ARTICLE TYPE

www.rsc.org/xxxxxx | XXXXXXXX

Photoelectrocatalytic Materials for Environmental Applications

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Received (in XXX, XXX) Xth XXXXXXXX 200X, Accepted Xth XXXXXXXX 200X First published on the web Xth XXXXXXXX 200X

5 DOI: 10.1039/b000000x

This review summarizes recent research on and development of semiconductor-based photocatalyst materials that are applicable to environmental remediation and/or chemical synthesis purposes. A wide variety of TiO_2 particles and/or films has been studied during the past 30 years because they are the most stable and powerful photocatalysts leading to the degradation of various organic

- ¹⁰ pollutants. The photocatalytic performance of other semiconductor materials such as ZnO, SnO_2 , WO_3 , Fe_2O_3 and CdS has also been intensively investigated. A general limitation in the efficiency of any photocatalytic process is the recombination of the photogenerated charge carriers, i.e., of electrons and holes, following bandgap illumination. Considerable efforts have been made to suppress this recombination and hence to enhance the charge carrier separation and the overall
- ¹⁵ efficiency by means of coupling of different semiconductors with desirable matching of their electronic band structures, or incorporation of noble metal nanoclusters onto the surface of semiconductor photocatalyst particles. Modification of the physicochemical properties, such as particle size, surface area, porosity and/or crystallinity of the semiconductor materials, and optimization of the experimental conditions, such as pH, illumination conditions and/or catalyst
- ²⁰ loading, during photocatalytic reactions have also been carefully addressed to achieve high reaction rates or yields. To utilize solar energy more efficiently, i.e., to extend the optical absorption of the mostly UV-sensitive photocatalysts into the visible light range, numerous research groups have contributed to developing novel visible light active photocatalysts. With the application of semiconductors with narrower bandgaps such as CdS, Fe_2O_3 and WO_3 being
- straightforward choices, doping of wide bandgap semiconductors like TiO_2 has been the most popular technique to enhance the catalysts' optical absorption abilities. Research on the mixedoxide-based semiconductor photocatalysts with deliberately modulated band structures has also attracted tremendous attention in the past decade, concentrating on, for example, the generation of H₂ and/or O₂ from H₂O splitting, and the degradation of organic pollutants under visible light
- ³⁰ irradiation. Both theoretical calculations and experimental results have convincingly shown that the developed materials can serve as highly efficient photocatalysts that are both environmentally and economically significant.

1. Introduction

Since the demonstration by Honda and Fujishima¹ of the ³⁵ photoelectrolysis of water using a TiO_2 electrode under an anodic bias potential, intensive research efforts have been devoted to the development of photocatalytic materials, with the aim of utilizing solar energy and thus addressing the increasing global concerns of environmental remediation and

- ⁴⁰ clean fuel production. Decades of efforts have successfully produced a wide range of efficient semiconductor-based photocatalytic materials. A timely review of these materials is therefore appropriate. Thorough discussions concerning the mechanism of photocatalytic reactions are not the purpose of
- ⁴⁵ the present review. The interested reader will find detailed mechanistic discussions in various focused reviews, for example, by Hoffmann *et al.*²⁻⁴ On the other hand, several reviews⁵⁻⁸ have recently been published specifically focusing on photocatalytic materials for solar hydrogen production. In
- ⁵⁰ this review, a wider range of recently developed photocatalytic semiconductor materials will be discussed with

particular emphasis on the improvement of their photocatalytic performance and on their visible-light-driven activities.

For a better understanding of the subsquent discussions, it will be crucial to clarify a few fundamental definitions that are most relevant to this context. The electronic energy structure within a semiconductor consists of three distinguished regimes, i.e., the conduction band (CB), the 60 valence band (VB) and the forbidden band. The forbidden band represents a region in which, for an ideal, undoped semiconductor, energy states do not exist. Energy states only exist above and below this region. Taking the energy level of the electron in the vacuum as reference and as the uppermost 65 level, the upper band is called the conduction band, and the lower one the valence band. In terms of energy, the difference between the upper edge of the valence band and the lower edge of the conduction band is called the bandgap (E_g) of the semiconductor. If the two levels can be described with the 70 same wave vector, the semiconductor is considered to have a direct bandgap; otherwise it has an indirect bandgap. The bandgap is one of the most critical parameters defining the

optical properties of semiconductors.

A semiconductor immersed into a solvent (in most cases water) and illuminated with photons exceeding its bandgap energy will be called a photocatalyst provided that at its surface it is able to catalyze reactions with $\Delta G < 0$ (e.g., the oxidation of organic compounds by molecular oxygen). In the case of endothermic reactions, such as the splitting of water into O₂ and H₂ that is found to occur at the semiconductor photocatalyst surface upon ultra-bandgap illumination, the

- ¹⁰ system can be viewed as "photosynthetic" and will be able to store part of the light energy in the form of chemical energy. Most studies of photocatalytic reactions are nowadays focused on particulate systems⁹⁻¹¹, employing either colloidal semiconductor particles or their suspensions, due to the ¹⁵ apparent reality that particles possess much higher surface
- areas (therefore higher yields from utilizing the incoming light energy, called photonic efficiency) than their bulk counterparts. The photocatalyst particles can actually be regarded as individual microelectrodes, always kept under
- ²⁰ open circuit potential, inside which charge carriers (electrons and holes) can be generated upon bandgap irradiation. The thus formed charge carriers then migrate to the surface to participate in possible chemical reactions with the surfaceadsorbed species. A series of reactions is given as follows to ²⁵ represent a simplified description of the events taking place
- on photocatalyst particles upon bandgap illumination²:

 $SC + hv (\geq E_g) \rightarrow h_{VB}^+ + e_{CB}^-$ (charge carrier generation) (1)

 $h_{\rm VB}^+ + e_{\rm CB}^- \rightarrow \rm SC + heat$ (bulk recombination) (2)

 $h_{\rm VB}^+ + \equiv \text{SC-OH} \rightarrow \equiv \text{SC-OH}^{\bullet+}$ (hole trapping) (3)

 $_{30} e_{CB}^{-} + \equiv \text{SC-OH} \rightarrow \equiv \text{SC-OH}/e_{tr}^{-}$ (electron trapping) (4)

 $\equiv \text{SC-OH}^{\bullet+} + \text{Red} \rightarrow \equiv \text{SC-OH} + \text{Red}^{\bullet+} \text{ (hole transfer) (5)}$

 $\equiv \text{SC-OH}/e_{\text{tr}} + \text{Ox} \rightarrow \equiv \text{SC-OH} + \text{Ox}^{\bullet} \quad (\text{electron transfer}) \quad (6)$

where "SC" denotes the semiconductor; e_{CB} is the photoexcited electron in the conduction band; h_{VB}^+ is the ³⁵ photoexcited hole in the valence band; SC-OH/ e_{tr}^- is the surface-trapped CB electron; SC-OH^{*+} is the surface-trapped VB hole (i.e., the surface-bound hydroxyl radical); Red and Ox are the electron donor and acceptor, respectively. It should be noted that the interfacial charge carrier transfer described

⁴⁰ by Eqs. (5) and (6) is generally much slower than the preceding events described by Eqs. (1-4). This is a highly simplified description of photocatalytic reactions that turns out to be rather more complicated if one takes a closer look.

2. Charge Transfer at Semiconductor Particles

⁴⁵ In photocatalytic reactions, the essential advantage of using semiconductor particles is their large surface area. In addition, the photogenerated charge carriers can easily reach the surface before they recombine, so that a high quantum yield (which will be defined later) can also be expected. However, two ⁵⁰ reactions, an oxidation and a reduction, must proceed simultaneously on the same particle surface (otherwise the particle will be charged, eventually leading to the overall reaction being stopped), as presented in Fig. 1. The slower process then determines the overall reaction rate. In this way, ⁵⁵ the particle behaves practically as a microelectrode kept always under the open circuit potential with the anodic and cathodic current being equal in magnitude.

Fig. 1 Charge carrier transfer on large (a) and small (b) semiconductor particles in the presence of an electron donor, D, and an acceptor, A. Reproduced with permission from ref. 12, Copyright 2001 Wiley-VCH.

Using larger-sized semiconductor particles, the partial currents in the dark are of rather limited magnitude under open circuit conditions, because the major carrier (e.g, the. 65 electrons in an n-type semiconductor) density at the surface is small due to the depletion layer beneath the electrode surface, as indicated in Fig. 1a. In contrast, no space charge region is formed in much smaller particles of size $d \leq d_{sc}$ (Fig. 1b, where d_{sc} is the thickness of the space charge region). Upon 70 light excitation, some minor carriers (e.g., the holes in n-type semiconductors) in larger particles are transferred to the electron donor in the solution, which results in a negative charging of the particle that alleviates the positive space charge. Accordingly, this event causes a flattening of the 75 energy bands (see the dashed line in Fig. 1a), equivalent to a negative shift of the rest potential of a bulk electrode under illumination. With much smaller semiconductor particles $(d \leq d_{sc})$, on the other hand, the photogenerated electrons and holes can be easily transferred to the surface and react with 80 the electron and hole acceptors, provided that the energy requirements are fulfilled. The average transit time, τ_{tr} , within a particle of diameter d can be obtained by solving Fick's diffusion law:

$$\tau_{\rm tr} = \frac{d^2}{4\pi^2 D} \quad (7)$$

ss in which *D* is the diffusion coefficient. Taking typical values of $D=0.1 \text{ cm}^2\text{s}^{-1}$ and d=20 nm, the average transmit time is about 1 picosecond, which is much shorter than the recombination time so that most charge carriers can reach the surface before recombination.

90 Quantum Size Effects

Nanosized semiconductor particles have been very popular as photocatalysts because of their large surface areas. Yet the most striking feature of the semiconductor nanoparticles is the remarkable change in their optical absorption spectra due to ⁹⁵ size reduction, compared with bulk materials.¹³⁻¹⁵ For example, the bandgap of CdS can be tuned between 2.5 and 4.5 eV as the size is varied from a macroscopic crystal down to the molecular regime. This interesting phenomenon has been addressed with success using the effective mass model. ¹⁰⁰ As mentioned earlier, in bulk semiconductors, light excitation results in the formation of electron-hole pairs, which experience a Coulomb interaction and can form excitons with

usually small bond energies (<0.03 eV) and large radii. The exciton radii can be determined based on the Bohr radius of an electron in an H atom modified by introducing the dielectric constant of the semiconductor and its reduced effective mass, $s m^*$, with the latter being given by

$$m^* = \left(\frac{1}{m_{\rm e}^*} + \frac{1}{m_{\rm h}^*}\right)^{-1}$$
 (8)

Using a "particle in a box" model with an infinite potential drop at the wall as the boundary condition, and taking into account that the exciton consists of an electron-hole pair, the

¹⁰ Schrödinger equation can be solved yielding the energy of the lowest excited state¹⁶⁻¹⁸, i.e., the lower edge of the conduction band, as

$$E(R) = E_{\rm g} + \frac{h^2}{8m_{\rm o}m^*R^2} - \frac{1.8{\rm e}^2}{\varepsilon R} \quad (9)$$

in which E_g is the bandgap energy; m_0 is the electron mass in ¹⁵ vacuum. According to Eq. (9), when a semiconductor has a reduced effective mass that is significantly smaller than the free electron mass, a large variation of its bandgap can be expected. Examples of such semiconductors are given: CdS $(m_e^*=0.21m_0, m_h^*=0.80m_0)$, CdSe $(m_e^*=0.13m_0,$ ²⁰ $m_h^*=0.45m_0)$, GaAs $(m_e^*=0.067m_0, m_h^*=0.082m_0)$ and ZnO $(m_e^*=0.24m_0, m_h^*=0.45m_0)$.^{19, 20} There are, however, semiconductors with larger effective mass in which quantization does not occur before its radius becomes extremely small, e.g., r < 5nm. One example is TiO₂, which

- ²⁵ has been the most intensively studied photocatalyst material during the past decades. Experimentally, TiO_2 particles synthesized with an average size between 5 and 20 nm were confirmed to exhibit the bandgap properties of the bulk solid. However, when the TiO_2 particle size is kept below 3 nm
- ³⁰ (i.e., corresponding to a few hundred TiO_2 molecules), the quantum size effect could be identified indicating a bandgap increase of ~0.25 eV.²¹ To explore the precise quantum size effect, it should be emphasized that bandgap shifts can only be measured with sufficient precision employing colloidal
- ³⁵ suspensions possessing a sufficiently narrow size distribution. Besides dispersed particles, techniques have also been available for the fabrication of semiconductor films consisting of nanocrystalline particles.²⁰ Such films may exhibit similar quantum size effects as individual particles, depending on the ⁴⁰ effective mass of the semiconductor as just described.

Accompanying the bandgap widening due to reduced particle size, electrons at the lower edge of the conduction band and holes at the upper edge of the valence band then possess higher negative and positive potentials, respectively.

 ⁴⁵ In consequence, electrons and holes have a higher reduction and oxidation power, respectively, in such quantized particles. Besides bandgap widening, variation in the semiconductor particle size also has possible interesting consequences on the

charge carrier transfer in photocatalytic reactions. For $_{50}$ instance, differences in the pathways of the photocatalytic reaction of acetic acid between a system using a TiO₂ bulk electrode short-circuited to a Pt electrode and that using Pt-

loaded TiO₂ particles provide a very suitable illustration of such size-dependent consequence.²² Using spatially separated 55 electrodes, acetic acid is oxidized by photogenerated holes at the illuminated TiO₂ electrode to form CH₃ radicals that then combine with each other to yield ethane, while H₂ evolves at the Pt electrode. Distinctively, in Pt-loaded TiO₂ particles, a photogenerated electron (most likely trapped at the Pt sites) 60 and a hole are able to reduce a proton and oxidize acetic acid to yield surface-adsorbed hydrogen, H_{ad}, and a CH₃[•] radical, respectively. Then, at adjacent TiO₂ and Pt sites, methane can be formed due to the reaction between neighboring H_{ad} and CH3. Another interesting consequence of the size effect 65 concerns the density of the photons absorbed by the semiconductor particles. Considering two colloidal solutions of different particle sizes and assuming that all photons are absorbed in both, the time interval between the absorption of the two photons in the smaller-particle solution can be 70 exceedingly larger than that in the bigger-particle solution. This difference can be very influential on these reaction pathways requiring multiple-electron transfer.

Photonic Efficiency and Quantum Yield in Photocatalytic Systems

⁷⁵ Extensive studies on heterogeneous photocatalysis have been undertaken worldwide, employing significantly diverse experimental conditions including illumination, photocatalyst preparation and reactor design. To make the experimental data comparable among various researchers, a unified,
⁸⁰ unambiguous definition of the efficiencies of the photocatalytic processes is compulsory.

The term photonic efficiency (η) is defined as the ratio of the rate of a photocatalytic reaction (usually the initial rate) to the rate of incident photons entering the system at a given wavelength interval. This parameter attracts considerable attention for photocatalysis applications in that it does provide a basis for engineering efficiency. Quantum yield, ϕ , is defined as the ratio of the quantity of the reactant molecules consumed or the product molecules formed to the quantity of so absorbed photons at a given wavelength. In practice, this ratio is often alternatively measured by the reaction rate and the absorption rate of the photon flow, i.e., the volumetric rate corresponding to a given reactant (or product) divided by the rate of photons absorbed in the system, as given by

$$\phi = r/I_{\rm a} \quad (10)$$

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in which r is the photocatalytic reaction rate and I_a is the absorbed photon flux. The latter can be obtained from

$$I_{\rm a} = I_0 \times F \quad (11)$$

in which I_0 is the incident photon flux, and F is the integrated ¹⁰⁰ absorption fraction in the system over the useful wavelength range as follows:

$$F = \frac{\int_{\lambda_{l}}^{\lambda_{2}} I_{\lambda} T_{\lambda}^{\mathrm{F}} f_{\lambda} \mathrm{d}\lambda}{\int_{\lambda_{l}}^{\lambda_{2}} I_{\lambda} T_{\lambda}^{\mathrm{F}} \mathrm{d}\lambda} \qquad (12)$$

where I_{λ} is the relative incident photon flux in the wavelength band, $d\lambda$; I_{λ}^{F} is the transmittance of the filter used in the experiment; and f_{λ} is the fraction of photons absorbed at wavelength λ as given by

$$f_{\lambda} = 1 - T_{\lambda} = 1 - 10^{-A_{\lambda}}$$
 (13)

in which T_{λ} and A_{λ} are the transmittance and absorbance, respectively, of the photocatalytic system at wavelength $\lambda \cdot I_0$ and F can be determined by actinometry and spectrophotometry, respectively.

10 3. Single Semiconductor Photocatalysts

3.1 TiO_2

The virtues of TiO₂, including high photostability (i.e., resistance to photocorrosion), low cost and non-toxicity, have led it to be widely used in photocatalytic applications, 15 including the degradation of organic pollutants in aqueous and gaseous phases, removal of heavy metals from contaminated

- waters, hydrogen gas generation from photocatalytic water splitting, etc. Studies of TiO₂ photocatalysis have been increasingly thriving since the first pioneering articles ₂₀ appeared in the 1970s.^{1, 23, 24} Anatase and rutile TiO₂ are
- commonly used as photocatalysts, with anatase showing a higher photocatalytic activity in most cases.¹³ The difference in their photocatalytic activity arises from their different lattice structures and electronic band structures.
- ²⁵ It has been generally accepted that upon bandgap illumination of TiO_2 particles the physical events simply proceed as follows: Firstly, electrons are raised into CB and holes left in VB of TiO_2 ; then, a portion of the electrons and holes successfully reach the particle surface where subsequent ³⁰ chemical reactions can take place. Experimental techniques²⁵⁻
- ²⁸, such as pulsed laser photolysis, transient absorption spectroscopy, and photoacoustic spectroscopy, are useful to probe the behavior of photogenerated charge carriers in the degradation of organic pollutants by aqueous colloidal
- suspensions of TiO_2 . Upon pulsed laser excitation, electrons and holes are generated inside a TiO_2 particle. Their subsequent behavior can then be probed by the transient absorption spectroscopy technique. To do this, it is necessary to identify the absorption bands of the electrons and holes.
- ⁴⁰ However, a precise assignment of the electron and hole absorption bands is rather difficult because their absorption spectra are very broad and the bands overlap each other in the visible wavelength range.²⁷ Optically transparent colloidal TiO₂ systems are best chosen to investigate the transient
- ⁴⁵ absorption of photogenerated charge carriers. Considerable progress in synthetic methods to produce extremely small TiO₂ clusters²⁹ makes it possible for such investigations to be carried out under well-defined experimental conditions.^{30, 31}
- Detailed spectroscopic investigations on aqueous colloidal ⁵⁰ TiO₂ suspensions upon bandgap irradiation in the absence of any hole scavengers showed that, while photogenerated electrons are trapped instantaneously, i.e., on the time scale of nanoseconds, holes can be trapped in electronically shallow or deep states. Deeply trapped holes are rather long-lived and

- ⁵⁵ inactive, while shallowly trapped holes, which are in a thermally activated equilibrium with free holes, exhibit a very high oxidation potential as probed by using dichloroacetate (DCA⁻) and thiocyanate (SCN⁻) as substrates²⁷. In a recent work by Yoshihara *et al.*³², the free and trapped electrons and ⁶⁰ trapped holes were identified employing transient absorption
- spectra. Their reactivity was evaluated by transient absorption spectroscopy in the presence of hole- and electron-scavengers indicating that the trapped electrons and holes are localized at the surface of the TiO_2 particles and the free electrons are 65 distributed in the bulk, as depicted in Fig. 2.

Fig. 2 Spatial distribution of photogenerated charge carriers in TiO₂. Reprinted with permission from ref. 32, Copyright 2004 ACS.

The primary cause for the photocatalytic activity of TiO_2 is ⁷⁰ believed to be the formation of $\cdot OH$ radicals³³⁻³⁷ by rapid conversion of photogenerated holes upon contact with the adsorbed H₂O molecules on TiO_2 according to the following reaction pathways:

$$\operatorname{TiO}_{2} + hv (\geq E_{g}) \rightarrow h_{VB}^{+} + e_{CB}^{-} \quad (14)$$
$$h_{VB}^{+} + e_{CB}^{-} \rightarrow \operatorname{TiO}_{2} + heat \quad (15)$$
$$h_{VB}^{+} + \equiv \operatorname{Ti}^{\mathrm{IV}}\mathrm{OH}/\mathrm{H}_{2}\mathrm{O} \rightarrow \equiv \operatorname{Ti}^{\mathrm{IV}}\mathrm{OH}^{\bullet+}/\mathrm{OH}^{\bullet+} + \mathrm{H}^{+} \quad (16)$$

The highly active ·OH radicals are capable of mineralizing most organic pollutant molecules. Oxygen molecules dissolved in H₂O, which usually serve as scavengers of ⁸⁰ photogenerated electrons, also lead to the formation of ·OH radicals. Other oxidizing routes have also been proposed, including direct oxidation by the photogenerated holes^{27, 32}, generation of oxidizing species from reactions involving intermediates formed in the solution³⁸, etc.

- Besides colloidal TiO₂, various nanosized TiO₂ particulate aqueous suspensions have also been used in photocatalytic degradation of organic molecules, such as methanol^{39, 40}, dichloroacetate, oxalic acid, phenols, dyes and other pollutants, including herbicides, pesticides and their of derivatives, etc. Commercially available TiO₂ products such as Degussa P25 and Sachtleben Hombikat UV100 have also been studied for different reactions^{39, 41-44}, with the former being regarded as a model photocatalyst widely used as a reference to be compared with other photocatalytic materials.
- ⁹⁵ The photocatalytic activity of TiO_2 towards a specific reaction depends on both its physicochemical properties^{45, 46} and external conditions. The influential physicochemical properties include the morphology, primary particle size, degree of aggregation, surface area, and crytalline structures,
- ¹⁰⁰ while the external conditions involve the irradiation intensity, the pH of the aqueous system, the presence/absence of electron/hole scavengers, and the bias potential if applied to TiO₂ film photoelectrodes. These factors often interactively affect the overall photocatalytic activity.²
- ¹⁰⁵ Particle size, degree of aggregation and surface area determine the adsorption ability of TiO_2 photocatalysts for substrate molecules, which has proved to be a prerequisite for

many photocatalytic reactions to proceed efficiently. Most currently used and commercially available photocatalyst powders, for example, consist of nanocrystalline primary particles that are aggregated to form secondary structures with

- ⁵ dimensions in the micrometer range. Aggregation of particles would inevitably reduce their total surface area exposed to the outer environment, leading to a lowered photocatalytic activity as observed in many reaction systems. Only in a certain special agglomerated fashion, i.e., adjacent crystallites
- ¹⁰ are aligned in a given crystallographic orientation to enable a strong electronic coupling between the primary particles, can the photocatalytic activity be maintained at a high level due to the so-called "antenna effect".^{36, 37, 47} As illustrated in Fig. 3, compared with randomly agglomerated TiO₂ particles, a chain
- $_{15}$ of well-aligned particles will act as the antenna system to transfer the photon energy from the spot of light absorption to the reaction site since the electron transfer resistance at the grain boundaries is now considerably reduced. This scenario explains how photons are accumulatively used on one TiO₂
- ²⁰ particle in such systems even at reduced photon flux from a laser pulse.

Fig. 3 Antenna effects of charge carrier transfer during Ag photodeposition in self-assembled TiO₂ aggretates. Reproduced with permission from ref. 47, Copyright 2007 Oldenbourg Wissenschaftsverlag GmbH.

Based on similar arguments, because of the attractive features of the high surface area (hence the high adsorption capacity) and crystallite alignment, mesoporous TiO_2 films ³⁰ with ordered structures have also been actively developed recently as efficient photocatalysts.⁴⁸⁻⁵⁶ The employed illumination mode can also affect the adsorption property of TiO_2 particles via a deaggregation scheme^{37, 40}, in which the high intensity, e.g., pulsed laser irradiation, exposes more

- ³⁵ surface area for adsorption originally blocked due to particleparticle aggregation. The deaggregation scheme is valid since most TiO_2 nanoparticles do not have a spherical shape, as revealed by a high-resolution transmission electron microscopy (HRTEM) study shown in Fig. 4, but they possess ⁴⁰ flat facets upon contact of which the number of adsorption
- ⁴⁰ flat facets upon contact of which the number of adsorption sites can be notably reduced.⁵⁷

Fig. 4 HRTEM images and reconstructed shapes of anatase TiO_2 nanoparticles: a), b) truncated cube; c), d) prism. Reproduced with permission from ref. 57, Copyright 2007 Wiley-VCH.

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More importantly, knowledge of the adsorption behavior of different molecules onto the TiO₂ surface provides more profound insight into the mechanisms of the corresponding photocatalytic reactions.⁵⁸⁻⁶² In this regard, Attenuated Total ⁵⁰ Reflection – Fourier Transform Infrared Spectroscopy (ATR-FTIR) serves as a powerful tool to probe the interactions between the TiO₂ surface and organic molecules, such as

carboxylic acids.⁶³⁻⁶⁵ For example, three forms of oxalate structures are formed upon chemisorption of oxalic acid on ⁵⁵ the TiO₂ surface in a low-pH aqueous system, as illustrated in Fig. 5, with complex (I) being the most stable and complex (III) being the least stable. Sequential ATR-FTIR spectra of these adsorbed oxalates under UV illumination suggest that the photocatalytic oxidation of oxalate proceeds through the 60 most stable surface complex, i.e., complex (I) in Fig. 5. Complexes (II) and (III) undergo structural rearrangements to replenish the surface availability of complex (I) during its oxidation.

Fig. 5 Schematic evolution of the surface composition of oxalates chemisorbed on TiO₂ surface during UV illumination. Reprinted from ref. 64, Copyright (2005), with permission from Elsevier.

The pH of the aqueous environment of the TiO₂ particles appears to be one of the most influential external conditions 70 determining their photocatalytic activity. Apparently, the surface adsorption behavior towards ionic species can be directly modified by changing the pH of the solution: at lower pH, the TiO₂ surface is protonated to be positively charged, which favors the adsorption of anionic species from the 75 solution; at higher pH, the surface is negatively charged thus repelling anionic species from approaching the surface. On the other hand, the pH also bears an influence on the levels of energy bands in TiO₂. The flatband potential, E_{fb} , of a single crystal TiO₂ photoelectrode varies with pH according to

$$E_{fb} = E_{fb(pH=0)} - 0.059 pH \quad (17)$$

where $E_{fb(pH=0)}$ is the flatband potential of the photoelectrode at 25 ${}^{0}C$ at pH 0. In other words, the flatband potential shifts cathodically by 59 mV upon changing the pH by one unit. The value of $E_{fb(pH=0)}$ in rutile TiO₂ photoelectrodes has been ss determined to be 0.06, -0.038 or -0.05 V (vs. NHE) by different researchers. Particulate TiO₂ also exhibits such a Nernstian pH-dependence at 25 ${}^{0}C$ as reported by Duonghong *et al.*⁶⁶ using colloidal TiO₂ composed mainly of amorphous and anatase TiO₂:

$$E_{fb}$$
 (TiO₂.particle) = -(0.12 ± 0.02) - 0.059 pH (18)

90

The difference between the $E_{fb(pH=0)}$ values of particulate and film photoelectrode TiO₂ can, for example, be explained by the different crystal structures of particles and electrodes. Anatase particles possess a larger bandgap than rutile particles 95 and electrodes. As the valence band position appears to be rather insensitive to the TiO₂ lattice structure, this difference is thus reflected in a more negative value of $E_{fb(pH=0)}$ of anatase particles than of rutile electrodes. Since the flatband potential is usually very close to the Fermi level of electrons 100 and the conduction band edge in n-type TiO₂, the pHdependence of E_{fb} also determines the position of the conduction band edge and hence the rate of interfacial electron transfer. Consequently, reduction reactions initiated by conduction band electrons will be more favored (i.e., occur 105 at a higher rate or yield) at high pH values while oxidation processes are favored at low pH values. Depending upon the desired reactions, the proper choice of pH will therefore be crucial for the overall process efficiency. Since this so-called Nerstian behavior is by no means limited to TiO₂ but is a 110 general phenomenon of almost any semiconductor/water interface, the above considerations can readily be generalized for all of the subsequently described systems.

3.2 ZnO

ZnO has a similar bandgap to that of TiO₂ as shown in Fig. 6 and is expected to exhibit similar photocatalytic capacity to ⁵ that of TiO₂, provided that this property is largely dependent on the energy level of CB and VB.⁶⁷ Therefore, it has been comparatively studied with TiO₂ in terms of its photocatalytic performance.⁶⁸⁻⁷⁵ The main drawback of particulate ZnO in an aqueous environment is, however, its chemical instability:

¹⁰ $ZnO+2H_{aq}^{+} \square Zn_{aq}^{2+}+H_2O$ (19) $ZnO+H_2O \square Zn(OH)$ (20)

$$2110 \cdot 11_2 \circ = 211 (\circ 11)_2 \cdot (20)$$

Hence, the pH-range in which ZnO is found to be stable is very limited.¹⁹

Fig. 6 CB and VB energy levels of several semiconductors. (The semiconductors are in contact with aqueous electrolyte at pH 1. The energy scale is indicated in electron volts using either the normal hydrogen electrode (NHE) or the vacuum level as reference. On the right, the standard potentials of several redox couples are presented against the
 standard hydrogen electrode potential.) Reprinted by permission from

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ZnO has shown photocatalytic activities in the reduction or oxidation of several compounds including organic dyes and pulp and paper bleaching effluents, etc.^{69, 70, 72, 76-82} Similar ²⁵ oxidation pathways to those of TiO₂ were confirmed in ZnO photocatalysts, including the formation of •OH radicals as well as the direct oxidation by photogenerated holes, etc. But the implementation of ZnO photocatalytic systems has not flourished like TiO₂ systems have, mainly because of their ³⁰ unsatisfying photostability. Under prolonged optical irradiation, ZnO suffers from photodecomposition, which is mainly attributed to the oxidation of ZnO from the solid phase into the aqueous phase by holes according to the following reaction⁸³:

$$ZnO+2h_{VB}^{+} \rightarrow Zn^{2+}+\frac{1}{2}O_{2}$$
 (21)

Although its photocatalytic application is not as successful as TiO_2 , ZnO has been attracting more and more attention in other fields, including sensors⁸⁴⁻⁸⁶, optoelectronics⁸⁷ and field emission units.⁸⁸⁻⁹⁰

40 3.3 SnO₂

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 SnO_2 is also an *n*-type semiconductor with a bandgap energy of ~3.8 eV, which corresponds to an optical absorption edge below 330 nm. However the CB position of SnO_2 is such that it is incapable of reducing oxygen molecules (Fig. 6).

⁴⁵ Therefore, in the past, semiconductors of such kind have not been considered as suitable photocatalysts that can be used individually. On the other hand, such materials may have an advantage regarding their band structures and can possibly provide another way to serve in photocatalytic systems, i.e., ⁵⁰ when coupled with other semiconductors with suitable

matching of band levels.⁹¹ This has been demonstrated in a number of publications⁹¹⁻⁹⁵, the details of which are given later. A much narrower bandgap of 2.53 eV was also reported for SnO₂, corresponding to an absorption edge of 490 nm.⁹³ ⁵⁵ Quite recently, an interesting type of SnO₂ photocatalyst, nanosized V-shaped bipods, was reported by Wang and coworkers⁹⁶, and the materials showed a broad photoresponse in the visible region up to ~550 nm. This was believed to be caused by the presence of oxygen vacancies, together with ⁶⁰ abundant surface states.

3.4 WO₃, Fe₂O₃ and CdS

WO₃, Fe₂O₃ and CdS are jointly discussed in this section simply because of their similar and relatively narrow bandgaps, 2.6, 2.1, and 2.25 eV, respectively, which make ⁶⁵ them capable of being excited by visible light. Fig. 6 shows that the upper edge of the VB of WO₃ is close to that of TiO₂, which exceeds the H₂O/O₂ oxidation potential. Thus, the photogenerated holes in WO₃ upon bandgap excitation are capable of oxidizing a wide range of compounds. The ⁷⁰ advantage of WO₃ as a photocatalyst is that the bandgap is only ~2.6 eV, which is ~0.6 eV narrower than TiO₂. Therefore, more visible light can be harnessed by WO₃ from the sunlight spectrum.⁹⁷ Another virtue of WO₃ is its remarkable photostability in acidic aqueous solutions making

⁷⁵ it a powerful photocatalyst, e.g., for the treatment of wastewater contaminated by organic acids.⁹⁸ For example, formic acid and Rhodamine B have been reported to be effectively degraded on WO₃ photoelectrodes.

Another important application of WO₃ is in photocatalytic 80 water splitting to produce hydrogen gas using visible solar light, due to its narrow bandgap. Earlier studies of the photoelectrochemical behavior of both polycrystalline and monocrystalline WO₃ provided instructive knowledge for the development of photocatalytic water-splitting systems.^{99, 100} 85 The difficulty in the overall water splitting (both reduction and oxidation of H₂O molecules are to be achieved) by WO₃ is that the lower edge of the CB lies below the redox potential of H₂O/H₂, as illustrated in Fig. 6. This means that the reduction of water molecules to generate hydrogen gas is ⁹⁰ thermodynamically unfavorable.¹⁰¹ Applying a bias potential to the system can overcome the energy barrier for the photogenerated electrons to be ejected into the adsorbed water molecules.97 Coupling with other semiconductor materials102 and doping by metal ions^{103, 104} are other alternatives to make 95 use of the oxidation power of WO₃ for water splitting. WO₃ has also been applied in electrochromic¹⁰⁵⁻¹⁰⁷ and photochromic¹⁰⁸⁻¹¹² devices, such as large area displays and "smart windows" because WO3 films can be switched between different optical states under different 100 electrochemical or optical conditions. The electrochromic effect is caused by the electrochemical reaction between the WO₃ electrode and protons in the electrolyte solution, under the influence of a bias potential to provide charge carriers (electrons in this case). The electrons can then create color 105 centers by reducing the W⁶⁺ species to W⁵⁺ species. The photochromism effect of WO₃ is due to the formation of an identical absorption band upon light irradiation.¹¹³ This process is completely reversible by exposing the reduced sample to oxygen gas.

The band structure of α -Fe₂O₃ is quite similar to that of WO₃, with the VB edge exceeding the standard redox ⁵ potential of H₂O/O₂ and the CB edge being lower than the standard redox potential of H₂/H₂O. Upon optical irradiation, the recombination of the photogenerated charge carriers is reported to be very rapid (within 1 ns) if no electron or hole scavengers are present in the electrolyte.¹¹⁴ In the presence of

- ¹⁰ appropriate scavengers, however, the holes can function as powerful oxidants, and the electrons as moderately powerful reductants. For example, S⁴⁺ species, such as aqueous SO₂, HSO₃⁻ and SO₃²⁻ etc, have been shown to be readily oxidized on the surface of α -Fe₂O₃.^{115, 116} Using Fe³⁺ as the electron ¹⁵ scavengers, α -Fe₂O₃ is capable of oxidizing H₂O to evolve oxygen gas.¹¹⁷ A bias potential can also help to achieve total H₂O splitting under visible irradiation.¹¹⁸ A number of organic compounds (e.g., salicylic acid¹¹⁹, phenols¹²⁰, azo dyes and 2-naphthol¹²¹) can also be photocatalytically
- $_{20}$ degraded on α -Fe₂O₃ photocatalysts, either by adding sacrificial scavengers or through the application of a bias potential, although the efficiency remains to be improved.

In the area of photoelectrochemistry, CdS has been the most heavily studied II-VI group semiconductor.¹²² It has a

- $_{25}$ higher VB edge as compared with the above-mentioned metal oxides, as shown in Fig. 6. This is because the VBs of metal oxides are mainly formed by O 2p states, while that of CdS is formed by S 2p states. The electronegativity of S is smaller than that of O, resulting in the different VB positions.
- ³⁰ Quantum size effects, represented by the markedly different properties of materials when their sizes decrease, are often emphasized in the study of CdS semiconductors. For example, the onset of light absorption by CdS varies significantly as the particles decrease in size. Moreover, this quantum size effect
- ³⁵ can be maintained during the assembly of CdS films from quantum-sized CdS particles.¹²³⁻¹²⁵ For example, assembly of *p*-aminothiophenol-capped CdS nanoparticles onto a *p*aminothiophenol-functionalized Au electrode was achieved by electropolymerization, resulting in flexible charge carrier
- ⁴⁰ behavior upon optical irradiation under a bias potential.¹²⁴ Chemoselective photocatalytic reduction of aromatic azides to aromatic amines was recently reported on CdS quantum dots in the presence of sacrificial electron donors.¹²⁶ As commonly seen in other low CB edge semiconductors, CdS also suffers
- ⁴⁵ from photocorrosion by photogenerated holes.¹²⁷ Moreover, as reported by Meissner *et al.*¹²⁸, there might even be fundamental problems concerning the principal ability of CdS to form molecular hydrogen from water in a photoelectrochemical cell based upon the position of its ⁵⁰ conduction band edge. This problem has been recently
- addressed by a new method for the preparation of CdS electrodes, meanwhile obtaining high photocatalytic activity for hydrogen production.¹²⁹

4. Coupled Semiconductor Photocatalysts

⁵⁵ Coupling between different semiconductors in photocatalytic systems was designed to alleviate the charge carrier recombination in individual photoelectrodes. A good matching of their CB and VB levels can realize a vectorial transfer of photogenerated charge carriers from one to the other as illustrated in Fig. 7, where the relative positions of the energy bands of the two particles are shown in terms of energetic rather than spatial level. After coupling in the shown manner, the energy gap between corresponding band levels drives the charge carriers from one particle to its neighbor to 65 form a spatial separation between electrons and holes. But coupling of semiconductors does not always enhance the charge separation, because the design of a coupled photoelectrode relies on the band structures of its components, which are determined by many other factors (e.g., surface 70 area, defect density, crystallinity and quantum size effects). More detailed aspects of such coupling effects will be discussed below in a few examples.

Fig. 7 Coupling two different semiconductor particles and charge carrier separation.

Other than the mutually photosensitive components, coupling between one photosensitive and another nonsensitive (e.g., very wide bandgap) semiconductor may also have positive effects on the photocatalytic performance of the ⁸⁰ sensitive one. For example, Kisch and Weiss^{130, 131} studied the SiO₂-supported CdS photoelectrode in an organic addition reaction and found that the enhanced photocatalytic activity was related to the changes in the bandgap and the flatband potential of CdS, which originate from an electronic ⁸⁵ semiconductor-support interaction mediated by [Si]-O-Cd-S bonds. The surface chemistry, in particular the acidity, can also be modified to benefit the performance of photocatalysts, as exemplified by TiO₂/SiO₂ and TiO₂/ZrO₂.^{132, 133}

4.1 TiO₂/WO₃

105

⁹⁰ The coupling scheme depicted in Fig. 7 has been achieved for WO₃/TiO₂ photoelectrodes. As shown in an earlier study¹³⁴ concerning the effect of adding WO₃ to TiO₂ on the photocatalytic activity of TiO₂, the observed enhanced photocatalytic degradation of 1,4-dichlorobenzene was
⁹⁵ explained by the increased electron transfer from TiO₂ to WO₃ via the formation of an intermediate W(V) species, together with the increased surface acidity in the coupled photoelectrode. Protonated surface hydroxyl groups, and hence the surface acidity, can promote the electron transfer ¹³⁵ In a study by Kwon *et al.*¹³⁶, the role of the increased surface acidity due to WO₃ addition was confirmed by treating the photocatalytic reactions on WO₃/TiO₂ electrodes using the Langmuir-Hinshelwood equation¹³⁷ as follows:

$$=\frac{kKC}{1+KC}$$
 (22)

r

where r is the rate of photocatalytic reaction; k is the reaction rate constant only related to the illumination source, the catalyst activity and the reaction media, but not to the structure of the reactants; K represents the equilibrium 110 adsorption constant and is a function of the reactant molecular structure; C denotes the concentration of the reactant. The magnitude of k is indicative of the decomposition rate of the adsorbed organics, which is closely related to the charge carrier separation and trapped charge density on the surface. ⁵ Meanwhile, K represents the adsorption efficiency of the

- organics, which is intimately related to the Lewis surface acidity of the particles. Therefore, the contribution to the enhanced photocatalytic activity by WO_3 incorporation can be divided into two aspects: 1) improved charge carrier
- ¹⁰ separation and 2) increased surface adsorption affinity. The authors suggested that under certain circumstances the second might be the predominant effect. Fuerte *et al.*¹³⁸ observed continuously enhanced photocatalytic activity in toluene degradation by TiO_2/WO_3 when the W concentration was
- ¹⁵ enhanced. They ascribed the effect to the creation of Wrelated trapping centers on the catalyst surface and intraband electronic states. As proposed by Miyaochi *et al.*¹³⁹ who studied the effect of layered WO₃/TiO₂ structures, both the surface hydrophilicity of the top TiO₂ layer and the
- ²⁰ photocatalytic efficiency for the oxidation of the test molecule methylene blue were increased, which was also explained by a charge carrier transfer between the TiO_2 and WO_3 layers. Similar effects were observed by Somasundaram *et al.* when they studied the photoaction spectra of TiO_2/WO_3 composite ²⁵ films.¹⁴⁰

The TiO_2/WO_3 coupling does not always enhance the photocatalytic activity of TiO_2 . For example, too much loading of WO₃ shows adverse effects because some W sites can act as charge recombination centers according to the ³⁰ following scheme¹⁴¹:

 $W^{6+} + \hat{e}_{(TiO_2)CB} \to W^{5+}$ (23) $W^{5+} + h^+_{(TiO_2)VB} \to W^{6+}$ (24)

Another negative example was reported to be due to the difference in WO₃ crystallinity. Higashimoto *et al.*¹⁴² studied ³⁵ two systems of TiO₂ coupled with either amorphous or crystalline WO₃. Their bandgap calculations on the two systems revealed different CB and VB positions of amorphous and crystalline WO₃, and so are the different CB positions between TiO₂ and WO₃ in the two systems, as depicted in ⁴⁰ Fig. 8. The band structures in the crystalline-WO₃/TiO₂ couple do not favor the separation of charge carriers. Although the CB electron transfer is favored in amorphous-WO₃/TiO₂, the bandgaps and band edge levels in WO₃ and TiO₂ may vary from sample to sample due to different ⁴⁵ preparation methods.^{142, 143} Therefore, the fabrication of

coupled semiconductors with controlled band structure properties is still a challenging task.

Fig. 8 Energetic diagram of amorphous- and crystalline-WO₃/TiO₂.
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4.2 TiO₂/SnO₂

As mentioned previously, SnO_2 has a very large bandgap (~3.8 eV) and has been traditionally viewed as a poor

⁵⁵ candidate for photocatalytic applications. However, coupling SnO₂ with other semiconductors can greatly enhance its photocatalytic activities in organic pollutant degradation^{91, 92, 144-148}, especially when an external bias potential is applied.⁹¹

Vinodgopal and Kamat⁹¹ reported a very rapid 60 decolorization of Acid Orange 7 using a coupled SnO₂/TiO₂ photoelectrode under a bias potential. They ascribed the enhanced degradation rate as improved charge separation due to good matching in the energy levels (E_{CB} for $SnO_2 = 0$ V vs. NHE at pH 7, while for TiO₂ E_{CB} = -0.5 V vs. NHE at pH 7). 65 The anodic bias potential was also reported to be responsible for the enhancement in photocatalytic activity by driving away the electrons into the conduction band of SnO₂, thus promoting the oxidation of dye molecules on the TiO₂ surface where photogenerated holes are more abundant. The 70 photoelectrocatalytic degradation of naphthol blue black by a similar system⁹² again was significantly improved compared with pure TiO₂, due to the enhanced charge separation between TiO₂ and SnO₂ nanoparticles. As the content of SnO₂ was increased, the influence of oxygen on both the 75 short-circuit photocurrent and the open-circuit photovoltage became less and less significant, indicating the rapid injections of electrons from TiO₂ into SnO₂ before recombination with holes or being scavenged by oxygen molecules. A scheme depicting this coupled photoelectrode is ⁸⁰ shown in Fig. 9. The network of three-dimensionally interconnected nanoparticles of both kinds generates sufficient contact points between these two kinds of particles and thus creates a large SnO₂/TiO₂ interface.

Fig. 9 Idealized photoinduced charge separation in a SnO₂/TiO₂ semiconductor film. Reproduced with permission from ref. 92, Copyright 1996 ACS.

Another coupling approach is to deposit one type of semiconductor film over another, thus a clear-cut two-90 dimensional interface layer will be achieved. Employing this approach, the charge carrier transfer between TiO_2 and SnO_2 was also confirmed as the dominant factor in the improved photocatalytic activity. Hattori et al.^{146, 149} prepared doublelayered SnO₂/TiO₂-coupled films (as shown in Fig. 10) and 95 studied their photocatalytic activity in both the oxidation of formic acid and 1,3,5,7-tetramethylcyclotetrasiloxane and the reduction of Ag⁺ and bis(2-dipyridyl)disulfide. By comparing the amount of CO_2 evolved, the photooxidation of formic acid on SnO₂/TiO₂-coupled films was confirmed to occur more 100 efficiently than on pure TiO₂ films. The degradation of 1,3,5,7-tetramethylcyclotetrasiloxane was also more efficient on the coupled SnO₂/TiO₂ films. On the other hand, photocatalytic reduction processes on SnO₂/TiO₂ couple were found to be less efficient than on pure TiO2 films. These 105 results are unanimously consistent with the vectorial charge carrier transfer as proposed earlier.91, 92 Note that the electrode substrates in these studies are non-conducting, therefore electrons transferred from TiO₂ into SnO₂ can only exit these layers via the edges of the SnO₂ layer in contact with the 110 electrolyte¹⁴⁶.

Fig. 10 SnO_2 and $\text{TiO}_2/\text{SnO}_2$ deposited on glass substrate. Reproduced from ref. 146 by permission of the Electrochemical Society.

Shang *et al.*¹⁵⁰ also confirmed the positive effect of the coupled semiconductors by the higher photocatalytic ⁵ degradation of formaldehyde on $\text{SnO}_2/\text{TiO}_2$ bilayers which were compared with pure TiO_2 . They further studied the effect of the thickness of the TiO_2 layer on the photocatalytic activity of the couple. As the TiO_2 thickness increased, the activity was found to decline, until a similar value as that of ¹⁰ the pure TiO_2 film was attained. As the TiO_2 layer became thicker, more electrons generated far away from the $\text{SnO}_2/\text{TiO}_2$ interface recombined with the holes before they could reach the region of the interface in which a gradient could "pull" them towards the SnO_2 CB. The outermost TiO_2 film. If TiO_2 was firstly deposited on the glass substrate, followed by depositing a SnO_2 layer over the TiO_2 film, the

- followed by depositing a SnO_2 layer over the TiO_2 film, the photocatalytic activity of this couple was much lower than that of the glass/SnO₂/TiO₂ configuration. This observation
- ²⁰ supports the coupling effect in that the electrons in the SnO_2 conduction band now could not be transferred into TiO_2 due to the energy barrier. More complex patterns can also be formed in combining SnO_2 and TiO_2 layers into a film photoelectrode.^{151, 152} As shown in Fig. 11, a first layer of ²⁵ SnO_2 followed by two layers of TiO_2 stripes orthogonal to
- $_{25}$ SnO₂ followed by two layers of TiO₂ stripes orthogonal to each other resulted in much higher activity, as compared with non-patterned structures.

Fig. 11 3D imaging of a cross-patterned SnO₂/TiO₂ coupled film. (The ³⁰ SnO₂ layer was at the bottom, with two orthogonal TiO₂ stripes on top.) Reprinted with permission from ref. 152, Copyright 2001 ACS.

4.3 TiO₂/CdS

The relative energy positions of CBs and VBs between CdS and TiO_2 are shown in Fig. 12. Both the CB and VB of CdS

- ³⁵ particles are higher than their counterparts in the TiO_2 particles.¹⁵³ The smaller bandgap of CdS (~2.5 eV) enables it to absorb visible light to generate electrons and holes. Subsequently the electrons will flow from the CB of CdS to the CB of the adjacent TiO₂, leaving the holes behind in the
- ⁴⁰ VB of CdS. The enhanced charge separation under visible light illumination has made the couple widely used in photo(electro)catalytic reactions, e.g., for the degradation of organic pollutants¹⁵⁴⁻¹⁵⁸, the production of hydrogen gas^{159, 160} and, in visible-light-driven solar cells, etc.¹⁶¹
- ⁴⁵ Studies on the coupling effect between CdS and TiO₂ can be traced back to the early 1980s, when the hydrogen generation via photocatalytic H₂S splitting by CdS was found to be enhanced upon the addition of TiO₂ particles.¹⁶² Spanhel *et al.*¹⁶³ also found a 10-fold increase in the quantum yield for
- ⁵⁰ the photoreduction of methyl viologen by coupled CdS/TiO₂. Evans *et al.*¹⁶⁴ suggested that the CB electron transfer from CdS to TiO₂ could be completed on a time scale of picoseconds, resulting in a significantly slower recombination for the charge carriers formed upon light absorption in CdS.
- Earlier research on TiO₂/CdS couples was mostly limited to colloidal systems, and CdS was usually the dominant

component. Subsequent research started to reverse this trend by using CdS as a "sensitizer". The small amount of CdS dispersed in a TiO₂ matrix can absorb visible light, making 60 the coupled photocatalyst sensitive to visible light. Yu et al.¹⁶⁵ prepared a CdS-sensitized TiO₂ nanocrystalline photocatalyst and obtained much higher activity toward the degradation of methylene blue under visible light illumination ($\lambda > 400$ nm) than with pure TiO2 or CdS due to the rectified electron 65 transfer from CdS to TiO₂, as shown by the formation of Ti³⁺ observed in the electron paramagnetic resonance (EPR) spectra.¹⁶⁶ Wang et al.¹⁶⁷ prepared a coupled TiO₂/CdS hydrogel with a CdS loading of only about 0.9%. The hydrogel consisted of uniform crystalline CdS particles (~2 $_{70}$ nm in size) well dispersed in TiO₂. At this size, the quantum size effect from CdS could be expected, i.e., the bandgap of CdS was widened to increase the energy difference between the CBs of CdS and TiO2. Meanwhile, the coupled semiconductor was still sensitive to visible light for the 75 degradation of methylene blue under visible light (with an excitation wavelength longer than 420 nm). The degradation mainly took place on the TiO₂ surface since most of the CdS surface was covered by the TiO₂ matrix.

$_{80}$ Fig. 12 Band positions in the coupled TiO_2/CdS system. Reproduced with permission from ref. 153.

Another benefit of a such-structured couple is that the surrounding TiO₂ matrix can protect the CdS quantum dots against photocorrosion, which has been a major problem for 85 CdS photocatalysts to be used in aqueous environments.¹⁶⁸ The effects of quantized TiO₂ particles were also studied in TiO₂/CdS couples. Sant and Kamat¹⁶⁹ prepared extremely small TiO₂ particles coupled with CdS. The quantum size effects from both TiO₂ and CdS were confirmed by the blue 90 shift of the absorption edges as the size of the particles decreased. When the TiO₂ size went down to about 0.5 nm, the bandgap of TiO_2 was widened by 0.85 eV. This in turn shifted the energy of the conduction band edge of TiO_2 by over 0.5 eV towards negative values. Such a shift in TiO₂ CB 95 now created an energy barrier for the electron transfer from CdS to TiO₂, because the CB edge of TiO₂ had become more negative than that of CdS. This was confirmed by the CdS emission spectra, i.e., the quenching of the CdS emission (the electron transfer from CdS to TiO₂) could no longer be 100 observed as the TiO₂ particle size dropped to 0.5 nm with the CdS size remaining unchanged, as illustrated in Fig. 13.

Fig. 13 Energy level diagram of quantized TiO₂/CdS coupled semiconductors. Reproduced from ref. 169, by permission of the PCCP owner societies.

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It is straightforward that an adequate physical and electric contact (e.g., an ohmic contact) between different semiconductors in a coupled semiconductor assembly is necessary for an effective transfer and hence a significant ¹¹⁰ separation of the charge carriers. Thus, many efforts have been dedicated to this regard. Jang *et al.*¹⁶⁰ prepared a coupled CdS/TiO₂ photocatalyst by coupling CdS nanoparticles with

 TiO_2 nanosheets to maximize the contact between the two phases. The such-coupled photocatalyst showed higher activity for hydrogen production and methylene blue degradation under visible light illumination ($\lambda > 420$ nm) than 5 did a physical mixture of CdS nanoparticles and TiO₂

- nanorods. Co-axial arrays of TiO_2/CdS sheath/core couples were also prepared to increase the contact interface¹⁷⁰, as shown in Fig. 14. The outer layer of the TiO_2 sheath was firstly grown as guided by an anodic aluminum oxide
- ¹⁰ template; then the CdS core was grown within the TiO_2 sheath. This coupling mode has been found to be highly favorable to the vectorial electron transfer between the co-axial CdS and TiO₂.

15 Fig. 14 SEM image of TiO₂/CdS nanocables prepared by templated liquid-phase deposition. Reprinted from ref. 170, Copyright (2005), with permission from Elsevier.

While the above-mentioned methods tried to couple TiO_2 with CdS via direct contact between hard particles, a "soft" ²⁰ coupling scheme was also proposed. Robel *et al.*¹⁶¹ used bifunctional organic molecules as the surface modifier to link CdSe quantum dots (QDs) with TiO_2 nanoparticles, as shown in Fig. 15. The optical absorption properties of the QDs remained unchanged but the emission yield decreased by ²⁵ ~80% when linked to TiO_2 . This indirectly proved the hypothesis that TiO_2 nanoparticles interact with the excited CdSe QDs via a vectorial electron transfer scheme. It should be emphasized that photoactivity depends strongly on the physicochemical properties of the coupled semiconductors,

³⁰ such as the surface area, porosity, adsorption capacity, distribution of the active sites, etc. Upon coupling, besides the vectorial charge transfer, the original properties of the components might also be modified. This complicates the comparison of photoactivity before and after coupling. In ³⁵ many cases, only the total photocatalytic activity, which is the

collective performance of many factors, was studied.

Fig. 15 TiO₂/CdSe couple linked by organic molecules: (a) particleparticle; (b) particle-film.¹⁶¹

40 5. Metal/Semiconductor Composites

- Combining noble metals with semiconductor photocatalysts^{171, 172} on a nanometer scale was proposed to enhance the photocatalytic activity due to their different Fermi levels, characterized by the work function of the metals ⁴⁵ and the band structure of the semiconductors. Upon contact, a Schottky-barrier can be formed between the semiconductor and the metal particle, leading to a rectified charge carrier transfer similar to that in the coupled semiconductors. ^{13, 173, 174} As shown in Fig. 16, irradiation by photons with higher
- ⁵⁰ energy than the semiconductor bandgap generates electrons in the CB of the semiconductor and raises its Fermi level to more negative values.¹⁷⁵ Then, the energetic difference at the semiconductor/metal interface drives the electrons from the CB of the semiconductor into the metal nanoparticles. The

55 Fermi level of the metal is thereby also negatively shifted so

that a secondary electron transfer can occur between the metal and electron acceptors in the redox couples from the surrounding electrolyte. A large number of reports on nanosized Ag, Au and Pt combined with photocatalysts such 60 as TiO_2 have indeed shown increased photoactivity that was consequently explained by this effect.^{176, 177}

Fig. 16 Electron transfer and Fermi level shift at a metal/semiconductor interface.¹⁷⁵

65 5.1 Ag/TiO₂

The combination of Ag and TiO₂ can be achieved in different manners. For instance, Ag nanoparticles can be deposited on the TiO₂ surface by photo-assisted reduction of Ag⁺ ions in aqueous solutions under UV illumination.^{178, 179} Ag/TiO₂ 70 core/shell structures can also be obtained, for example, by firstly reducing Ag⁺ ions to form an Ag core and then hydrolyzing titanium-(triethanolaminato)isopropoxide to form a TiO₂ shell around the Ag particles.^{180, 181} In the absence of electron scavengers, such materials have shown the ability to 75 store the photogenerated electrons transferred from TiO₂ to the Ag cores upon UV excitation, as shown in Fig. 17. The electron transfer continues until a Fermi level equilibrium is established between Ag and TiO₂. The shift in the surface plasmon resonance band is used to measure the number of 80 electrons stored in the Ag core, with an estimation of about 66 electrons per Ag/TiO₂ core/shell structure. This electron storage ability shows the importance of such structures in photon energy conversion by storing electrons during excitation and delivering them back in the dark. Their 85 photocatalytic activity is limited, however, as indicated by a C_{60}/C_{60} probe under UV irradiation.¹⁸¹ Similar electron transfer and Fermi-level equilibration were observed in noble metal/ZnO nanocomposites.182

90 Fig. 17 Electron accumulation in an Ag/TiO₂ core-shell particle under UV irradiation. Reprinted with permission from ref. 180, Copyright 2004 ACS.

High photoactivity of Ag/TiO₂ nanocomposites has been reported, for example, in the decoloration of methyl orange 95 solutions.¹⁸³ This was attributed to the multi-heterojunctions formed by Ag/TiO2 (anatase), Ag/TiO2 (rutile) and anatase/rutile, etc. Although anatase TiO₂ has been known to be more active than rutile TiO2, their coexistence has a positive effect on the photocatalytic activity, as exemplified 100 by the highly active Degussa P25 with a two-phase formula.¹⁸⁴ Ag nanoparticles were also intercalated between TiO₂ nanosheets, and a larger photocurrent could be obtained as compared with pure TiO₂ films.¹⁸⁵ This was explained by the enhanced photoelectron conduction between TiO₂ layers 105 due to metallic Ag. Under visible light irradiation (wavelengths longer than 470 nm), photooxidation of Rhodamine B by Ag/TiO₂ can be achieved due to the following mechanisms¹⁸⁶: 1) The dye molecules are photosensitive and can be excited to generate electrons that 110 are then transferred to the TiO_2 CB; 2) TiO_2 under visible light illumination only acts as the electron acceptor from the excited dye due to its large bandgap; 3) the Ag nanoparticles attract the electrons from the TiO_2 CB due to the Schottky barrier effect; 4) Ag nanoparticles can also act as efficient dye-adsorption sites, where oxidant species can be formed ⁵ from electron scavenging by adsorbed oxygen molecules.

- Under a bias potential, Ag/TiO_2 thin film photoelectrodes on ITO glass can efficiently degrade formic acid. Both Ag loading and the bias potential are responsible for the increased activity. Ag not only traps the photoelectrons from TiO₂ but
- ¹⁰ also assists the bias electric field to drive the photoelectrons into the external circuit.

Photocatalytic reduction has also been studied employing Ag/TiO_2 nanocomposite powders with very small Ag clusters (diameter ~ 1.5 nm) and low Ag loading (~0.24wt%) prepared ¹⁵ by a photo-assisted deposition method.¹⁸⁷⁻¹⁸⁹ The composite showed very high efficiency in the photocatalytic reduction of

- nitrobenzene and bis(2-dipyridyl)disulfide. The Ag^0 nanoclusters attracting the photoelectrons from the TiO₂ CB worked as selective adsorption/reduction sites for
- ²⁰ nitrobenzene and bis(2-dipyridyl)disulfide, while the TiO_2 surface with trapped photogenerated holes served as oxidation sites. The high efficiency of such reactions was explained by the combined effects of selective adsorption and rectified charge separation. Photoactivity enhancement was also
- ²⁵ observed in the photoreduction of selenate ions by Ag/TiO_2 .¹⁹⁰ Without Ag, the selenate was firstly reduced by photoelectrons to Se⁰. Then, upon the exhaustion of the selenate in the solution, the as-formed Se⁰ was further reduced to H₂Se. In the presence of Ag, the selenate was directly
- ³⁰ reduced to H_2Se . The photoelectrons were thought to be transferred from TiO₂ to Se⁰ via Ag. The accumulation of electrons in Se⁰ before the exhaustion of Se(VI) led to the reduction of Se⁰ to Se²⁻. It is necessary to take into account the reaction kinetics to elucidate the mechanism of this ³⁵ photoreduction process, in addition to thermodynamics considerations (i.e., the Fermi level differences between TiO₂, Ag, Se⁴⁺/Se⁰ and Se⁰/Se²⁻, etc.).

It is the contact between metallic particles and semiconductors that forms the Schottky barrier between them, ⁴⁰ but noble metals do not always exist in the pure metallic form in their composite. Certain parts of the metals can be oxidized to form ions. Xin *et al.*¹⁹¹ reported three types of silver species, including Ag₂O, AgO and Ag⁰, in the Ag/TiO₂ composites prepared by a sol-gel method. At lower Ag

- ⁴⁵ loadings (< 0.3mol%), silver mainly exists as Ag_2O and AgO, whereas at higher loadings (up to 5 mol%), all three types exist with Ag^0 being the dominant one. Ag_2O may introduce impurity band levels within the material. The oxygen-related surface states are multiple due to various valence states of Ag
- ⁵⁰ species. Two O1s peaks from Ag-O and Ag⁰-adsorbed O were confirmed in addition to the lattice O, surface bridging O and the surface hydroxyl O in TiO₂. The improved photocatalytic degradation of Rhodamine B by Ag/TiO₂ indicates that both oxidized and metallic silver can effectively capture the
- ⁵⁵ photogenerated electrons and enhance the photoactivity of TiO_2 . Kumar *et al.*¹⁹² studied the photoaxidation of aniline using Ag/Ag⁺-loaded TiO_2 and found an improvement in the photoactivity due to similar reasons.

Noble metal nanoparticles are expected to undergo 60 morphology transformation after long time exposure to light.^{184, 193-196} For example, Ag particles 40-60 nm in size in water can be fragmented into smaller particles when exposed to highly energetic laser pulses.¹⁹⁷ Photoinduced structural changes were also observed in Ag nanoparticles deposited on 65 glass.¹⁹⁸ Moreover, optical irradiation was used for synthesis purposes to convert Ag nanoparticles into triangular nanoprisms with special optical properties.¹⁹⁹ The size and morphology dependency of the catalytic activity of nanomaterials has been well emphasized in the literature.²⁰⁰⁻ 70 204 Moreover, the electron or hole scavengers in solution can also affect the oxidation or reduction of the metals.²⁰⁵ For example, in an Ag/TiO₂-nanorod composite, the Ag particles diminished upon UV irradiation with oxygen as electron scavengers in the solution.²⁰⁶ Recognition of such problems is importance in designing great high-efficiency 75 of nanocomposite photocatalysts.207

Photochromic materials, which change their colors reversibly in response to light, can be used in smart windows, displays and memory devices.²⁰⁸ While conventional 80 photochromic materials respond monochromatically, multicolor-photochromism often requires combinations of different materials or filters. If this can be achieved on a single material, photochromic devices would find broader applications such as in rewritable color copy paper, electronic 85 paper and multi-wavelength optical memory.²⁰⁹ Tatsuma and coworkers²¹⁰⁻²¹² recently explored an interesting property of Ag/TiO₂ film, as shown in Fig. 18. The film color was initially brownish-gray. Upon visible light irradiation, it was changed to be identical to the incident light and could be 90 changed back to brownish-gray under UV light. This multicolor response arose from the broad absorption of the Ag/TiO2 film ranging from 350 to 700 nm, due to the diversity in size and morphology of Ag particles and to the high refractive index of the TiO₂ matrix.

95

Fig. 18 Multi-colored Ag/TiO₂ film. Reprinted by permission from Macmillan Publishers Ltd.: [Nature Materials] (ref. 210), copyright (2003).

5.2 Au/TiO₂

100 Despite its bulk inertness, Au nanoparticles with diameters smaller than 5 nm on TiO₂ supports have shown high catalytic activity in chemical reactions such as low-temperature CO oxidation²¹³⁻²¹⁵, water-gas-shift reactions and epoxidation of propylene.²¹⁶ Au nanoparticles are also able to enhance 105 photocatalytic reactions if incorporated into photocatalysts like TiO₂.²¹⁷ For example, Au/TiO₂ photoelectrodes under visible light irradiation generate photocurrents due to Au surface plasmon resonance. Photoelectrocatalytic production of hydrogen gas using Au/TiO₂ film electrodes was also ¹¹⁰ attempted.²¹⁸ Different preparation methods such as impregnation, photodeposition, deposition-precipitation and sol-gel have been employed to achieve Au/TiO₂ composites. Their photoactivity indeed showed a dependence on the preparation methods. Mechanisms on the role of Au 115 nanoparticles were investigated by the aid of electrochemical, photochemical and spectroelectrochemical probing techniques.^{218, 219} For example, due to the stability of C_{60}^{-} in N_2 and the ease to follow its optical absorption at 1075 nm, C_{60}/C_{60}^{-} redox couples were used as a convenient probe to s determine the Fermi levels of the Au/TiO₂ composite system.

- According to the report by Subramanian *et al.*^{175, 220}, the Fermi-level shift in Au/TiO₂ composites showed a size dependency (20 mV for 8 nm, 40 mV for 5 nm and 60 mV for 3 nm Au particles). The influence of the Au particle size on
- ¹⁰ the photoelectrochemical behavior of the respective Au/TiO₂ system was probed by isolating the individual charge transfer steps as shown in Fig. 19. Upon UV irradiation in the presence of ethanol, photoelectrons were trapped in Ti^{4+} sites in the TiO₂ nanoparticle suspension. After addition of Au
- ¹⁵ nanoparticles with controlled size, the trapped electrons were then transferred to Au, as indicated by the decreased blue coloration. Once C_{60} was introduced, the electrons trapped at the Au nanoparticles were further transferred to reduce C_{60} to form C_{60}^{-} as confirmed by the quantifiable increase in the
- ²⁰ 1075 nm absorption intensity. This probing technique is very helpful for understanding photoreduction processes on these nanocomposite materials.

Fig. 19 Photoelectron transfer in Au/TiO_2 probed by C_{60}/C_{60} couple.25Reprinted with permission from ref. 175, Copyright 2004 ACS.

Au/TiO₂ nanocomposites have shown high activity in photocatalytic degradation of various organic compounds. Li et al.²²¹ studied photooxidation of methylene blue by Auloaded TiO₂ in aqueous solutions. The high Schottky barrier 30 existing between TiO₂ and Au nanoparticles facilitated the photoelectron transfer out of the TiO₂ CB and enhanced the electron/hole separation. Meanwhile, the existence of ionic Au⁺ and Au³⁺ species served as traps for charge carriers, which also contributed to the charge separation. Au loading 35 should be controlled properly to achieve the optimum performance. This is because Au ionic impurity levels can also act as charge recombination centers, which becomes relevant particularly at very high Au loadings. A similar tendency was found in Au/TiO₂ thin film composites with Au $_{40}$ deposited over the TiO₂ layer via electron beam evaporation.²²² With these structures, the highest photoactivity for methyl orange degradation was obtained at a

- surface Au concentration of about 0.8 μ g cm⁻². The Au particle size also affected the performance. As the Au ⁴⁵ concentration increased, its particle size also increased to benefit the photoelectron transfer because the distance between the trapped electrons and remaining holes became larger. Very high Au loadings, however, resulted in a high coverage of the TiO₂ surface area, leaving a smaller surface
- $_{50}$ exposed for light absorption and methyl orange adsorption. Compared with bare TiO₂, enhancement in phenol photodegradation was also reported with Au/TiO₂ thin film electrodes.²²³

Based on their experimental results concerning ethanol and ⁵⁵ methanol photooxidation by Au/TiO₂ composites under visible light illumination, Tatsuma *et al.*²²⁴ proposed a plasmon-induced charge separation scheme. They observed a interesting phenomenon in which the photoelectrons were excited from Au nanoparticles and transferred to the TiO₂ ⁶⁰ CB.^{175, 182} Meanwhile, the oxidized Au species accepted electrons from the donor molecules present in the solution to recover the charge balance. The process is illustrated in Fig. 20.

5 Fig. 20 Charge separation upon visible-light irradiation on Au/TiO₂. Reprinted with permission from ref. 224, Copyright 2005 ACS.

The photocatalytic activity of Au/TiO_2 nanocomposites mainly depends on the effectiveness of the electron transfer between Au and TiO_2 resulting in an improved electron-hole ⁷⁰ separation. The charge transfer behavior is dictated by the specific electronic structures of both Au and TiO_2 . The socalled Schottky barrier effect only provides the conceptual explanations on how the charge transfer proceeds. Other factors such as the particle sizes, lattice defects, oxygen ⁷⁵ vacancies, surface states in both components²²⁵ and the chemical environment surrounding the heterojunctions, etc. also influence the characteristics of the heterojunctions within the composite materials.

5.3 Pt/TiO₂

- ⁸⁰ Platinization of semiconductor photocatalysts like TiO₂ has become a routine practice to enhance photoactivity.²²⁶⁻²²⁸ Pt nanoparticles showed very fast electron trapping from semiconductor CB upon light excitation.¹⁸² Other factors such as selective adsorption of reactants at the Pt surface may also ⁸⁵ contribute to the observed activity enhancement. There were also cases in which Pt-loading showed no positive effects on photocatalytic performance.^{141, 184, 229} This indicates that the charge carrier transfer in a Pt/semiconductor composite is as complicated as in the Ag and Au counterparts.
- ⁹⁰ Platinized TiO_2 has long been used as a photocatalyst for a variety of reactions.^{40, 230-232} The role of Pt nano-contacts as electron traps was confirmed by transient absorption spectra analysis of Pt/TiO₂ powders.²³³ As shown in Fig. 21, in addition to the normal decay of the transient absorption of the
- ⁹⁵ trapped CB electrons in TiO_2 at 600 nm due to the electron/hole recombination following 390 nm excitation, a new decay component lasting a few picoseconds was observed and interpreted as the photoelectron migration from TiO_2 to Pt. In pure TiO_2 samples, no such decay occurred within 25
- ¹⁰⁰ picoseconds. This clearly proved that the charge carrier separation can be enhanced by Pt trapping of the electrons from the TiO₂ CB. Consistent with this mechanism, a recent study²³⁴ revealed that the photoluminescence of Pt/TiO₂ under UV irradiation was blue-shifted upon increasing Pt content.
- ¹⁰⁵ The excited electrons accumulated in the Pt particles possess higher energy, so that the electron/hole recombination emitted shorter-wavelength luminescence, as compared with that for pure TiO_2 .
- Fig. 21 Transient absorption spectra of irradiated TiO₂ and Pt/TiO₂. Reprinted from ref. 233, Copyright (2001), with permission from Elsevier.

Bahnemann *et al.*²³¹ studied the surface trapping of photoelectrons and holes in a platinized TiO₂ sol and assigned the trapping mode to different scavengers by the laser flash photolysis technique combined with transient absorption ⁵ spectroscopy. Anpo *et al.*²³⁵ compared the effect of Pt loading on the photoactivity for the hydrogenation of CH₃C=CH and C₃H₆ by TiO₂ and ZnO and found that Pt increased the photoactivity of both catalysts. Electron trapping by adsorbed protons on Pt may be responsible for this enhancement. A

- ¹⁰ comparative study on photocatalytic H₂ generation between Pt/TiO₂ and Au/TiO₂ powders suggested that Pt can be a better trapping site for photoelectrons than is Au.²¹⁷ Another comparison was made between Ag/TiO₂, Pt/Ag/TiO₂ and Pt/TiO₂ catalysts for the photocatalytic dehydrogenation of 1-
- ¹⁵ propanol.²³⁶ In Pt/Ag/TiO₂, the photoelectrons can be effectively transferred from TiO₂ via Ag to Pt clusters where chemically dissociated hydrogen was adsorbed to generate H₂. Favorable adsorption of reactants on Pt clusters was also confirmed in the photooxidation of CO.¹⁹⁴ Uchida *et al.*²³⁷
- $_{20}$ proposed a novel configuration of Pt/TiO₂ electrodes for the photodegradation of 1,2,4-trichlorobezene (TCB). As shown in Fig. 22, TiO₂ and PTFE particles were first deposited together on an ITO substrate via an electrophoretic method. Then Pt nanoparticles were photo-deposited into the
- ²⁵ TiO₂/PTFE matrix. PTFE showed affinity towards both O₂ and TCB, which led to efficient TCB adsorption and photoelectron consumption for O₂ reduction. Pt particles promoted the electron transfer within the matrix and their reaction with O₂ molecules.
- ³⁰ Zhao *et al.*²³⁸ studied the photo-destruction of sulforhodamine-B in Pt/TiO₂ suspension under visible light. The electrons excited from dye molecules were accepted by Pt islands. The accumulated electrons then reacted with O₂ to form O₂· and ·OH, which ultimately caused the self-
- as destruction of the dye molecules. Photocatalytic destruction of oxalic acid²³⁹ and H₂ generation²⁴⁰ from an aqueous methanol solution were also promoted by platinizing TiO₂. Under anoxic conditions, products from photocatalytic reactions using Pt/TiO₂ may be different from those using pure TiO₂.
- ⁴⁰ For example, although the reaction rate of alkylamine degradation was increased by the presence of Pt, some undesirable toxic byproducts were also generated.²²⁷ Quan *et al.*²⁴¹ reported a synergetic effect on the photoelectrocatalytic degradation of 2,4-dichlorophenoxyacetic acid using a
- ⁴⁵ Pt/TiO₂/Ti electrode. The degradation efficiency was higher than the sum of the individual photocatalytic and electrochemical efficiencies. Suppression of the charge carrier recombination benefits from the trapping of photoelectrons by Pt while the charge carrier separation is improved by the ⁵⁰ external bias potential.

Fig. 22 Pt-loaded TiO₂-PTFE film photoelectrode deposited on ITO glass substrate. Reprinted from ref. 237, Copyright (1998), with permission from Elsevier.

55 6. Doped Semiconductor Photocatalysts

Wide bandgap semiconductor materials have long served as

active photocatalysts. But their main drawback is actually the wide bandgap, as it only allows very limited utilization of solar energy. Accordingly, the red-shift of their absorption ⁶⁰ edge into the visible light region has been widely attempted. Sensitization by dye molecules has shown encouraging results in dye-sensitized solar cells.^{49, 67, 242-244} However, in most photocatalytic systems, the dyes are usually not stable once the photocatalyst is exposed to bandgap illumination. Another

- ⁶⁵ way to shift the absorption towards the visible region is to dope the semiconductors with ionic species.²⁴⁵ Although not all the results were successful, quite a few studies provided very encouraging results for the development of visible-lightactive photocatalysts. While the light absorption edge could
- ⁷⁰ be red-shifted by this type of doping, the photoactivity after doping may not necessarily be improved. The measured absorption spectra of a photocatalyst are the overlapped results from several absorption bands of different origins, such as intrinsic bulk absorption, surface states absorption, ⁷⁵ and absorptions from defects, etc. As a result, the absorption by intra-bandgap states may not form sufficiently strong oxidants for certain reactions. The absorption spectra for a photocatalyst should not be expected to match entirely with the action spectra of its photocatalytic performance. Although ⁸⁰ numerous theoretical and experimental results concerning doped photocatalysts have already been published, a clear

mechanistic understanding of the role of dopants and the

behavior of the photocatalysts is far from being established.

6.1 Non-Metal-Doped Semiconductor Photocatalysts

85 Earlier studies²⁴⁶⁻²⁴⁸ on anionic doping used N-containing TiO₂ obtained from calcination of titanium hydroxide/NH₄Cl (or NH₄OH), thermal oxidation of TiN, or chemical vapor deposition with titanium(IV) isopropoxide and nitrous oxide. Other choices of dopants included C, F, S and P, etc., which 90 have been subject to investigations on optical absorption, photocatalytic activity and/or band structure calculations. Nitrogen has been the most intensively studied non-metal-ion dopant for TiO₂, as can be seen from the increasing number of publications every year on N-doped TiO₂. Even for this single 95 dopant, various mechanisms have been proposed to explain its effect on the light absorption and photoactivity of N-doped TiO₂, i.e., the bandgap narrowing by overlapping between N 2p and O 2p orbitals^{249, 250}, creation of oxygen vacancies²⁵¹, ²⁵², generation of intra-bandgap surface states, or combined ¹⁰⁰ effects among them.²⁵³ A schematic diagram shown in Fig. 23 displays these possible mechanisms.²⁵¹

Fig. 23 Various schemes of band structure change of: (a) Pure anatase TiO₂; (b) Doped-TiO₂ with localized dopant levels near the CB and VB edges; (c) Bandgap narrowing due to VB broadening; (d) Localized dopant levels and electronic transitions to the CB; (e) Electronic transitions of dopant levels near the VB edge to corresponding excited states for Ti³⁺ and F⁺ centers. Reprinted with permission from ref. 251, Copyright 2006 ACS.

110 6.1.1 Bandgap Narrowing

Asahi and coworkers²⁵⁰ published results from both theoretical density-of-states (DOS) calculations of the band structures and photocatalytic experiments of non-metal-ion

doped TiO₂ in 2001. They claimed that among C, N, F, P and S, the most effective substitutional dopant was N for the bandgap narrowing of TiO₂. As shown in Fig. 24, the calculated p states from N dopants mix with O 2p states from TiO₂ to parameter the

- ${}_{5}$ TiO₂ to narrow the bandgap and effectively transfer the photoexcited charge carriers to the reactive sites at the TiO₂ surface within their lifetime. Although doping by S shows a similar bandgap narrowing, the ionic radius of S is too big to enable it to be substituted into the TiO₂ lattice. (This may not
- ¹⁰ be a serious problem if S-doped TiO₂ is prepared by thermal oxidation of TiS₂ instead of using S to attack the O in the TiO₂ lattice.²⁵⁴) The states introduced by C and P are energetically too deep in the bandgap of TiO₂ to promptly transfer the charge carriers to the surface reactive sites.
- ¹⁵ Calculations on interstitial N doping and substitutional-andinterstitial N doping indicate the existence of molecular dopants with bonding states quite similar to those of NO and N_2 molecules. Such dopants give rise to bonding states below the O 2p valence bands and antibonding states deep in the
- $_{\rm 20}$ bandgap (Fig. 24B, $N_{\rm i}\text{-}doped$ and $N_{\rm i+s}\text{-}doped)$, which hardly interact with the band states of TiO_2 and therefore are not effective in transferring the photogenerated charge carriers. This argument was confirmed by testing the visible-light-driven photocatalytic degradation of aqueous methylene blue
- ²⁵ and gaseous acetaldehyde and XPS analysis of the atomic-N peak area (corresponding to a binding energy of 396 eV²⁴⁷), because the N-doped TiO₂ sample with the highest fraction of the atomic N state (the area of the 396 eV peak over the total area of 396, 400 and 402 eV peaks; the latter two peaks
- ³⁰ correspond to the molecularly chemisorbed states²⁴⁷) shows the highest photocatalytic degradation rate. Contrary opinions exist about whether substitutional or interstitial N-doping is more effective. Diwald *et al.*²⁵⁵ doped TiO₂(110) single crystals with N by an NH₃ treatment at 870 K and found that ³⁵ it is the interstitial nitrogen that was responsible for the red-
- shift of the light absorption down to a lower energy.

The work by Asahi *et al.*²⁵⁰ inspired a new tide of research to find visible-light-active photocatalysts based on doped ⁴⁵ TiO₂, which seemed to be able to benefit from the guidance of theoretical calculations although their reliability could not be easily estimated. Umebayashi *et al.*²⁵⁶ found that the mixing of S 3*p* states with the VB of anatase TiO₂ resulted in the bandgap narrowing of S-doped TiO₂, which is consistent with ⁵⁰ Asahi and coworkers' results. Based on first-principles

- calculations, Yamamoto *et al.*²⁵⁷ also obtained a bandgap narrowing of rutile TiO_2 induced by S doping. Based on plane-wave-based pseudopotential density functional theory calculations, Tian and Liu²⁵⁸ presented a similar bandgap
- ⁵⁵ narrowing by mixing O 2p with S 3p states in S-doped anatase TiO₂. Recently, Wang and Louis²⁵⁹ recalculated the band structures of C, N and S-doped TiO₂, showing that their dopant of choice was C for the development of visible-light-

active TiO₂-based photocatalysts, in contrast to the suggestion ⁶⁰ by Asahi *et al.* that the energy states induced by C do not effectively overlap and mix with O 2*p* states. These groups of researchers do share a common recognition concerning the bandgap narrowing by mixing the O 2*p* orbitals with the introduced energy states near the VB edge of TiO₂. ⁶⁵ Umebayashi *et al.*²⁶⁰ experimentally investigated the optical properties of S-doped anatase TiO₂ prepared by annealing TiS₂. The diffuse reflectance spectra showed that the absorption edge was shifted towards the lower energy region due to the bandgap narrowing by mixing S 3*p* states with the

TiO₂ VB. By studying the visible-light-activity of C-doped TiO₂ made from thermal oxidation of TiC powders, Irie *et al.*²⁶¹ suggested that the bandgap narrowing could be seen even at a low carbon loading (~0.32%). It is obvious from these results that considerable hesitation concerning the ⁷⁵ reliability of theoretical calculations, aiming for the prediction of the electronic band structures of doped semiconductors, is most certainly indicated because the predictions of these studies do not agree with each other. Moreover, a large number of experiments seem to prove that it is not by bandgap ⁸⁰ narrowing but by newly formed localized energy states that the visible-light absorption of doped-TiO₂ is enhanced.

6.1.2.1 States Close to the Conduction Band Edge

Color centers are one type of the intra-bandgap energy state in ss semiconductor materials. Color centers are formed in a metal oxide upon the loss of an oxygen atom. The electron pair that remains trapped at the cavity gives rise to an F center; a positively charged F⁺ center is equivalent to a single electron residing at the oxygen vacancy. The electron-pair deficient 90 oxygen vacancy is referred to as a doubly charged F⁺⁺ center; the electrons left in the cavity can also react with adjacent Ti⁴⁺ ions to give Ti³⁺ centers.^{262, 263}

In most fluoride (F^{-})-doped TiO₂ photocatalysts, the main reason for the improved light absorption was the color centers 95 formed upon F⁻ incorporation. For example, Li et al.²⁶⁴ studied F-doped TiO₂ from spray pyrolysis of H₂TiF₆ and found high photocatalytic activity in the decomposition of gaseous acetaldehyde under both UV and visible light irradiation. XPS analysis revealed two types of color centers 100 in the sample, i.e., the oxygen vacancies with either two trapped electrons (F centers) or one trapped electron (F⁺ centers). As indicated in the excitation/emission pathways shown in Fig. 25, both types of color centers formed trapped states below the CB edge of TiO₂ (0.53 eV for F centers and 105 0.84 eV for F⁺ centers, respectively) as deduced from the photoluminescence spectra. Ho and coworkers²⁶⁵ prepared hierarchical-structured F-doped TiO₂ nanospheres exhibiting visible light photoactivity, which was also explained by the extrinsic absorption resulting from the color centers formed 110 upon F-doping. Ihara et al.²⁵² prepared an N-doped TiO₂ photocatalyst by calcination of the hydrolysis products of $Ti(SO_4)_2$ with ammonia. The resulting powder showed visible light absorption between 400 and 550 nm that was interpreted as being due to the creation of oxygen vacancies preferably at 115 the grain boundaries of TiO_2 . These oxygen vacancies were thought, in turn, to reduce the cation charge and coordination number, leading to localized states between the CB and VB of TiO_2 (without pinning their positions) and thus allowing excitation pathways to be initiated with sub-bandgap energy.²⁶⁶ Lin *et al.*²⁶⁷ quantified the position of the donor ⁵ states introduced by oxygen vacancies by theoretical calculations as being localized at 0.15-0.30 eV below the CB edge. Martyanov *et al.*²⁶⁸ prepared oxygen-deficient TiO₂ by annealing TiO and Ti₂O₃ powders under O₂ atmosphere. In this way, the interference from N-doping on oxygen vacancies

¹⁰ could be excluded since no N was involved in the preparation of TiO_2 .

Fig. 25 Possible energy states between the CB and VB of Fluorine-doped TiO₂. Reprinted from ref. 264, Copyright (2005), with permission from Elsevier.

Oxygen vacancies were also said to be responsible for the visible-light-activity of C- and S-doped TiO₂. Li *et al.*²⁶⁹ prepared C-doped titania by carbonization of anatase TiO₂, and the product showed optical absorption bands up to 700 nm ²⁰ and much higher photooxidation activity for gas-phase benzene than pure TiO₂ under artificial solar irradiation. These observations were explained by the presence of oxygen vacancies and the formation of Ti³⁺ levels between the CB and VB. Yu and coworkers²⁷⁰ observed considerable anti-bacterial

- ²⁵ photoactivity of S-doped TiO_2 for killing bacteria under visible light illumination that was explained by the formation of intra-bandgap S⁶⁺ states close to the CB edge of TiO₂. Ohno *et al.*^{271, 272} proposed that sulfur incorporated into a TiO₂ lattice mainly substitutes S⁴⁺ for Ti⁴⁺ based on XPS
- $_{30}$ analysis (the S⁶⁺ peaks found in their XPS spectra were claimed to be sulfuric acid adsorbed on the TiO₂ surface). First-principles calculations carried out by the authors indicate the formation of S⁴⁺ states near the CB edge of TiO₂ that account for the visible light absorption and photoactivity
- ³⁵ for 2-propanol decomposition. Note that S dopants do not always substitute for Ti with the specific doping mode depending largely on the methods of preparation.^{254, 273} Theoretical calculations also showed that oxygen vacancies in TiO₂ lattices were also able to accommodate S atoms.²⁷⁴
- ⁴⁰ Visible-light-active P-doped TiO₂ was also prepared and it was reported that phosphorus atoms exist in their pentavalent form and act as impurity levels to trap photogenerated electrons.²⁷⁵ Based on the common features reported for most doped TiO₂ photocatalysts, i.e., the formation of oxygen
- ⁴⁵ vacancies and color centers that are inevitably due to a partial reduction of TiO_2 at a certain point during the preparations of the materials, Serpone^{251, 276} argued that the red-shift of the absorption edge is indeed caused by such color centers (Fig. 23e).
- 50 6.1.2.2 States Close to the Valence Band Edge

Theoretical calculations by Lin *et al.*²⁶⁷ suggested that N-doping did not narrow the bandgap of TiO₂ by mixing O 2p with N 2p orbitals, even at much higher N concentrations than those used by Asahi *et al.*²⁵⁰. Instead, their calculations

ss predicted that the N 2*p* states are localized near the top of the VB of TiO₂. Only at very high dopant levels (~20%) would the N 2*p* states mix with the O 2*p* orbitals, leading to bandgap

narrowing. However, in practice, too much N loading results in the formation of TiN, which is not transparent in the visible 60 region. Moreover, it is questionable whether or not a semiconductor can maintain its chemical and electronic structural integrity after incorporating a large amount of foreign dopants.²⁵¹ The highest experimentally achieved N loading in TiO₂ was reported to be $8\%^{277}$, which is far below 65 the amount required for bandgap narrowing as calculated by Lin et al.²⁶⁷ While dopant loading is pertinent to the properties of the doped materials, their distribution within the materials, which is closely related to the preparation methods, should never be ignored. As shown by Takeshita and 70 coworkers,²⁵⁴ even with similar sulfur loadings in TiO₂, different distributions of S resulted in significant differences in their photoactivity under visible light illumination. Di Valentin et al.²⁷⁸ conducted density functional theory (DFT) calculations revealing that besides the substitutional N 2p 75 states, states formed by interstitial N are located higher than substitutional N 2p states above the VB edge and are expected to contribute to the red-shift of the absorption edge. However, these interstitial N dopants might behave as strong hole trapping sites thus reducing the direct oxidizing power of 80 doped TiO₂.²⁷⁹

Theoretical calculation results predicting the localized states above the VB edge have been confirmed by some photocatalytic experiments N-doped using TiO₂ photoelectrodes. Nakamura et al.280 determined the mid-85 bandgap surface state positions by studying the photooxidation of various hole scavengers (e.g., SCN, Br and I^{-} , etc.) with unique oxidation potentials, under both UV and visible light irradiation. The estimated energy levels of the surface states are shown in Fig. 26. Hence, the possibility of a 90 bandgap narrowing resulting from an overlapping between O 2p and N 2p orbitals was excluded by the observed oxidizing power variation of the photogenerated holes under different irradiation conditions.

95 Fig. 26 The band structure of N-doped TiO₂ with the oxidation potentials of a few redox couples. Reprinted with permission from ref. 280, Copyright 2004 ACS.

Miyauchi et al.²⁸¹ supported this conclusion by testing the photoactivity of N-doped TiO2 under visible light 100 illumination. compared They the photocatalytic decomposition of 1-propanol under UV and visible light illumination and found that the reaction rate under UV irradiation is much higher than that under visible light illumination. If the visible-light-activity of N-doped TiO₂ ¹⁰⁵ were due to the mixing of N 2p with O 2p levels, then the photoactivity should not differ much under these different irradiation conditions. However, the quantum yield (defined as the number of oxidized 1-propanol molecules per absorbed photon) of N-doped TiO_2 is lower than that of pure TiO_2 110 under UV irradiation. This observation suggested a negative effect of N-doping, i.e., the energy states formed by doping acted as the recombination centers for electrons and holes and should thus be located in the mid-bandgap region between VB and CB.

The possible role of dopant species as recombination centers was also confirmed by other researchers. Lindgren *et al.*²⁸² studied the photoelectrochemical *i*-*V* characteristics of a N-doped TiO₂ film electrode under modulated irradiation. As 5 shown in Fig. 27, white light caused hardly any photoresponse from the un-doped TiO₂ film electrode (Fig. 27a), whereas there was an obvious photoresponse with the N-doped TiO₂ film electrode (Fig. 27b). Pronounced photocurrent transients were seen in a wide bias-potential range around the

- ¹⁰ photocurrent onset, indicated by the circle in Fig. 27b. The transients together with the nearly linear increase in the photocurrent under a positive bias-potential are typical indicators of a high electron/hole recombination rate under stable irradiation.
- 15

Fig. 27 i-V characteristics of pure TiO₂(a) and N-doped TiO₂(b) irradiated by white light. Reprinted with permission from ref. 282, Copyright 2003 ACS.

Sakthivel and Kisch²⁵³ prepared nitrogen-doped ²⁰ (0.08~0.13wt%) titania by hydrolysis of TiCl₄ with nitrogencontaining bases, followed by a 400 ⁰C calcination in air. Diffuse reflectance spectra showed that the catalyst could absorb visible light (a wavelength between 400 and 520 nm). The bandgap energy of the doped TiO₂ was estimated to be

- $_{25}$ 3.12 eV by plotting the modified Kubelka-Munk function in relation to the photon energies. This bandgap is slightly smaller than that of pure anatase TiO₂ and was ascribed to bandgap narrowing due to a modest anodic shift in the CB edge. Since the light absorption edge was 520 nm (2.39 eV,
- ³⁰ which is much smaller than 3.12 eV), the authors proposed that some localized energy states above the VB edge must exist. The positions of these states were determined by measuring the wavelength-dependence of the photooxidation of different charge carrier scavengers. The final band structure

³⁵ suggested by these authors is shown in Fig. 28.

Fig. 28 Electrochemical potentials (versus NHE) for band edges, surface states (shaded areas) and oxygen reduction at pH 7 for TiO₂ and N-doped TiO₂. Reproduced with permission from ref. 253, Copyright 2003 Wiley-VCH.

6.2 Transition-Metal-Doped Semiconductor Photocatalysts

In transition-metal-doped semiconductors, there are also two different positions that the dopant ions can occupy in a semiconductor lattice, i.e., substitutional and interstitial. If the

- ⁴⁵ ionic radius of the dopant is similar to that of the matrix cation, the dopant will conveniently take the substitutional mode; if the dopant radius is much smaller than the matrix cation, interstitial doping is also possible.²⁸³ Some studies even suggest that interstitial doping is possible for dopant ions
- ⁵⁰ larger than the matrix cation.²⁸⁴ Note that the dopant ions should be within an appropriate concentration to exclude phase separation between the dopant and the matrix.^{285, 286} Compared with the valence states of the matrix cations, cationic dopants can be divided into two categories: those
- ss with valence states higher than those of the matrix cations, and those valence states that are lower than those of the

matrix cations. In the TiO_2 matrix, these two types of dopants behave in distinctly different ways, i.e., the higher-valence dopants act as electron donors and are therefore called *n*-type 60 dopants, while the lower-valence dopants act as electron acceptors and are called *p*-type dopants.

Transition metal dopants influence wide bandgap semiconductor photocatalysts with at least two effects^{283, 287}: changing the bulk electronic structure of the matrix ⁶⁵ semiconductor (resulting in, e.g., changes in the position of the Fermi level, the formation of new energy levels by the interaction of the dopant with the matrix lattice, changes in the electron conductivity within the matrix semiconductor^{288, 289}), and/or modification of the surface properties. The latter

⁷⁰ can be linked with the variations of the thickness of the space charge layer, changes in the concentration of surface states, and the initiation of photocorrosion processes.^{290, 291} Studies focused on metal-ion-doped photocatalysts can be traced back to the 1980s.^{226, 292} Electron paramagnetic resonance (EPR)

⁷⁵ was applied by researchers to study the doped TiO_2 to discriminate the various doping modes in both anatase and rutile TiO_2 . Since then, doping of photocatalysts with metal ions has been investigated extensively with the consequence that nearly all metals in the periodic table of elements have ⁸⁰ been tried as dopants.^{176, 283, 287, 291, 293-325} In this section, only some mechanistic principles and a few examples based on doped-TiO₂ have been selected to illustrate the influence of metal-ion dopants on photocatalysts.

6.2.1 Formation of New Energy Levels

- ⁸⁵ Upon metal-ion doping, new energy states can be formed either within or beyond the bandgap of semiconductors. The diagram in Fig. 29 qualitatively provides a scenario illustrating where the dopant levels could be within the energy diagram of a metal-ion-doped TiO₂.²⁸³
- ⁹⁰ The most frequently employed valence states of Cr and Fe ions are Cr^{3+} and Fe^{3+} , respectively. If these cations are incorporated into the TiO₂ lattice by substituting Ti⁴⁺ cations, the electroneutrality as a whole requires the simultaneous formation of oxygen vacancies, the amount of which should ⁹⁵ be equal to half of the substitutional trivalent cation dopants incorporated at Ti⁴⁺ sites, as shown in Eq. (25):

$$M_2O_3 \rightarrow 2 \mid M^{III} \mid'_{Ti} + V_0^{\bullet \bullet} + 3O_0$$
 (25)

where M refers to the corresponding metals (Fe or Cr); V_0 " represents the oxygen vacancy, the energy level of which lies ¹⁰⁰ slightly below the CB edge as shown in Fig. 29; O_0 denotes the oxygen atom at its normal lattice site. Consequently, only a fraction of the dopant centers will have a full-coordination sphere of lattice oxygen atoms, while the other dopant centers are in the position of having an oxygen vacancy at a nearest ¹⁰⁵ neighbor site. Similarly, for pentavalent dopants such as V⁵⁺, the following equation holds:

$$2M_2O_5 \rightarrow 4 |M|_{Ti}^{5\bullet} + 5V_{Ti}^{4'} + 10O_0$$
 (26)

where $V_{Ti}^{4'}$ represents cation vacancies that are good hole acceptors (as shown in Fig. 29, after excitation holes in the ¹¹⁰ VB can be trapped at these sites to form $V_{Ti}^{"'}$ and $V_{Ti}^{"}$ states above the VB edge); $|M|_{Ti}^{5^{\bullet}}$ denotes the defect sites that are good electron acceptors (upon acceptance of one or two photoelectrons, V⁴⁺ and V³⁺ states can be formed within the bandgap).

5

Fig. 29 Energy states in TiO₂ after being doped by Fe, Cr and V ions. Reprinted with permission from ref. 283, Copyright 1994 ACS.

6.2.2 Enhanced Visible Light Absorption

Due to the formation of intra-bandgap energy levels, the light 10 absorption edge can be red-shifted by electronic transitions from the VB to these levels and/or from these levels to the CB. In Cr^{3+} -doped TiO₂, both the Cr^{3+} states and the visible light activity were confirmed by many research groups.³²⁶⁻³²⁸ Zhu et al.³²⁹ prepared Cr³⁺-doped TiO₂ by a sol-15 gel/hydrothermal procedure and observed visible light absorption at a doping level between 0.15-0.30%. An absorption shoulder at around 450 nm was ascribed to the excitation of Cr³⁺ resulting in CB electrons. Lu and coworkers³³⁰ prepared Cr³⁺-doped TiO₂ by a diffusion-20 doping-sensitization technique. Their products showed an absorption edge at around 750 nm. Ghicov et al.³³¹ recently reported enhanced visible light absorption up to 520 nm by TiO_2 nanotubes doped with Cr^{3+} by ion-implantation. Although during ion-implantation a certain amount of defects 25 was created that could potentially act as recombination

was created that could potentially act as recombination centers, such adverse effects could be minimized by reannealing the doped TiO₂ samples. Umebayashi *et al.*³²⁶ also reported that Cr-dopant levels appeared close to the VB edge of TiO₂ following material preparation by an ion ³⁰ implantation method.

In Fe³⁺-doped TiO₂, the red-shift of the absorption edge was ascribed to the excitation of 3d-Fe³⁺ electrons to the CB of TiO₂, or the charge transfer between dopant ions (Fe²⁺ and Fe⁴⁺) via the CB.^{294, 332} Wang and coworkers^{36, 37, 333} described as a sol-gel method to prepare Fe(III)-doped TiO₂ nanopowders with high uniformity of Fe(III) distribution throughout the TiO₂ matrix, which was considered to be responsible for the high quantum efficiency of the materials in the photocatalytic oxidation of methanol to form formaldehyde. Yamashita and 40 coworkers³³⁴ prepared iron-doped TiO₂ by ion-implantation and reported a visible light absorption up to 600 nm. Jeong *et*

- $al.^{335}$ observed a red-shift in the absorption edge of Fe-doped TiO₂ films deposited on glass substrates. Zhou *et al.*³³⁶ prepared mesoporous Fe-doped TiO₂ powders and found that ⁴⁵ the absorption was red-shifted as the dopant concentration
- increased from 0.05atm% to 0.25atm%. Zhang and coworkers³³⁷ prepared Fe-doped TiO₂ supported on activated carbon. It also showed a red-shift in its light absorption edge. Very recently, Wang *et al.*³³⁸ demonstrated that Fe³⁺-doped
- ⁵⁰ TiO₂ nanopowders prepared by plasma oxidative pyrolysis could degrade methyl orange under visible light irradiation. Nahar *et al.*³³⁹ prepared Fe-doped TiO₂ by calcination of Fe_xTiS₂ (x varies from 0.002 to 0.01). The material was able to photocatalytically degrade phenol under visible light
- ⁵⁵ illumination (405-436 nm). Teoh *et al.*³⁴⁰ prepared Fe-doped TiO₂ by flame spray pyrolysis. It showed considerable activity in the degradation of oxalic acid under visible light

illumination above 400 nm. Other metal (e.g., Mn³⁴¹, V, Co³⁴², Ni^{313, 320}, Mg¹⁰⁴ and Pt^{314, 343, 344}) ion-doped ⁶⁰ photocatalysts were also found to exhibit visible-light activities. Although quite a large number of examples exist in the literature on materials exhibiting enhanced light absorption properties, it should be pointed out that the absorption of light is a necessary but not a sufficient condition ⁶⁵ to promote photocatalytic activity.³⁴²

6.2.3 Changing the Lifetime of Charge Carriers and Photocatalytic Activity

Metal-ion dopants can greatly alter the lifetime of photogenerated charge carriers and thus photocatalytic ⁷⁰ activities.³⁴⁵ At appropriate concentrations, the dopants can selectively trap one charge carrier and allow another one to reach the particle surface to be able to take part in the desired redox reactions. For example, Grätzel *et al.*³⁴⁶ demonstrated by electron paramagnetic resonance measurements that doping ⁷⁵ of colloidal TiO₂ particles with Fe³⁺ and V⁴⁺ resulted in a drastic augmentation in the lifetime of the photogenerated electron/hole pairs upon bandgap irradiation, which would recombine within a few nanoseconds without these dopants. Quite a few photocatalytic activity measurements of metal-⁸⁰ ion-doped TiO₂ also confirmed the enhancement of charge carrier lifetimes and the corresponding photocatalytic activity.^{325, 347}

On the other hand, dopant ions can also act as recombination centers for the photoelectrons and holes and 85 thus decrease the photocatalytic performance.^{226, 341} The frequently reported decrease in photoactivity of metal-iondoped TiO₂ with increasing dopant concentration above a certain doping level is a good illustration of this phenomenon. In fact, visible-light photoactivity could hardly be observed in 90 a Fe³⁺-doped TiO₂ at a Fe loading of 10wt%, although the visible light absorption was very considerable. Radecka et al.³⁴⁸ studied the photoelectrochemical behavior of Cr³⁺-doped ${\rm TiO}_2$ electrodes and found that the addition of ${\rm Cr}^{3+}$ led to an increase in the recombination of photogenerated charge 95 carriers, and therefore the energy conversion efficiency for the doped electrodes was lower than that of an undoped TiO₂ electrode. Wilke and Bruer²⁹¹ examined the relationship between dopant concentration, charge carrier lifetime and photocatalytic performance of Cr³⁺- and Mo⁵⁺-doped TiO₂. ¹⁰⁰ Their study revealed that in both Cr^{3+} and Mo^{5+} -doped TiO₂, the lifetime of the charge carriers was drastically decreased from about 90 µs for pure TiO₂ down to about 25 µs at a dopant concentration of 1atm%. Meanwhile, the photocatalytic activity decreased to a low level with dopant 105 concentrations below 1atm% for both systems. This was ascribed to the substitutional doping by the cations that act as recombination centers. Wang and coworkers³³⁸ studied the photodegradation of methyl orange by both pure and Fe³⁺doped TiO₂ nanopowders under UV irradiation and found that 110 the photoactivity of the former is higher than that of the latter, which was explained by the more serious recombination loss of the charge carriers in Fe^{3+} -doped TiO₂.

All the examples given above seemingly suggest that a direct relationship exists between the charge carrier lifetime ¹¹⁵ and the photoactivity of metal-ion-doped photocatalysts. The

longer the lifetime, the higher the photoactivity. However, such a statement should not be generalized because the relationship between the charge carrier lifetime and the photoactivity is not straightforward and unambiguous. As *s* pointed out by Bahnemann and coworkers²⁷, photogenerated

- holes could be trapped either deeply or shallowly. Those deeply trapped holes that were rather long-lived exhibited almost no activity, i.e., they were not able to oxidize dichloroacetate (DCA⁻). Shallowly trapped holes, on the other
- ¹⁰ hand, were able to oxidize DCA⁻ almost instantaneously $(t_{1/2} < 5 \ \mu s)$. Moreover, there are also other effects caused by metal-ion doping on the photoactivity of catalysts, such as changes in the surface hydrophilicity^{349, 350}, changes in the adsorption ability towards reactant molecules, shifting of
- ¹⁵ Fermi levels²⁸⁷, changes in the thickness of the space charge region near the surface, and induction of crystalline phase transitions within the catalysts.³⁴² Sometimes these factors may exhibit opposite effects when present simultaneously.^{295, 349}
- ²⁰ Although the different ways to increase the efficiency of photocatalysts, e.g., coupled semiconductors, deposition of noble metals, and doping, have been discussed here separately, these techniques can also be combined to achieve synergetic effects in improving photocatalytic performance. In
- ²⁵ a recent report, Tada *et al.*³⁵¹ showed that an Au/TiO₂ photocatalyst was capable of effectively photoreducing elemental S to S²⁻ in an aqueous environment.³⁵² Based on this finding, the authors prepared an Au/CdS/TiO₂ nanocomposite photocatalyst by the selective deposition of CdS on Au
- ³⁰ deposited on the surface of TiO_2 nanoparticles. Convincing evidence was presented that a vectorial electron transfer takes place from TiO_2 via-Au-to CdS under irradiation, as a result of the simultaneous excitation of CdS and TiO_2 . Under these reaction conditions, the CdS surface was found to
- ³⁵ predominantly function as the reductive site leaving the exposed TiO_2 surface as the oxidizing site, as probed by the photodeposition of Pt selectively on the CdS surface. This observation is in clear contrast with the simple electrochemical picture in which, according to the energetic
- $_{40}$ positions of CB and VB in TiO₂ and CdS (cf. Fig. 6), the former should be the place for the reduction processes and the latter for the oxidation reactions.

7. Mixed Transition Metal Oxide Photocatalysts

- The development of mixed transition metal oxide (i.e., binary, ⁴⁵ ternary or quaternary) photocatalysts is a newer research subject than that of their single-oxide counterparts (e.g., TiO_2).³⁵³⁻³⁵⁵ In particular, application of mixed oxide photocatalysts in visible-light-driven H₂ and/or O₂ generation has been very actively addressed during recent years, although
- ⁵⁰ the choice of applicable materials for direct photocatalytic H_2O splitting (in no need of sacrificing agents) under visible light is still limited.^{6, 356} Photocatalytic degradation of organic compounds using mixed oxides under visible light illumination has also been frequently reported in the literature.
- ⁵⁵ The most attractive feature of using mixed transition metal oxides as photocatalysts results from at least two important aspects: 1) their capability of absorbing photons in the visible

light range ($\lambda > 420$ nm) due to appropriately modulated electronic band structures, and 2) the vast possibilities of combinations of different elements, thus providing a wide range of photocatalyst candidates. Theoretically, calculations of the electronic band structures of the photocatalysts, although often underestimating their bandgaps³⁵⁷, provide a powerful tool in the prediction and design of visible-lightcost active photocatalysts. As often practiced with their singleoxide counterparts, modifications of the mixed oxide materials to enhance their photocatalytic performances have as well been attempted by various techniques, such as doping^{358, 359}, coupling of different semiconductors³⁶⁰, and 70 introducing nanoclusters as trapping sites³⁵⁵ for the charge carriers.

In addition to the mixed oxides, the recent literature also presents a number of other complex semiconductors as photocatalysts under visible light irradiation, such as mixed ⁷⁵ sulfides (e.g., $ZnIn_2S_4^{361}$, $Zns-CuInS_2-AgInS_2$ solid solutions³⁶², $Cd_xCu_yZn_{1-x-y}S^{363}$), oxynitrides (e.g., $TaON^{364}$, $Zr_2ON_2^{365}$, $Y_2Ta_2O_5N_2^{366}$, $Nb_2Zr_6O_{17-x}N_x^{367}$), and oxyhalides (e.g., $Bi_4NbO_8Cl^{368}$, $xBiOBr-(1-x)BiOI^{369}$). A few materials from this category will also be analyzed in the ⁸⁰ following discussions.

7.1 Band Structures and Optical Properties

The optical absorption property and the photocatalytic activity of a semiconductor are essentially related to its electronic band structure. If one expects the semiconductor to be an ss efficient photocatalyst under visible light illumination, the following requirements should be met³⁷⁰: 1) a narrow bandgap (usually < 3.0 eV); 2) suitable potentials of the conduction and/or valence band edges; and 3) high mobility of the photogenerated charge carriers within in the conduction 90 and/or valence bands.

In most cases, mixed oxide photocatalysts that are efficient under visible light illumination, possess narrowed bandgaps due to either the elevation of the valence band edge caused by the hybridization between the O 2p orbitals and the newly ⁹⁵ introduced orbitals (which ought to have a more negative potential than that of O 2p), or the lowering of the conduction band edge contributed by the introduced components in the materials.³⁵⁶ Calculations of their electronic band structures, although often predicting much smaller bandgaps than those ¹⁰⁰ experimentally determined from optical absorption spectra³⁷¹. ³⁷², are nonetheless very helpful to interpreting the band structure formation and the electronic/optical properties of the

materials. Bi³⁺-containing mixed oxides can serve as excellent ¹⁰⁵ examples to illustrate the mechanism of bandgap narrowing. Kudo *et al.*³⁵³ synthesized and comparatively studied the optical absorption properties of two types of BiVO₄, one with a tetragonal structure and the other exhibiting a monoclinic structure. Their different bandgaps, i.e., 2.9 eV for the ¹¹⁰ tetragonal and 2.4 eV for the monoclinic structure, respectively, arise from the unequal participation of Bi 6s orbitals in the formation of the valence bands. With the bottom of the conduction band being composed of V 3*d* orbitals in both cases, the top of the valence band in the tetragonal BiVO₄ consists only of O 2p orbitals, while in the monoclinic case it contains both O 2p and Bi 6s orbitals, resulting in a negative shift of the valence band edge to allow the absorption of longer-wavelength photons than in the ⁵ former case. Slightly different values of the bandgap energies

- of BiVO₄, e.g., 2.34 eV for the monoclinic structure and 3.11 eV for the tetragonal structure, respectively, were recently reported by other researchers³⁷³ when they employed different synthesis methods.
- ¹⁰ Sayama *et al.* studied the photoelectrochemical decomposition of H_2O on $BiVO_4$ electrodes and argued that the difference in the bandgap (i.e., 0.3 eV) between $BiVO_4$ and WO_3 results from different potentials of their valence band edges³⁷⁴, consistent with the report by Kudo *et al.*³⁵³ The
- ¹⁵ authors also conducted comparative tests on YVO_4 and InVO₄ electrodes, both of which showed much lower activity towards H₂O splitting. This indicates that the Bi orbitals possibly played a significant role in defining the high efficiency of BiVO₄ electrodes.
- ²⁰ Bi^{3+} has also been found to be responsible for the bandgap narrowing of other mixed oxide semiconductors. For instance, the valence band of $CaBi_2O_4$ is composed of hybridized Bi 6s and O 2p orbitals³⁷⁵, resulting in a shift of the valence band edge towards more negative potentials. It appears to be, in
- ²⁵ fact, a common feature of mixed oxide semiconductors containing Bi^{3+} , that the valence band involves the hybridization between the Bi 6*s* and O 2*p* orbitals. In contrast, in Bi^{5+} -containing materials, this hybridization is rather limited because the Bi 6*s* orbitals are now empty. However,
- ³⁰ the empty 6*s* orbitals of Bi^{5+} can possibly provide a way to tune the conduction band edge potential, as reported recently by Tang *et al.*³⁷⁰ The authors synthesized $BaBiO_3$ containing both Bi^{3+} and Bi^{5+} via a soft chemical method and discovered an impressive visible-light-response under illumination even
- as at $\lambda > 600$ nm. Their calculations using plane-wave-based density functional theory suggested that the top of the valence band is composed of Bi³⁺ 6s and O 2p orbitals, while the bottom of the conduction band contains the 6s orbitals originating from Bi⁵⁺. Details of the density contour maps of
- ⁴⁰ the LUMO (lowest unoccupied molecular orbital, i.e., the bottom of the conduction band) and HOMO (highest occupied molecular orbital, i.e., the top of the valence band) orbitals in BaBiO₃ are presented in Fig. 30. Clearly, the HOMO is composed solely of Bi³⁺ 6s and O 2p orbitals, while the
- ⁴⁵ LUMO consists of both Bi^{5+} 6s and 6p orbitals besides O 2p orbitals. This is in vast contrast to Bi^{3+} -containing oxides, such as $BiVO_4$ and $CaBi_2O_4$ whose the conduction bands are formed exclusively from V 3d orbitals ($BiVO_4$) or Bi 6p orbitals ($CaBi_2O_4$), respectively. The coexistence of these two
- ⁵⁰ types of Bi cations results in a considerably narrowed bandgap, i.e., 2.05 eV, as experimentally derived from its optical absorption spectrum.³⁷⁰

A bandgap narrowing by shifting the conduction band edge towards more positive potentials has also been attempted by ⁵⁵ other research groups. Kako and coworkers³⁷⁶ studied the optical absorption behavior of NaBiO₃, which exhibits a sharp absorption edge at around 470 nm, corresponding to a bandgap of ~2.6 eV. Calculations of its electronic structure

revealed that the hybridization between Na 3*s* and O 2*p* orbitals occurred at the bottom of the conduction band (accounting for the bandgap narrowing), while a flat structure of O 2*p* orbitals was observed at the top of the valence band. Ouyang *et al.*³⁷⁷ compared the band structures between AgAlO₂ and Ag₂CrO₄ and concluded that the lower edge of the conduction band in AgAlO₂ mainly consists of empty Ag 5*s*5*p* orbitals, while in Ag₂CrO₄ the lower edge is formed by the hybridization of Ag 5*s*, 5*p* and Cr 3d orbitals. This leads to a much narrower bandgap in Ag₂CrO₄ (1.75 eV) as compared with that of AgAlO₂ (2.95 eV).

With more metal ion components present, the electronic structures of ternary and even more complex oxide semiconductors can be, unsurprisingly, more flexibly modulated than can their binary oxide counterparts. A few examples of ternary and quaternary oxide materials will be 75 presented here to illustrate the multiplicity of their band structures.

Fig. 30 Density contour maps of the LUMO orbitals (a) and of the HOMO orbitals (b) in BaBiO₃. Reprinted with permission from ref. 370, Copyright 2007 ACS.

Tang et al.³⁷⁸ prepared AgInW₂O₈ powders exhibiting activity for O₂ evolution under visible light illumination. The authors speculated that the top of the valence band consists of hybridized Ag 4d and O 2p orbitals with its Fermi level being s more positive than the H_2O oxidation potential (*E*=1.23 V vs. NHE). The conduction band of AgInW₂O₈, on the other hand, has a complicated structure due to the coexistence of three types of metal ions. Consequently, the bottom of the conduction band consists of both W 5d orbitals and hybridized 90 In 5s and Ag 5s orbitals. When illuminated by visible light, the photogenerated electrons were excited only to the W 5d orbitals, with their potential being more positive than that required for the H_2O reduction reaction (*E*=0 V vs. NHE). Under full arc (i.e., both UV and visible light) irradiation, 95 however, the electrons can be further promoted to the hybridized In 5s and Ag 5s band, which has a sufficiently negative potential to reduce H₂O.³⁷⁹

Kim *et al.*³⁸⁰ prepared a single-phase PbBi₂Nb₂O₉, which exhibits a sharp absorption edge at ~500 nm. This narrow bandgap is reported to result from a shift of the top of the valence band towards more negative potentials as compared with simple metal oxides. The valence band of AgInW₂O₈ is formed by the hybridization of O 2*p*, Bi 6*s* and Pb 6*s* orbitals.

The valence band of $Zn_{2.5}VMoO_8^{381}$ is composed by 105 contributions from both Zn 3*d* and O 2*p* orbitals, although their hybridization does not elevate the valence band edge because the Zn 3*d* orbitals are lower in potential than the O 2*p* orbitals. Yet the hybridization itself still facilitates the hole transfer within the valence band. The conduction band of 110 Zn_{2.5}VMoO₈, however, is composed of disordered V 3*d* and Mo 4*d* orbitals, both of which possess a potential that is more positive than the potential of the H₂O reduction reaction. Therefore, even under UV irradiation in the presence of CH₃OH as the sacrificial agent, this material could not 115 generate H₂ from H₂O. Being composed of four types of metal ions, In₁₂NiCr₂Ti₁₀O₄₂³⁸² has a valence band consisting of O 2*p* orbitals hybridized with occupied Ni 3*d* and Cr 3*d* orbitals, both of which are located above the O 2*p* orbitals. In fact, ⁵ these 3*d* orbitals are spread over different potential levels and hybridize quite well. To be more precise, the top of the valence band was assigned to be due mainly to the Cr 3*d* states, followed by the Ni 3*d* states at more positive potential. The conduction band, on the other hand, is formed primarily

- ¹⁰ from empty Ti 3d and In 5s orbitals, in combination with empty Ni 3d b_{2g} and Cr 2d e_g orbitals. With such a band structure, the bandgap of $In_{12}NiCr_2Ti_{10}O_{42}$ is found to be as narrow as 2.14 eV.
- $Ca_{1-x}Bi_xV_xMo_{1-x}O_4$ solid solutions were found to have 15 bandgap energies between 2.34 and 2.7 eV, monotonically dependent on the variation of x, i.e., the concentration of Bi and V in the materials.³⁸³ The valence band in these materials was regarded as the result of the hybridization between Bi 6s and O 2p orbitals, similar to the case of BiVO₄.³⁷⁵ The
- ²⁰ contribution of Bi 6*s* orbitals to the valence band becomes more dominant as the content of Bi ions is increased. The bottom of the conduction band results from the mixed V 3*d* and Mo 4*d* orbitals, which can also be shifted by adjusting the composition of the material. Similar band shifts were achieved
- ²⁵ in other mixed oxide solid solutions as well, such as $(AgNbO_3)_{1-x}(NaNbO_3)_x^{384}$, $Na_{1-x}La_xTa_{1-x}Co_xO_3^{385}$ and $(Ag_{0.75}Sr_{0.25})(Nb_{0.75}Ti_{0.25})O_3^{386}$. These results indicate that the band structures of complex solid solutions can be feasibly modulated by controlling the synthesis recipe.

30 7.2 Factors Determining the Photocatalytic Properties

7.2.1 Effects of Band Structures

Calculations of the electronic band structures of mixed oxide photocatalysts indicate that the hybridization between different orbitals of the component ions can change the

- ³⁵ potentials of the conduction and/or valence band edges. This in turn will enable the materials to absorb longer-wavelength photons, hence exhibiting photocatalytic activity under visible light irradiation. Besides narrowing the bandgap, the orbital hybridization can render band structures with different
- ⁴⁰ configurations, i.e., flat or abrupt. This can also influence the photocatalytic performance of the materials, because the effective masses of the charge carriers, and therefore their mobilities, are sensitive to the band configurations.

Usually, the charge carriers are highly mobile in the $_{45}$ hybridized conduction or valence bands. In many Bi³⁺- containing mixed oxides, for example, the transfer of holes in the valence band can be improved by the hybridization between Bi 6*s* and O 2*p* orbitals, as proposed by a number of research groups.³⁷⁴⁻³⁷⁶ The mobility of electrons in the so conduction band of NaBiO₃ was also increased due to the

hybridization between Na 3s and O 2p orbitals.³⁷⁶

On the other hand, Ouyang *et al.*³⁸⁷ reported a reduced charge carrier mobility in AgAlO₂. While the mobility of the electrons in its conduction band (mainly composed of Ag 5s5p

ss orbitals) is still high, the mobility of the holes in the valence band (hybridized Ag 4d and O 2p orbitals) is lowered due to the very flat configuration. The holes are easily localized at Ag- or O-sites, or move very slowly when being transferred along the O-Ag-O chains.

⁶⁰ Furthermore, an indirect bandgap structure can also be beneficial to the suppression of the charge carrier recombination.^{372, 387}

7.2.2 Effects of Physicochemical Properties

Other than the intrinsic band structures, the physicochemical 65 properties, e.g., the crystallinity, the particle size, and the surface area, of mixed oxide semiconductors can also significantly influence their photocatalytic activities.356, 358 A wide range of mixed oxides has been produced by solid-state reaction (SSR) routes³⁵⁵, which require very high reaction 70 temperatures (usually above 1000 °C) thus reducing the surface area of the catalysts to even below 1 m²/g. Compared with the typical surface area of traditional photocatalysts such as TiO₂, i.e., $50\sim 200 \text{ m}^2/\text{g}$, the small surface area will undoubtedly limit their surface adsorption capacity and the 75 overall photocatalytic performance in many reactions. Novel preparation techniques, such as sonochemical^{388, 389}, sol-gel³⁹⁰. and deposition-precipitation³⁹¹ methods, have recently been proposed and tested to achieve high-surface-area products. High crystallinity is also indispensible for an efficient transfer ⁸⁰ of charge carriers. Fortunately, most of the currently employed preparation methods are also able to deliver highly crystalline products.

Zhou *et al.*³⁸⁹ employed a sonochemical route to synthesize $BiVO_4$, which possesses a surface area 16 times larger than ⁸⁵ that obtained using the SSR route. Its photocatalytic activity in the decoloration of methyl orange under visible light irradiation was found to be much higher than that of the SSR product. Ultrasound-assisted methods have also been used to prepare Bi_2MO_6 (M=W, Mo) photocatalysts, as reported by ⁹⁰ Zhou *et al.*³⁹² Highly crystalline Bi_2WO_6 nanoplates (~100 nm in size) and Bi_2MOO_6 nanoparticles (~150 nm in size) were obtained after calcination at ~500 ^{0}C .

Zhang *et al.*³⁹³ prepared nanometer-sized $InVO_4$ particles by calcination at ~600 0 C. Instead of using commercial In_2O_3 ⁹⁵ or $In(OH)_3$ (both hardly soluble in most inorganic and organic acids) as the precursor, they produced fresh $In(OH)_3$ precipitates that were dissolved together with V_2O_5 in diethylenetriaminepentaacetic acid yielding a transparent solution upon heating. The dried residues from this solution ¹⁰⁰ were then subject to calcination in air to yield the final products. Their photocatalytic activities in the degradation of formaldehyde were once again found to be much higher than those of the corresponding SSR product.

A non-aqueous sol-gel method was proposed by Zhang and ¹⁰⁵ coworkers³⁹⁰ to synthesize InNbO₄ with particle sizes of 10~30 nm and a BET surface area of ~54 m²/g. The key parameter of this synthesis was the exceptionally low calcination temperature, i.e., 200 ⁰C, at which, however, highly crystalline nanoparticles can still be obtained, as ¹¹⁰ indicated in the TEM images shown in Fig. 31. The photocatalytic activity of the material towards the degradation of Rhodamine B was found to be much higher than that of its bulk counterpart under visible light irradiation ($\lambda > 420$ nm). **Fig. 31** TEM (a) and HRTEM (b) images of InNbO₄ nanoparticles synthesized via a non-aqueous sol-gel method. Reproduced with permission from ref. 390, Copyright 2007 Wiley-VCH.

Li and Ye³⁹¹ prepared Pb₃Nb₄O₁₃/fumed silica composite ⁵ photocatalysts via a deposition-precipitation method. The photocatalysts exhibited notably improved activities in the degradation of Rhodamine B, as compared with that of unsupported Pb₃Nb₄O₁₃. Due to the high surface area of the fumed silica, the adsorption uptake of Rhodamine B onto the

- ¹⁰ composite catalysts was found to be more than 5 times higher than that of bare $Pb_3Nb_4O_{13}$. Interestingly, the reaction mechanisms in the two cases were different. The degradation in the unsupported case mainly proceeded via the typical photocatalytic pathways. In the supported case, however, the
- ¹⁵ improved photocatalytic activities after introducing fumed SiO_2 were explained by the strengthened interaction between the adsorbed Rhodamine B molecules and the nearby active $Pb_3Nb_4O_{13}$ sites.

7.3 Applications of Mixed-Oxide Photocatalysts

20 7.3.1 Overall H₂O Splitting

Thermodynamically, when the conduction band edge of a photocatalyst has a more negative potential than the H_2O/H_2 redox potential (i.e., 0 eV vs. NHE), the material is expected to be able to generate H_2 from H_2O under bandgap

- ²⁵ illumination; when its valence band edge has a more positive potential than that of the H_2O/O_2 potential (i.e., 1.23 eV vs. NHE), it can catalyze the evolution of O_2 from H_2O . Hence, the theoretically required bandgap of a photocatalyst for the overall splitting of H_2O is at least 1.23 eV. However,
- ³⁰ considering the overall H_2O splitting reaction to form H_2 and O_2 in a photocatalysis scheme, at least two electrons and four holes are needed on the surface of the photocatalyst. Such a multiple charge carrier system might involve a broad range of energy, as predicted by the gradual, rather than sharp, onset of
- ³⁵ the optical absorption. Together with the bandgap energy, $E_{\rm g}$, an extra phonon energy, $E_{\rm p}$, which accounts for the conservation of the momentum, is required to induce the optical absorption, as pointed out by Orenstein.³⁹⁴ In other words, higher energy than the bandgap itself seems to be ⁴⁰ necessary to fulfill the requirement of an overall

photocatalytic H₂O splitting reaction.³⁵⁶

Mixed oxide semiconductors apparently provide a much higher flexibility of tuning the bandgaps than their singleoxide counterparts. Therefore, with appropriate bandgaps, a 45 wide range of mixed oxides are expected to be applicable to the visible-light-driven splitting of H₂O. Although most of the hitherto investigated mixed oxides possess bandgaps notably larger than 1.23 eV, the choice of suitable materials for the overall splitting of pure H₂O is very limited ^{355, 356}, due to the

- so following reasons: 1) the mismatching of the band edge potentials with the H₂O reduction/oxidation reactions, 2) the extremely low efficiencies of charge carrier separation and/or surface reactions, 3) the fast back reaction to form H₂O again, and 4) the insufficient stability against photocorrosion in the ⁵⁵ presence of O₂.^{395, 396}
 - Visible-light-driven generation of H_2 and O_2 from pure H_2O to produce stoichiometric amounts of H_2 and O_2 with

promising stability has only been achieved on a few materials, including $In_{1-x}Ni_xTaO_4$ and $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$.³⁹⁷⁻³⁹⁹ Co-60 catalysts such as Ni/NiO, RuO₂ and/or noble metal nanoclusters are routinely deposited on the surface of the photocatalysts to serve as the active H₂ evolution sites, thus increasing the overall reaction rate.

Zou et al.³⁵⁵ synthesized an Ni-doped indium-tantalum-65 oxide, $In_{1-x}Ni_xTaO_4$ (x=0~0.2), via the SSR route and reported a quantum yield of ~0.66% for the direct splitting of water under visible light ($\lambda > 420$ nm) irradiation. The presence of RuO₂ or NiO_x nanoparticles on the surface of In₁. $_xNi_xTaO_4$ is necessary to act as electron transfer catalysts at 70 the cathodic sites for the H₂O reduction. The photocatalytic activity was found to vary with the changing of x. In the presence of RuO₂ as the co-catalyst, undoped InTaO₄ catalyzes the evolution of H_2 and O_2 at rates of 0.75 and 0.35 μ mol/h, respectively; while when NiO_v is used as the co-75 catalyst, the reaction rates are 3.2 and 1.1 µmol/h, respectively. Doping of InTaO₄ by nickel significantly enhances the reaction rate, i.e., 5~10 times, depending on the dopant concentration. The highest activity was achieved with *x*=0.1.

- Very recently, Maeda and coworkers^{397, 399} reported a solid 80 solution of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ that catalyzed the overall water splitting at a quantum efficiency of 2.5% (illumination wavelength 420~440 nm) when its surface was loaded with nanoparticles of rhodium-chromium mixed oxide. The 85 material was prepared by the nitridization of a mixture of Ga₂O₃ and ZnO powders under NH₃ flow at 1123 K, resulting in a yellow powder with an absorption edge at around 510 nm. Density functional theory calculations indicated that the bottom of the conduction band of (Ga1- $_{90 x}Zn_{x}(N_{1-x}O_{x})$ mainly consisted of Ga 4s and 4p orbitals, while the top of the valence band was formed by N 2p and Zn 3d orbitals, hence resulting in a narrowed bandgap. Both the particle size and the loading of the co-catalyst, i.e., a Rh(III)-Cr(III) mixed oxide, seem to considerably influence the 95 reaction rate. The maximum activity was achieved at 1wt% Rh and 1.5wt% Cr, with a particle size of 15-20 nm. The authors also examined another type of co-catalyst, i.e., noble metal/Cr₂O₃ core/shell nanoparticles⁴⁰⁰ prepared by a two-
- step photodeposition method. The noble metal cores and ¹⁰⁰ Cr_2O_3 shells were deposited selectively at the reduction sites on the surface of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$. Coating the core metal particles by Cr_2O_3 appeared to effectively suppress the back reaction of re-forming H₂O over the metal particle surface, thus leading to improved activity, as compared with that using ¹⁰⁵ only noble metal particles as the co-catalyst.

 $MIn_{0.5}Nb_{0.5}O_3$ (M=Ca, Sr, Ba) powders⁴⁰¹ were also found to be able to generate H₂ from pure water under visible light irradiation ($\lambda > 420$ nm), although the reaction rate was very limited, i.e., below 0.18 µmol/h at a catalyst loading of ~2 g/L. ¹¹⁰ An interesting phenomenon is that no O₂ gas was detected within the reaction system. Similar results were also obtained from the pure H₂O splitting experiments using InMO₄ (M=Ta, Nb, V) photocatalysts.⁴⁰² Some researchers ascribed the absence of O₂ to its adsorption onto the surface of the ¹¹⁵ photocatalysts^{13, 378}, which is observable from the measurement of the DC magnetic susceptibility of the photocatalysts before and after the photocatalytic reactions.

Regarding photocatalyst materials that are inherently unable to catalyze the pure H₂O splitting due to inappropriate ⁵ band edge levels, application of a bias potential on the photocatalyst electrodes can help to adjust the band levels, as

- exemplified by WO₃ and Fe₂O₃ photoelectrodes.⁴⁰³ Moreover, the overwhelming recombination of charge carriers, which restricts the overall activity, can also be efficiently suppressed
- ¹⁰ by applying a bias potential. One example in the context of mixed oxides is the monoclinic $BiVO_4$, as mentioned earlier³⁵³. This material shows no activity in the photocatalytic H₂O reduction to evolve H₂ under visible light irradiation, apparently due to the low potential of the
- ¹⁵ conduction band edge. However, when a bias potential is applied, the conduction band edge can be shifted towards more negative potentials sufficient to reduce water under visible light illumination. Sayama *et al.*³⁷⁴ reported an excellent incident photon-to-current efficiency (IPCE=29% at
- ²⁰ 420 nm) for the decomposition of water using nanocrystalline BiVO₄ film electrodes under a 1.3 V bias potential (vs. a Ag/AgCl reference electrode).

7.3.2 Evolution of $H_2 \mbox{ or } O_2$

Compared with the photocatalytic H_2 production, research on ²⁵ the materials for only O_2 evolution is equally important in the fundamental understanding of their properties (e.g., crystalline and electronic structures, optical and photocatalytic properties). Yet in the light of providing solutions to the problem of "clean energy", efforts devoted to developing

- ³⁰ photocatalysts for H_2 evolution seem more prominent, both economically and environmentally. Despite the fact that many materials were developed for the visible-light-driven H_2O oxidation to produce O_2 , the details of all the studies in this field will not be covered in this review. Instead, a few mixed
- $_{35}$ oxides and chalcogenides for H_2 evolution have been selected as the focus of this section. In most cases, both co-catalysts and sacrificing agents are needed to achieve high efficiency in H_2 generation.

In₁₂NiCr₂Ti₁₀O₄₂ was investigated by Wang *et al.*³⁸² for 40 visible-light-driven H₂ evolution from an aqueous solution of methanol using 0.2wt% Pt as the co-catalyst. With a very narrow bandgap, i.e., 2.14 eV, its absorption spectrum is in good accordance with its photocatalytic action spectrum. The evolution of H₂ can be observed under illumination starting 45 approximately at its absorption edge, i.e., 560 nm.

Tian *et al.*³⁵⁷ investigated photocatalytic H_2 evolution under visible light illumination employing $K_4Ce_2Nb_{10}O_{30}$ as the photocatalyst. Even though this material possesses a very narrow bandgap, i.e., 1.8 eV (corresponding to an absorption

- so edge of ~690 nm), its conduction band edge still holds an appropriate potential level for H_2O reduction from an aqueous Na_2SO_3 solution. The authors also pointed out the role played by Ce in the band structure configuration, based on density functional theory calculations. While the widely distributed
- ss Ce 4*f* states in the valence band are well hybridized with the Nb 4*d* and O 2*p* states, the unoccupied Ce 4*f* states in the conduction band are narrowly localized. This feature implies their reduced effectiveness in photocatalysis, because it is

more difficult to transfer the photoexcited electrons from the $_{60}$ highly localized Ce 4*f* orbitals to the surface of the catalyst.

Yi and Ye³⁸⁵ measured the rates of H₂ evolution over single-phase Na_{1-x}La_xTa_{1-x}Co_xO₃ solid solutions from CH₃OH/H₂O mixtures under visible light irradiation ($\lambda > 420$ nm). They found that the reaction rates are closely related to ⁶⁵ the value of *x*, i.e., the concentration of Co in the solid solutions. Density of states calculations reveal that the split Co 3*d* states contribute, by hybridization with the O 2*p* orbitals, to the formation of both the LUMO and HOMO, as displayed in Fig. 32. When the Co concentration is too low, it ⁷⁰ is insufficient to induce the density of states needed for the maximum H₂ evolution rate, whereas a too high Co concentration would result in unsuitable redox potentials.

Fig. 32 Density of states of NaTaO₃ (a) and Na_{0.9}La_{0.1}Ta_{0.9}Co_{0.1}O₃ (b). Reprinted with permission from ref. 385. Copyright 2007, American Institute of Physics.

The single-phase oxide, PbBi₂Nb₂O₉, synthesized by Kim et al.³⁸⁰ achieves a quantum yield of 0.95% in photocatalytic H₂ evolution from an aqueous methanol solution under visible ⁸⁰ light illumination ($\lambda > 420$ nm). More impressively, its quantum yield for O₂ formation is about 29%, using AgNO₃ as the sacrificial electron accepting agent.

Wang et al.⁴⁰⁵ comparatively investigated photocatalytic H₂ evolution rates using three isostructural oxide semiconductors, ⁸⁵ i.e., $In_6NiTi_6O_{22}$, $In_3CrTi_2O_{10}$, and $In_{12}NiCr_2Ti_{10}O_{42}$, possessing bandgaps of 2.48, 2.0 and 2.14 eV, respectively. Interestingly, these materials exhibited very different activities in photocatalytic H_2 evolution. $In_{12}NiCr_2Ti_{10}O_{42}$, in which both Ni and Cr are present as minor cations, had the 90 highest activity (~8.2 µmol/h) at a catalyst loading of 1.85 g/L, while the H₂ evolution rates of the other two materials were only ~0.3 (In₆NiTi₆O₂₂) and 0.2 µmol/h (In₃CrTi₂O₁₀). To explain this considerable difference, the authors proposed that the presence of either Ni or Cr does not form continuous 95 conduction or valence bands, as depicted in Fig. 33a and b. In contrast, the coexistence of Ni and Cr establishes continuous bands (Fig. 33c), which is well known to be crucial for improving the mobility of the photogenerated charge carrier, and hence the photocatalytic activities.

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Fig. 33 Schematic band structures of $In_6NiTi_6O_{22}$ (a), $In_3CrTi_2O_{10}$ (b), and $In_{12}NiCr_2Ti_{10}O_{42}$ (c). Reprinted with permission from ref. 405, Copyright 2007 ACS.

Lei *et al.*³⁶¹ synthesized a cubic spinel-phase chalcogenide, ¹⁰⁵ ZnIn₂S₄, which functions actively in photocatalytic H₂ production from an Na₂S-Na₂SO₃ aqueous solution under visible light irradiation. As deduced from the diffuse reflectance spectra, its bandgap is 2.3 eV, corresponding to an absorption edge at 570 nm. The high photocatalytic activity of ¹¹⁰ this material can be related, at least partially, to its high surface area (i.e., 103 m²/g) being the result of a novel hydrothermal synthesis, which is about two orders of magnitude higher than that of the products from the SSR regime. Stability tests were also conducted on this catalyst, which demonstrated that more than 8.7 mmol H_2 was steadily produced with 0.3 g catalyst (with Pt as the co-catalyst) within 150 hours of illumination.

Besides H_2O , other materials can also serve as the H source s for photocatalytic H_2 generation, including hydrogen sulfide,

a highly polluting gas released routinely from petroleum, natural gas and the coal industries. Kanade *et al.*³⁶⁷ synthesized an oxynitride, $Nb_2Zr_2O_{17-x}N_2$, by thermal ammonolysis of $Nb_2Zr_6O_{17}$, which performs actively as a H₂

¹⁰ production photocatalyst from H_2S splitting under visible light irradiation. At a catalyst loading of 2.0 g/L, a quantum yield as high as 13.5% was obtained in an aqueous KOH solution under constant H_2S flow (2.5 ml/min) when a 420 nm cutoff filter was used.

15 7.3.3 Degradation of Organic Compounds

Many research groups have studied the photocatalytic degradation of organic compounds under visible light irradiation to examine the activities of mixed transition metal oxide semiconductor materials. A wide range of compounds

- ²⁰ has been used as the organic substrates, including primarily organic dyes such as methylene blue^{406, 407}, methyl orange³⁷⁷, ⁴⁰⁸, Rhodamine B⁴⁰⁹, together with some other pollutants (e.g., benzene³⁷⁷, CHCl₃, chlorophenol⁴¹⁰) and a few simpler molecules such as CH₃CHO⁴¹¹ and 2-propanol.^{359, 412} In the
- ²⁵ case of dye degradation, most researchers focused on the decoloration kinetics, while only a few examined the total destruction of the dyes.

It has long been recognized that three reaction pathways possibly exist that may account for dye decomposition: 1)

- ³⁰ photocatalytic degradation, 2) photosensitization-induced reaction and 3) direct photolysis. These reaction routes have been observed in many mixed-oxide photocatalytic systems. For instance, $CaIn_2O_4^{413}$ has an absorption edge of ~480 nm, but it can catalyze the degradation of methylene blue when a
- ³⁵ 580 nm cutoff filter is used. The reaction pathway was explained by the dye-photosensitization scheme. The electrons excited from the ground state (via the intramolecular π - π * transition) of the adsorbed dye molecules can be instantaneously injected into the conduction band of the
- ⁴⁰ semiconductor particles. Subsequently, the trapped electrons can react with adsorbed O_2 molecules to generate O_2^{+} as the oxidizing species for further destruction of the dyes. In contrast, in the degradation of Alizarin Red dye catalyzed by AgAlO₂, the change in its photocatalytic properties closely
- ⁴⁵ followed the variation of the light wavelength, suggesting that this process is an intrinsic photocatalytic reaction, but not a dye-assisted photocatalytic reaction.³⁸⁷ In addition, as elucidated in many reports^{370, 414}, direct photolysis of dyes is another possible reaction pathway, during which the electron
- transfer from the excited dyes to O_2 takes place to form oxidizing singlet oxygen atoms. Nevertheless, it is usually the photocatalytic reaction routes that are considered to play a major role in the overall degradation.

Fu *et al.*⁴⁰⁹ carefully monitored variations in the total ⁵⁵ organic carbon (TOC) and the concentrations of NH_4^+ and NO_3^- during the degradation of Rhodamine B catalyzed by Bi₂WO₆ nanoparticles under visible light illumination. The authors clarified that the total mineralization of the dyes was much slower than the initial decoloration process. TOC ⁶⁰ measurement results indicated a two-stage mineralization mechanism: 1) the ring cleavage in the first place and, 2) subsequent oxidation of the fragments. The dyephotosensitization pathway was also confirmed in this report.

- To test the activities of a series of Ag-based oxides, i.e., 65 AgAlO₂, AgCrO₂ and Ag₂CrO₄, Ouyang *et al.*³⁷⁷ employed two types of compounds, i.e., methyl orange and gaseous benzene as the organic substrates. Ag₂CrO₄ with a bandgap of 1.75 eV was found to be the most active photocatalyst for the destruction of both substrates under visible light irradiation up 70 to 570 nm. It is worth mentioning that Ag₂CrO₄ was found to perform much more efficiently than traditional Degussa P25 powder in the decomposition of gaseous benzene under full arc irradiation, even though its surface area is lower than that of P25 by one order of magnitude.
- ⁷⁵ BaBiO₃, another novel material with a very narrow bandgap (2.05 eV), exhibited considerable activity in the destruction of acetaldehyde and methylene blue.³⁷⁰ The efficiency of the acetaldehyde conversion into CO₂ remained at a high level when the wavelength of the irradiation light ⁸⁰ was changed from 350 nm (~75%) to ~550 nm (~60%). Using a 440 nm cutoff filter, a CO₂ conversion yield of more than 80% could be achieved within one hour of illumination. In the degradation of methylene blue, on the other hand, total decoloration (containing a factor of pure photolysis efficiency ⁸⁵ of ~20%) using a 420 nm cutoff filter was achieved within one hour.

Li *et al.*³⁸⁴ investigated the dependence of the rate of photocatalytic isopropanol oxidation upon the composition of the $(AgNbO_3)_{1-x}(NaNbO_3)_x$ solid solutions. The authors ⁹⁰ explicitly correlated the composition parameter, *x*, with both the physicochemical properties (e.g., particle size, surface area, and capacity of isopropanol adsorption) and the electronic band structures of the catalysts. The value of *x*=0.4 was considered as the optimum composition, under which the ⁹⁵ competition among the optical absorption, surface area and the oxidizing power of the material was balanced to achieve the highest efficiency.

The photocatalytic activity in the CO₂ evolution from CH₃CHO decomposition over another solid solution, ¹⁰⁰ (Ag_{0.75}Sr_{0.25})_{1-x}(Ag_{0.75}Sr_{0.25})O₃, under visible light irradiation was examined by Wang *et al.*³⁸⁶ The authors reported a quantum efficiency of 1.48% at $\lambda = 440$ nm, which tripled that of N-doped TiO₂ at $\lambda = 436$ nm (0.42%)²⁵⁰, although the BET surface area of (Ag_{0.75}Sr_{0.25})₁. ¹⁰⁵ _x(Ag_{0.75}Sr_{0.25})O₃ (~1 m²/g) was much smaller than that of TiO_{2-x}N_x (~67 m²/g).

Oxyhalide-based materials were also tested for photocatalytic degradation of organic compounds under visible light irradiation. As described in a report by Wang *et* $al.^{369}$, xBiOBr-(1-x)BiOI was most active when x=0.25 for methyl orange degradation at $\lambda > 420$ nm. Another Bi-based narrow-bandgap (2.38 eV) oxychloride, Bi₄NbO₈Cl, exhibiting a layered structure, was tested for the destruction of the same dye by Lin *et al.*³⁶⁸ The material performed well ¹¹⁵ under visible light irradiation, due to, at least partially, the internal electric fields between the [Bi₂O₂] and [Cl] layers in the crystalline structure of Bi₄NbO₈Cl.

Photoelectrocatalytic experiments employing mixed oxide electrodes were also conducted to investigate their activities under visible light illumination. Zhao *et al.*^{410, 415} investigated

- ⁵ the degradation of triazine-containing azo dyes, i.e., anionic reactive brilliant red K-2G, reactive brilliant red X-3B, and reactive yellow KD-3G, using γ -Bi₂MoO₆ films (bandgap 2.67 eV) as the photoelectrodes. The authors applied a 3.0 V (vs. SCE) bias potential, which by itself could induce the
- ¹⁰ electrooxidation of the dyes. Synergetic effects between the electrooxidation and photocatalysis were confirmed based upon the degradation kinetics and the TOC variation. In particular, after analyzing the degradation intermediates, the authors proposed that the destruction of K-2G proceeds first
- ¹⁵ through the cleavage of the azo bond leading to the decoloration, followed by the opening of the phenyl and naphthalene ring for further degradation. Similar synergetic effects were also observed by Zhao *et al.*⁴¹⁰ when they studied the photocatalytic oxidation of 4-chlorophenol using Bi₂WO₆
- ²⁰ nanoflake films under bias potentials. It was commonly recognized that electrooxidation in the dark resulted in the deactivation of the electrode surface due to the electropolymerization of the intermediate radicals on the surface, a process frequently encountered in the electrooxidation of
- 25 organic pollutants. The synergetic effects were then interpreted by the fact that the photogenerated charge carriers can efficiently react with the intermediate radicals, thus reactivating the electrode surface.

8. Concluding Remarks

- ³⁰ The photocatalytic oxidation of mainly organic pollutants in water and air as an advanced oxidation process has been proved to be an effective technique for environmental remediation. To develop efficient photocatalytic systems, high-quality semiconductor-based materials have been
- as actively studied in recent years. Among a wide spectrum of semiconductors, TiO_2 has attracted significant attention over the past decades due to its excellent performance as a photocatalyst under UV light irradiation. The development of synthesis methods for various nanostructures based on TiO_2
- ⁴⁰ allows further enhancement of the photocatalytic performance of TiO₂. Considerable efforts have also been expended on the development of visible-light-sensitive materials to extend the usable solar energy spectrum. For example, photocatalysts based on mixed oxide semiconductors have attracted
- ⁴⁵ considerable attention during the past ten years. Studies in this field have brought profound understanding to materials science, which continuously contributes to the design of visible-light-sensitive photocatalysts. These efforts are of special environmental and economic significance in the
- ⁵⁰ context of solving several environmental problems, e.g., seeking "clean energy". Although the photocatalysts reviewed here only cover a small portion of the full range of applicable materials, theoretical and experimental evidence has accumulated confirming that such materials can serve as the
- ⁵⁵ basis upon which highly efficient photocatalysts for solar energy utilization can be developed.

Notes

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65 References

- 1. A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37-38.
- M. R. Hoffmann, S. T. Martin, W. Y. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, 95, 69-96.
- 3. A. G. Agrios and P. Pichat, *J. Appl. Electrochem.*, 2005, **35**, 655-663.
- 4. M. Kaneko and I. Okura, *Photocatalysis: Science and Technology*, Kodansha: Tokyo; Springer: Berlin, New York, 2002.
- 5. F. E. Osterloh, Chem. Mat., 2008, 20, 35-54.
- R. van de Krol, Y. Q. Liang and J. Schoonman, J. Mater. Chem.,
 2008, 18, 2311-2320.
- B. D. Alexander, P. J. Kulesza, L. Rutkowska, R. Solarska and J. Augustynski, *J. Mater. Chem.*, 2008, 18, 2298-2303.
- K. Rajeshwar, N. R. de Tacconi and C. R. Chenthamarakshan, *Chem. Mat.*, 2001, 13, 2765-2782.
- D. F. Ollis, E. Pelizzetti and N. Serpone, *Environ. Sci. Technol.*, 1991, 25, 1522-1529.
- 10. H. Gerischer, *Electrochim. Acta*, 1995, 40, 1277-1281.
- 11. H. Gerischer and A. Heller, *J. Electrochem. Soc.*, 1992, **139**, 113-118.
- 85 12. R. Memming, Semiconductor Electrochemistry, WILEY-VCH Verlag GmbH, Weinheim, 2001.
- 13. A. L. Linsebigler, G. Q. Lu and J. T. Yates, *Chem. Rev.*, 1995, **95**, 735-758.
- 14. A. P. Alivisatos, J. Phys. Chem., 1996, 100, 13226-13239.
- 90 15. A. P. Alivisatos, *Science*, 1996, **271**, 933-937.
 - 16. L. E. Brus, J. Chem. Phys., 1983, 79, 5566-5571.
 - 17. L. E. Brus, J. Chem. Phys., 1984, 80, 4403-4409.
 - R. Rossetti, J. L. Ellison, J. M. Gibson and L. E. Brus, J. Chem. Phys., 1984, 80, 4464-4469.
- 95 19. D. W. Bahnemann, C. Kormann and M. R. Hoffmann, *Journal of Physical Chemistry*, 1987, **91**, 3789-3798.
- 20. E. M. Wong and P. C. Searson, *Appl. Phys. Lett.*, 1999, **74**, 2939-2941.
- C. Kormann, D. W. Bahnemann and M. R. Hoffmann, J. Phys.
 Chem., 1988, **92**, 5196-5201.
 - B. Kraeutler and A. J. Bard, J. Am. Chem. Soc., 1978, 100, 4317-4318.
 - 23. S. N. Frank and A. J. Bard, J. Am. Chem. Soc., 1975, 97, 7427-7433.
 - 24. S. N. Frank and A. J. Bard, J. Am. Chem. Soc., 1977, 99, 303-304.
- 105 25. D. Bahnemann, A. Henglein, J. Lilie and L. Spanhel, Journal of Physical Chemistry, 1984, 88, 709-711.
 - 26. D. Bahnemann, A. Henglein and L. Spanhel, *Faraday Discussions* of the Chemical Society, 1984, **78**, 151-163.
- 27. D. W. Bahnemann, M. Hilgendorff and R. Memming, J. Phys.
 110 Chem. B, 1997, 101, 4265-4275.

- N. Murakami, O. O. P. Mahaney, T. Torimoto and B. Ohtani, *Chem. Phys. Lett.*, 2006, **426**, 204-208.
- 29. D. W. Bahnemann, Isr. J. Chem., 1993, 33, 115-136.
- N. Serpone, D. Lawless, R. Khairutdinov and E. Pelizzetti, J. Phys. Chem., 1995, 99, 16655-16661.
- D. P. Colombo Jr and R. M. Bowman, J. Phys. Chem., 1995, 99, 11752-11756.
- T. Yoshihara, R. Katoh, A. Furube, Y. Tamaki, M. Murai, K. Hara, S. Murata, H. Arakawa and M. Tachiya, *J. Phys. Chem. B*, 2004, 108, 3817-3823.
- 33. R. Enriquez, A. G. Agrios and P. Pichat, *Catal. Today*, 2007, **120**, 196-202.
- 34. C. S. Turchi and D. F. Ollis, J. Catal., 1990, 122, 178-192.

40

- 35. R. M. Gao, J. Stark, D. W. Bahnemann and J. Rabani, J. 15 Photochem. Photobiol. A-Chem., 2002, **148**, 387-391.
 - C. Y. Wang, C. Bottcher, D. W. Bahnemann and J. K. Dohrmann, J. Mater. Chem., 2003, 13, 2322-2329.
 - 37. C. Y. Wang, R. Pagel, J. K. Dohrmann and D. W. Bahnemann, *C. R. Chim.*, 2006, **9**, 761-773.
- 20 38. C. Richard and P. Boule, Sol. Energy Mater. Sol. Cells, 1995, 38, 431-440.
- C. Y. Wang, J. Rabani, D. W. Bahnemann and J. K. Dohrmann, J. Photochem. Photobiol. A-Chem., 2002, 148, 169-176.
- 40. C. Y. Wang, R. Pagel, D. W. Bahnemann and J. K. Dohrmann, *J. Phys. Chem. B*, 2004, **108**, 14082-14092.
- 41. T. Torimoto, N. Nakamura, S. Ikeda and B. Ohtani, *Phys. Chem. Chem. Phys.*, 2002, **4**, 5910-5914.
- 42. C. Wang, D. W. Bahnemann and J. K. Dohrmann, *Water Sci. Technol.*, 2001, **44**, 279-286.
- 30 43. U. Siemon, D. Bahnemann, J. J. Testa, D. Rodriguez, M. I. Litter and N. Bruno, J. Photochem. Photobiol. A-Chem., 2002, 148, 247-255.
- 44. A. Y. Nosaka, T. Fujiwara, H. Yagi, H. Akutsu and Y. Nosaka, J. *Phys. Chem. B*, 2004, **108**, 9121-9125.
- 35 45. S. T. Cheng, C. R. Chenthamarakshan, N. R. de Tacconi and K. Rajeshwar, *Res. Chem. Intermed.*, 2007, 33, 225-237.
 - D. Gumy, S. A. Giraldo, J. Rengifo and C. Pulgarin, *Appl. Catal. B-Environ.*, 2008, **78**, 19-29.
 - D. Friedmann, H. Hansing and D. Bahnemann, Z. Phys. Chemie-Int. J. Res. Phys. Chem. Chem. Phys., 2007, 221, 329-348.
- 48. D. M. Antonelli and J. Y. Ying, Angew. Chem.-Int. Edit. Engl., 1995, **34**, 2014-2017.
- U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer and M. Gratzel, *Nature*, 1998, **395**, 583-585.
- 45 50. E. L. Crepaldi, G. Soler-Illia, D. Grosso, F. Cagnol, F. Ribot and C. Sanchez, *J. Am. Chem. Soc.*, 2003, **125**, 9770-9786.
 - 51. J. C. Yu, J. G. Yu and J. C. Zhao, *Appl. Catal. B-Environ.*, 2002, **36**, 31-43.
- 52. J. G. Yu, J. C. Yu, W. K. Ho and Z. T. Jiang, *New J. Chem.*, 2002,
 26, 607-613.
- 53. J. Tang, Y. Y. Wu, E. W. McFarland and G. D. Stucky, *Chemical Communications*, 2004, 1670-1671.
- 54. H. Choi, E. Stathatos and D. D. Dionysiou, *Appl. Catal. B-Environ.*, 2006, **63**, 60-67.
- 55 55. J. H. Pan and W. I. Lee, Chem. Mat., 2006, 18, 847-853.

- Y. Sakatani, D. Grosso, L. Nicole, C. Boissiere, G. Soler-Illia and C. Sanchez, *J. Mater. Chem.*, 2006, 16, 77-82.
- 57. A. Feldhoff, C. Mendive, T. Bredow and D. Bahnemann, *ChemPhysChem*, 2007, **8**, 805-809.
- 60 58. M. A. Blesa, A. D. Weisz, P. J. Morando, J. A. Salfity, G. E. Magaz and A. E. Regazzoni, *Coordination Chemistry Reviews*, 2000, **196**, 31-63.
 - A. D. Weisz, A. E. Regazzoni and M. A. Blesa, *Solid State Ion.*, 2001, 143, 125-130.
- 65 60. A. D. Weisz, A. E. Regazzoni and M. A. Blesa, *Croat. Chem. Acta*, 2007, **80**, 325-332.
 - C. B. Mendive, T. Bredow, A. Feldhoff, M. Blesa and D. Bahnemann, *Physical Chemistry Chemical Physics*, 2008, 10, 1960-1974.
- 70 62. D. V. Kozlov, E. A. Paukshtis and E. N. Savinov, *Appl. Catal. B-Environ.*, 2000, **24**, L7-L12.
 - P. Z. Araujo, C. B. Mendive, L. A. G. Rodenas, P. J. Morando, A. E. Regazzoni, M. A. Blesa and D. Bahnemann, *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 2005, 265, 73-80.
 - C. B. Mendive, D. W. Bahnemann and M. A. Blesa, *Catal. Today*, 2005, **101**, 237-244.
 - C. B. Mendive, T. Bredow, M. A. Blesa and D. W. Bahnemann, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3232-3247.
- 80 66. D. Duonghong, J. Ramsden and M. Gratzel, J. Am. Chem. Soc., 1982, 104, 2977-2985.
- 67. M. Gratzel, Nature, 2001, 414, 338-344.

- 68. C. Richard, New J. Chem., 1994, 18, 443-445.
- 69. A. A. Khodja, T. Sehili, J. F. Pilichowski and P. Boule, J. *Photochem. Photobiol. A-Chem.*, 2001, **141**, 231-239.
- L. Q. Jing, B. F. Xin, F. L. Yuan, B. Q. Wang, K. Y. Shi, W. M. Cai and H. G. Fu, *Appl. Catal. A-Gen.*, 2004, 275, 49-54.
- O. Seven, B. Dindar, S. Aydemir, D. Metin, M. A. Ozinel and S. Icli, *J. Photochem. Photobiol. A-Chem.*, 2004, 165, 103-107.
- 90 72. N. Daneshvar, D. Salari and A. R. Khataee, J. Photochem. Photobiol. A-Chem., 2004, **162**, 317-322.
- S. Sakthivel, B. Neppolian, M. V. Shankar, B. Arabindoo, M. Palanichamy and V. Murugesan, *Sol. Energy Mater. Sol. Cells*, 2003, 77, 65-82.
- 95 74. M. C. Yeber, J. Rodriguez, J. Freer, N. Duran and H. D. Mansilla, *Chemosphere*, 2000, **41**, 1193-1197.
 - L. Amalric, C. Guillard and P. Pichat, *Res. Chem. Intermed.*, 1994, 20, 579-594.
- 76. A. Akyol, H. C. Yatmaz and M. Bayramoglu, *Appl. Catal. B- Environ.*, 2004, 54, 19-24.
 - H. C. Yatmaz, A. Akyol and M. Bayramoglu, *Ind. Eng. Chem. Res.*, 2004, 43, 6035-6039.
 - S. Chakrabarti and B. K. Dutta, J. Hazard. Mater., 2004, 112, 269-278.
- ¹⁰⁵ 79. L. Q. Jing, Z. L. Xu, Y. G. Du, X. J. Sun, L. Wang, X. Q. Zhou, H. Y. Shan and W. M. Cai, *Chem. J. Chin. Univ.-Chin.*, 2002, **23**, 871-875.
 - S. Sakthivel, B. Neppolian, M. Palanichamy, B. Arabindoo and V. Murugesan, *Water Sci. Technol.*, 2001, 44, 211-218.
- 110 81. S. Sakthivel, B. Neppolian, M. Palanichamy, B. Arabindoo and V. Murugesan, *Indian J. Chem. Technol.*, 1999, 6, 161-165.

- C. Richard, A. M. Martre and P. Boule, *J. Photochem. Photobiol. A-Chem.*, 1992, 66, 225-234.
- A. Fujishima, T. Kato, E. Maekawa and K. Honda, Bulletin of The Chemical Society of Japan, 1981, 54, 1671-1674.
- 5 84. Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, X. L. He, J. P. Li and C. L. Lin, *Appl. Phys. Lett.*, 2004, **84**, 3654-3656.
- U. Ozgur, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho and H. Morkoc, *J. Appl. Phys.*, 2005, 98, 103.
- 10 86. S. J. Pearton, D. P. Norton, K. Ip, Y. W. Heo and T. Steiner, *Prog. Mater. Sci.*, 2005, **50**, 293-340.
- X. D. Wang, C. J. Summers and Z. L. Wang, *Nano Lett.*, 2004, 4, 423-426.
- S. A. Studenikin, N. Golego and M. Cocivera, J. Appl. Phys., 1998,
 84, 2287-2294.
- Y. Li, G. W. Meng, L. D. Zhang and F. Phillipp, *Appl. Phys. Lett.*, 2000, 76, 2011-2013.
- Y. C. Kong, D. P. Yu, B. Zhang, W. Fang and S. Q. Feng, *Appl. Phys. Lett.*, 2001, **78**, 407-409.
- 20 91. K. Vinodgopal and P. V. Kamat, *Environ. Sci. Technol.*, 1995, 29, 841-845.
- K. Vinodgopal, I. Bedja and P. V. Kamat, *Chem. Mat.*, 1996, 8, 2180-2187.
- 93. C. Wang, J. C. Zhao, X. M. Wang, B. X. Mai, G. Y. Sheng, P. Peng
 and J. M. Fu, *Appl. Catal. B-Environ.*, 2002, **39**, 269-279.
- W. Cun, X. M. Wang, B. Q. Xu, J. C. Zhao, B. X. Mai, P. Peng, G. Y. Sheng and H. M. Fu, *J. Photochem. Photobiol. A-Chem.*, 2004, 168, 47-52.
- 95. M. L. Zhang, T. C. An, X. H. Hu, C. Wang, G. Y. Sheng and J. M.
 Fu, *Appl. Catal. A-Gen.*, 2004, **260**, 215-222.
- 96. G. Wang, W. Lu, J. H. Li, J. Choi, Y. S. Jeong, S. Y. Choi, J. B. Park, M. K. Ryu and K. Lee, *Small*, 2006, 2, 1436-1439.
- C. Santato, M. Odziemkowski, M. Ulmann and J. Augustynski, J. Am. Chem. Soc., 2001, 123, 10639-10649.
- 35 98. D. Monllor-Satoca, L. Borja, A. Rodes, R. Gomez and P. Salvador, *ChemPhysChem*, 2006, 7, 2540-2551.
 - 99. G. Hodes, D. Cahen and J. Manasson, Nature, 1976, 260, 312-313.
- 100. K. L. Hardee and A. J. Bard, J. Electrochem. Soc., 1977, **124**, 215-224.
- 40 101. W. Gissler and R. Memming, J. Electrochem. Soc., 1977, 124, 1710-1714.
 - 102. R. Abe, T. Takata, H. Sugihara and K. Domen, *Chemical Communications*, 2005, 3829-3831.
- 103. A. Hameed, M. A. Gondal and Z. H. Yamani, *Catal. Commun.*, 2004, **5**, 715-719.
- 104. D. W. Hwang, J. Kim, T. J. Park and J. S. Lee, *Catal. Lett.*, 2002, 80, 53-57.
- 105. S. H. Baeck, K. S. Choi, T. F. Jaramillo, G. D. Stucky and E. W. McFarland, *Adv. Mater.*, 2003, **15**, 1269-1273.
- 50 106. S. Badilescu and P. V. Ashrit, Solid State Ion., 2003, 158, 187-197.
 - 107. S. Papaefthimiou, G. Leftheriotis and P. Yianoulis, *Electrochim. Acta*, 2001, 46, 2145-2150.
 - K. Kim, C. Seo and H. Cheong, *Journal of the Korean Physical Society*, 2006, 48, 1657-1660.
- 55 109. N. Xu, M. Sun, Y. W. Cao, J. N. Yao and E. G. Wang, Appl. Surf. Sci., 2000, 157, 81-84.

- 110. L. Y. Su, J. H. Fang and Z. H. Lu, Mater. Chem. Phys., 1997, 51, 85-87.
- 111. C. Bechinger, E. Wirth and P. Leiderer, *Appl. Phys. Lett.*, 1996, 68, 2834-2836.
- Y. Shigesato, Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers, 1991, 30, 1457-1462.
- C. Bechinger, G. Oefinger, S. Herminghaus and P. Leiderer, J. Appl. Phys., 1993, 74, 4527-4533.
- 65 114. B. C. Faust, M. R. Hoffmann and D. W. Bahnemann, J. Phys. Chem., 1989, 93, 6371-6381.
 - 115. S. N. Frank and A. J. Bard, J. Phys. Chem., 1977, 81, 1484-1488.
 - 116. J. K. Leland and A. J. Bard, J. Phys. Chem., 1987, 91, 5076-5083.
 - 117. T. Ohmori, H. Takahashi, H. Mametsuka and E. Suzuki, *Phys. Chem. Chem. Phys.*, 2000, **2**, 3519-3522.
 - 118. S. U. M. Khan and J. Akikusa, J. Phys. Chem. B, 1999, 103, 7184-7189.
 - B. Pal and M. Sharon, J. Chem. Technol. Biotechnol., 1998, 73, 269-273.
- 75 120. C. Pulgarin and J. Kiwi, *Langmuir*, 1995, 11, 519-526.

- 121. T. Kawahara, K. Yamada and H. Tada, J. Colloid Interface Sci., 2006, 294, 504-507.
- B. Ohtani, J. Kawaguchi, M. Kozawa, Y. Nakaoka and Y. Nosaka, J. Photochem. Photobiol. A-Chem., 1995, 90, 75-80.
- 80 123. T. Hirai, Y. Bando and I. Komasawa, J. Phys. Chem. B, 2002, 106, 8967-8970.
 - 124. E. Granot, F. Patolsky and I. Willner, J. Phys. Chem. B, 2004, 108, 5875-5881.
- R. Baron, C. H. Huang, D. M. Bassani, A. Onopriyenko, M. Zayats
 and I. Willner, *Angewandte Chemie-International Edition*, 2005, 44, 4010-4015.
 - 126. M. Warrier, M. K. F. Lo, H. Monbouquette and M. A. Garcia-Garibay, *Photochem. Photobiol. Sci.*, 2004, 3, 859-863.
- 127. D. Meissner and R. Memming, J. Phys. Chem., 1988, **92**, 3476-3483.
- 128. D. Meissner, R. Memming, B. Kastening and D. Bahnemann, *Chem. Phys. Lett.*, 1986, **127**, 419-423.
- 129. D. W. Jing and L. J. Guo, J. Phys. Chem. B, 2006, 110, 11139-11145.
- 95 130. H. Weiss, A. Fernandez and H. Kisch, Angewandte Chemie-International Edition, 2001, 40, 3825-3827.
 - 131. H. Kisch and H. Weiss, Adv. Funct. Mater., 2002, 12, 483-488.
 - 132. X. Z. Fu, L. A. Clark, Q. Yang and M. A. Anderson, *Environ. Sci. Technol.*, 1996, **30**, 647-653.
- 100 133. M. E. Zorn, D. T. Tompkins, W. A. Zeltner and M. A. Anderson, *Appl. Catal. B-Environ.*, 1999, 23, 1-8.
 - 134. Y. R. Do, W. Lee, K. Dwight and A. Wold, *J. Solid State Chem.*, 1994, **108**, 198-201.
- 135. J. Papp, S. Soled, K. Dwight and A. Wold, *Chem. Mat.*, 1994, 6, 496-500.
 - 136. Y. T. Kwon, K. Y. Song, W. I. Lee, G. J. Choi and Y. R. Do, J. Catal., 2000, 191, 192-199.
 - 137. H. Hidaka, J. Zhao, E. Pelizzetti and N. Serpone, J. Phys. Chem., 1992, 96, 2226-2230.
- 110 138. A. Fuerte, M. D. Hernandez-Alonso, A. J. Maira, A. Martinez-Arias, M. Fernandez-Garcia, J. C. Conesa, J. Soria and G. Munuera, *J. Catal.*, 2002, **212**, 1-9.

- 139. M. Miyauchi, A. K. Nakajima, T. Watanabe and K. Hashimoto, *Chem. Mat.*, 2002, **14**, 4714-4720.
- 140. S. Somasundaram, N. Tacconi, C. R. Chenthamarakshan, K. Rajeshwar and N. R. de Tacconi, *J. Electroanal. Chem.*, 2005, 577, 167-177.
- 141. V. Keller, P. Bernhardt and F. Garin, J. Catal., 2003, 215, 129-138.
- 142. S. Higashimoto, M. Sakiyama and M. Azuma, *Thin Solid Films*, 2006, **503**, 201-206.
- 143. M. Miyauchi, A. Nakajima, K. Hashimoto and T. Watanabe, *Adv. Mater.*, 2000, **12**, 1923-1927.
- 144. B. Levy, W. Liu and S. E. Gilbert, J. Phys. Chem. B, 1997, 101, 1810-1816.
- 145. N. Kanai, T. Nuida, K. Ueta, K. Hashimoto, T. Watanabe and H. Ohsaki, *Vacuum*, 2004, **74**, 723-727.
- 15 146. A. Hattori, Y. Tokihisa, H. Tada and S. Ito, J. Electrochem. Soc., 2000, 147, 2279-2283.
 - 147. I. Bedja and P. V. Kamat, J. Phys. Chem., 1995, 99, 9182-9188.
 - 148. P. V. Kamat, in *Molecular Level Artificial Photosynthetic Materials*, 1997, pp. 273-343.
- 20 149. A. Hattori, Y. Tokihisa, H. Tada, N. Tohge, S. Ito, K. Hongo, R. Shiratsuchi and G. Nogami, J. Sol-Gel Sci. Technol., 2001, 22, 53-61.
 - 150. J. Shang, W. Q. Yao, Y. F. Zhu and N. Z. Wu, Appl. Catal. A-Gen., 2004, 257, 25-32.
- 25 151. L. X. Cao, H. B. Wan, L. H. Huo and S. Q. Xi, J. Colloid Interface Sci., 2001, 244, 97-101.
 - 152. T. Kawahara, Y. Konishi, H. Tada, N. Tohge and S. Ito, *Langmuir*, 2001, **17**, 7442-7445.
- 153. S. Srinivasan, J. Wade and E. K. Stefanakos, *Journal of Nanomaterials*, 2006, **2006**, 87326(87321-87327).
- 154. A. Kumar and A. K. Jain, J. Mol. Catal. A-Chem., 2001, 165, 265-273.
- 155. H. B. Yin, Y. Wada, T. Kitamura, T. Sakata, H. Mori and S. Yanagida, *Chem. Lett.*, 2001, 334-335.
- 35 156. Y. Bessekhouad, D. Robert and J. Weber, J. Photochem. Photobiol. A-Chem., 2004, 163, 569-580.
 - 157. J. C. Tristao, F. Magalhaes, P. Corio and M. T. C. Sansiviero, J. Photochem. Photobiol. A-Chem., 2006, 181, 152-157.
 - Y. Bessekhouad, N. Chaoui, M. Trzpit, N. Ghazzal, D. Robert and J. V. Weber, J. Photochem. Photobiol. A-Chem., 2006, 183, 218-224.
- 159. W. W. So, K. J. Kim and S. J. Moon, Int. J. Hydrog. Energy, 2004, 29, 229-234.
- 160. J. S. Jang, S. H. Choi, H. Park, W. Choi and J. S. Lee, J. Nanosci. Nanotechnol., 2006, 6, 3642-3646.
- ⁴⁵ 161. I. Robel, V. Subramanian, M. Kuno and P. V. Kamat, J. Am. Chem. Soc., 2006, **128**, 2385-2393.
 - 162. N. Serpone, E. Borgarello and M. Gratzel, ChemPhysChem, 1983.
 - 163. L. Spanhel, H. Weller and A. Henglein, J. Am. Chem. Soc., 1987, 109, 6632-6635.
- 50 164. J. E. Evans, K. W. Springer and J. Z. Zhang, J. Chem. Phys., 1994, 101, 6222-6225.
 - 165. J. C. Yu, L. Wu, J. Lin, P. Li and Q. Li, *Chemical Communications*, 2003, 9, 1552-1553.
 - 166. L. Wu, J. C. Yu and X. Fu, Journal of Molecular Catalysis A:
- 55 *Chemical*, 2006, **244**, 25-32.

- 167. J. Y. Wang, Z. H. Liu, Q. Zheng, Z. K. He and R. X. Cai, *Nanotechnology*, 2006, **17**, 4561-4566.
- 168. Y. Bessekhouad, N. Chaoui, M. Trzpit, N. Ghazzal, D. Robert and J. V. Weber, *TiO2 electrode; Photoelectrochemical oxidation; Microwave; Hydrothermal treatment,* 2006, **183**, 218-224.
 - 169. P. A. Sant and P. V. Kamat, *Phys. Chem. Chem. Phys.*, 2002, 4, 198-203.
 - 170. M. C. Hsu, I. C. Leu, Y. M. Sun and M. H. Hon, J. Cryst. Growth, 2005, 285, 642-648.
- 65 171. P. Pichat, New J. Chem., 1987, 11, 135-140.
 - 172. B. Ohtani, M. Kakimoto, S. Nishimoto and T. Kagiya, J. Photochem. Photobiol. A-Chem., 1993, **70**, 265-272.
 - 173. K. D. Schierbaum, U. K. Kirner, J. F. Geiger and W. Gopel, Sens. Actuator B-Chem., 1991, 4, 87-94.
- 70 174. Y. M. Gao, W. Lee, R. Trehan, R. Kershaw, K. Dwight and A. Wold, *Mater. Res. Bull.*, 1991, 26, 1247-1254.
 - 175. V. Subramanian, E. E. Wolf and P. V. Kamat, J. Am. Chem. Soc., 2004, **126**, 4943-4950.
 - 176. J. G. Yu and X. J. Zhao, Rare Metal Mat. Eng., 2000, 29, 390-393.
- 75 177. T. Sano, N. Negishi, D. Mas and K. Takeuchi, J. Catal., 2000, 194, 71-79.
 - 178. A. Sclafani, M. N. Mozzanega and P. Pichat, J. Photochem. Photobiol. A-Chem., 1991, 59, 181-189.
 - 179. D. Friedmann, H. Hansing and D. Bahnemann, Zeitschrift fur Physikalische Chemie, 2007, **221**, 329-348.
 - 180. T. Hirakawa and P. V. Kamat, Langmuir, 2004, 20, 5645-5647.

- 181. T. Hirakawa and P. V. Kamat, J. Am. Chem. Soc., 2005, 127, 3928-3934.
- 182. A. Wood, M. Giersig and P. Mulvaney, J. Phys. Chem. B, 2001, 5 105, 8810-8815.
- 183. J. G. Yu, J. F. Xiong, B. Cheng and S. W. Liu, Appl. Catal. B-Environ., 2005, 60, 211-221.
- 184. B. Sun, A. V. Vorontsov and P. G. Smirniotis, *Langmuir*, 2003, 19, 3151-3156.
- 90 185. J. X. He, P. J. Yang, H. Sato, Y. Umemura and A. Yamagishi, J. *Electroanal. Chem.*, 2004, **566**, 227-233.
 - 186. H. M. Sung-Suh, J. R. Choi, H. J. Hah, S. M. Koo and Y. C. Bae, J. Photochem. Photobiol. A-Chem., 2004, 163, 37-44.
- 187. H. Tada, K. Teranishi, Y. Inubushi and S. Ito, *Langmuir*, 2000, 16, 3304-3309.
 - 188. H. Tada, T. Ishida, A. Takao and S. Ito, *Langmuir*, 2004, **20**, 7898-7900.
 - 189. H. Tada, K. Teranishi and S. Ito, Langmuir, 1999, 15, 7084-7087.
- 190. T. T. Y. Tan, C. K. Yip, D. Beydoun and R. Amal, *Chem. Eng. J.*,
 2003, **95**, 179-186.
 - 191. B. F. Xin, L. Q. Jing, Z. Y. Ren, B. Q. Wang and H. G. Fu, J. Phys. Chem. B, 2005, 109, 2805-2809.
 - 192. A. Kumar and N. Mathur, Appl. Catal. A-Gen., 2004, 275, 189-197.
 - 193. E. Stathatos and P. Lianos, Langmuir, 2000, 16, 2398-2400.
- 105 194. H. Einaga, M. Harada, S. Futamura and T. Ibusuki, J. Phys. Chem. B, 2003, 107, 9290-9297.
 - 195. K. Kawahara, K. Suzuki, Y. Ohka and T. Tatsuma, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3851-3855.
- 196. C. S. Ah, H. S. Han, K. Kim and D. J. Jang, *J. Phys. Chem. B*, 2000,
 104, 8153-8159.

- 197. P. V. Kamat, M. Flumiani and G. V. Hartland, J. Phys. Chem. B, 1998, 102, 3123-3128.
- 198. K. Murakoshi, H. Tanaka, Y. Sawai and Y. Nakato, J. Phys. Chem. B, 2002, 106, 3041-3045.
- ⁵ 199. R. C. Jin, Y. W. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz and J. G. Zheng, *Science*, 2001, **294**, 1901-1903.
- 200. N. R. Jana, T. K. Sau and T. Pal, J. Phys. Chem. B, 1999, 103, 115-121.
- 201. A. Roucoux, J. Schulz and H. Patin, *Chem. Rev.*, 2002, **102**, 3757-3778.
- 202. N. Pradhan, A. Pal and T. Pal, Langmuir, 2001, 17, 1800-1802.
- 203. R. Narayanan and M. A. El-Sayed, J. Am. Chem. Soc., 2003, 125, 8340-8347.
- 204. P. D. Cozzoli, E. Fanizza, R. Comparelli, M. L. Curri, A. Agostiano and D. Laub, *J. Phys. Chem. B*, 2004, **108**, 9623-9630.
- 205. V. Subramanian, E. E. Wolf and P. V. Kamat, *Langmuir*, 2003, 19, 469-474.
- 206. P. D. Cozzoli, R. Comparelli, E. Fanizza, M. L. Curri, A. Agostiano and D. Laub, J. Am. Chem. Soc., 2004, **126**, 3868-3879.
- 20 207. L. Z. Zhang and J. C. Yu, Catal. Commun., 2005, 6, 684-687.
 - 208. J. N. Yao, K. Hashimoto and A. Fujishima, *Nature*, 1992, **355**, 624-626.
 - 209. M. Irie, Chem. Rev., 2000, 100, 1685-1716.
- 210. Y. Ohko, T. Tatsuma, T. Fujii, K. Naoi, C. Niwa, Y. Kubota and A.
 ²⁵ Fujishima, *Nat. Mater.*, 2003, **2**, 29-31.
- 211. K. Naoi, Y. Ohko and T. Tatsuma, J. Am. Chem. Soc., 2004, 126, 3664-3668.
- 212. K. Naoi, Y. Ohko and T. Tatsuma, *Chemical Communications*, 2005, 1288-1290.
- 30 213. J. D. Grunwaldt, M. Maciejewski, O. S. Becker, P. Fabrizioli and A. Baiker, *J. Catal.*, 1999, **186**, 458-469.
- 214. M. A. Bollinger and M. A. Vannice, Appl. Catal. B-Environ., 1996, 8, 417-443.
- 215. S. S. Lee, C. Y. Fan, T. P. Wu and S. L. Anderson, J. Am. Chem.
- 35 *Soc.*, 2004, **126**, 5682-5683.
 - 216. T. Hayashi, K. Tanaka and M. Haruta, J. Catal., 1998, 178, 566-575.
 - 217. G. R. Bamwenda, S. Tsubota, T. Nakamura and M. Haruta, J. Photochem. Photobiol. A-Chem., 1995, **89**, 177-189.
- ⁴⁰ 218. G. Zhao, H. Kozuka and T. Yoko, *Thin Solid Films*, 1996, **277**, 147-154.
 - 219. Y. Nakato, K. Ueda, H. Yano and H. Tsubomura, J. Phys. Chem., 1988, 92, 2316-2324.
- 220. M. Jakob, H. Levanon and P. V. Kamat, *Nano Lett.*, 2003, **3**, 353- 100 358.
- 221. X. Z. Li and F. B. Li, Environ. Sci. Technol., 2001, 35, 2381-2387.
- 222. I. M. Arabatzis, T. Stergiopoulos, D. Andreeva, S. Kitova, S. G. Neophytides and P. Falaras, J. Catal., 2003, 220, 127-135.
- 223. R. S. Sonawane and M. K. Dongare, J. Mol. Catal. A-Chem., 2006,
 243, 68-76.
- 224. Y. Tian and T. Tatsuma, J. Am. Chem. Soc., 2005, 127, 7632-7637.
- 225. K. Okazaki, Y. Morikawa, S. Tanaka, K. Tanaka and M. Kohyama, *Phys. Rev. B*, 2004, **69**, 8.
- 226. J. G. Highfield and P. Pichat, New J. Chem., 1989, 13, 61-66.
- 55 227. J. S. Lee and W. Y. Choi, *Environ. Sci. Technol.*, 2004, **38**, 4026-4033.

- 228. T. A. Egerton and J. A. Mattinson, J. Photochem. Photobiol. A-Chem., 2008, 194, 283-289.
- 229. A. Linsebigler, C. Rusu and J. T. Yates, J. Am. Chem. Soc., 1996,
 118, 5284-5289.
- A. Henglein, B. Lindig and J. Westerhausen, J. Phys. Chem., 1981, 85, 1627-1628.
- 231. D. W. Bahnemann, A. Henglein and L. Spanhel, J. Phys. Chem., 1984, 88, 709-711.
- 65 232. D. W. Bahnemann, J. Mönig and R. Chapman, J. Phys. Chem., 1987, 91, 3872-3788.
 - 233. A. Furube, T. Asahi, H. Masuhara, H. Yamashita and M. Anpo, *Chem. Phys. Lett.*, 2001, **336**, 424-430.
- 234. H. Nakajima, T. Mori and M. Watanabe, *J. Appl. Phys.*, 2004, **96**, 70 925-927.
 - 235. M. Anpo, K. Chiba, M. Tomonari, S. Coluccia, M. Che and M. A. Fox, *Bulletin of the Chemical Society of Japan*, 1991, **64**, 543-551.
 - 236. A. Sclafani and J. M. Herrmann, *J. Photochem. Photobiol. A-Chem.*, 1998, **113**, 181-188.
- 75 237. H. Uchida, S. Katoh and M. Watanabe, *Electrochim. Acta*, 1998, 43, 2111-2116.
 - 238. W. Zhao, C. C. Chen, X. Z. Li, J. C. Zhao, H. Hidaka and N. Serpone, *J. Phys. Chem. B*, 2002, **106**, 5022-5028.
 - 239. V. Iliev, D. Tomova, L. Bilyarska, A. Eliyas and L. Petrov, *Appl. Catal. B-Environ.*, 2006, **63**, 266-271.
- 240. T. Sreethawong, Y. Suzuki and S. Yoshikawa, C. R. Chim., 2006, 9, 307-314.
- 241. X. Quan, S. Chen, J. Su, J. W. Chen and G. H. Chen, Sep. Purif. Technol., 2004, 34, 73-79.
- 85 242. P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi and M. Gratzel, *Nat. Mater.*, 2003, 2, 402-407.
- 243. A. Kay and M. Gratzel, Chem. Mat., 2002, 14, 2930-2935.
- 244. B. Oregan and M. Gratzel, Nature, 1991, 353, 737-740.
- 245. G. Bindaar, M. P. Dareedwards, J. B. Goodenough and A. Hamnett, *Journal of the Chemical Society-Faraday Transactions I*, 1983, **79**, 1199-1213.
 - 246. S. Sato, Chem. Phys. Lett., 1986, 123, 126-128.

- 247. N. C. Saha and H. G. Tompkins, J. Appl. Phys., 1992, 72, 3072-3079.
- 95 248. D. H. Lee, Y. S. Cho, W. I. Yi, T. S. Kim, J. K. Lee and H. J. Jung, *Appl. Phys. Lett.*, 1995, **66**, 815-816.
 - 249. T. Morikawa, R. Asahi, T. Ohwaki, K. Aoki and Y. Taga, *Jpn. J. Appl. Phys. Part 2 Lett.*, 2001, **40**, L561-L563.
 - 250. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, 2001, **293**, 269-271.
 - 251. N. Serpone, J. Phys. Chem. B, 2006, 110, 24287-24293.
 - 252. T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto and S. Sugihara, *Appl. Catal. B-Environ.*, 2003, 42, 403-409.
- 253. S. Sakthivel and H. Kisch, ChemPhysChem, 2003, 4, 487-490.
- 105 254. K. Takeshita, A. Yamashita, T. Ishibashi, H. Onishi, K. Nishijima and T. Ohno, J. Photochem. Photobiol. A-Chem., 2006, 177, 269-275.
 - 255. O. Diwald, T. L. Thompson, T. Zubkov, E. G. Goralski, S. D. Walck and J. T. J. Yates, *J. Phys. Chem. B*, 2004, **108**, 6004-6008.
- 110 256. T. Umebayashi, T. Yamaki, H. Itoh and K. Asai, *Appl. Phys. Lett.*, 2002, **81**, 454-456.

- 257. T. Yamamoto, F. Yamashita, I. Tanaka, E. Matsubara and A. Muramatsu, *Mater. Trans.*, 2004, **45**, 1987-1990.
- 258. F. H. Tian and C. B. Liu, J. Phys. Chem. B, 2006, 110, 17866-17871.
- 5 259. H. Wang and J. P. Lewis, J. Phys.-Condes. Matter, 2006, 18, 421-434.
- 260. T. Umebayashi, T. Yamaki, S. Tanaka and K. Asai, *Chem. Lett.*, 2003, **32**, 330-331.
- 261. H. Irie, Y. Watanabe and K. Hashimoto, *Chem. Lett.*, 2003, **32**, 772773.
- 262. T. C. Lu, S. Y. Wu, L. B. Lin and W. C. Zheng, *Physica B*, 2001, 304, 147-151.
- 263. D. Li, H. Haneda, S. Hishita and N. Ohashi, *Chem. Mat.*, 2005, **17**, 2596-2602.
- 15 264. D. Li, H. Haneda, S. Hishita, N. Ohashi and N. K. Labhsetwar, J. Fluor. Chem., 2005, **126**, 69-77.
 - 265. W. Ho, J. C. Yu and S. Lee, *Chemical Communications*, 2006, 1115-1117.
- 266. S. A. Bilmes, P. Mandelbaum, F. Alvarez and N. M. Victoria, J.
 20 Phys. Chem. B, 2000, 104, 9851-9858.
- 267. Z. S. Lin, A. Orlov, R. M. Lambert and M. C. Payne, J. Phys. Chem. B, 2005, 109, 20948-20952.
- 268. I. N. Martyanov, S. Uma, S. Rodrigues and K. J. Klabunde, *Chemical Communications*, 2004, 2476-2477.
- 25 269. Y. Z. Li, D. S. Hwang, N. H. Lee and S. J. Kim, *Chem. Phys. Lett.*, 2005, **404**, 25-29.
 - 270. J. C. Yu, W. K. Ho, J. G. Yu, H. Yip, P. K. Wong and J. C. Zhao, *Environ. Sci. Technol.*, 2005, **39**, 1175-1179.
- 271. T. Ohno, T. Mitsui and M. Matsumura, *Chem. Lett.*, 2003, **32**, 364-365.
- 272. T. Ohno, M. Akiyoshi, T. Umebayashi, K. Asai, T. Mitsui and M. Matsumura, *Appl. Catal. A-Gen.*, 2004, **265**, 115-121.
- 273. T. Ohno, T. Tsubota, M. Toyofuku and R. Inaba, *Catal. Lett.*, 2004, 98, 255-258.
- 35 274. J. A. Rodriguez, J. Hrbek, J. Dvorak, T. Jirsak and A. Maiti, *Chem. Phys. Lett.*, 2001, **336**, 377-384.
 - 275. Q. Shi, D. Yang, Z. Y. Jiang and J. Li, J. Mol. Catal. B-Enzym., 2006, 43, 44-48.
- 276. V. N. Kuznetsov and N. Serpone, J. Phys. Chem. B, 2006, 110, 25203-25209.
- 277. T. L. Ma, M. Akiyama, E. Abe and I. Imai, *Nano Lett.*, 2005, 5, 2543-2547.
- 278. C. Di Valentin, G. Pacchioni, A. Selloni, S. Livraghi and E. Giamello, J. Phys. Chem. B, 2005, 109, 11414-11419.
- 45 279. M. Mrowetz, W. Balcerski, A. J. Colussi and M. R. Hoffman, J. Phys. Chem. B, 2004, 108, 17269-17273.
 - 280. R. Nakamura, T. Tanaka and Y. Nakato, J. Phys. Chem. B, 2004, 108, 10617-10620.
- 281. M. Miyauchi, A. Ikezawa, H. Tobimatsu, H. Irie and K. Hashimoto, *Phys. Chem. Chem. Phys.*, 2004, **6**, 865-870.
- 282. T. Lindgren, J. M. Mwabora, E. Avendano, J. Jonsson, A. Hoel, C. G. Granqvist and S. E. Lindquist, J. Phys. Chem. B, 2003, 107, 5709-5716.
- 283. N. Serpone, D. Lawless, J. Disdier and J. M. Herrmann, Langmuir,
- 55 1994, **10**, 643-652.

- 284. S. I. Shah, W. Li, C. P. Huang, O. Jung and C. Ni, Proc. Natl. Acad. Sci. U. S. A., 2002, 99, 6482-6486.
- 285. J. A. Wang, R. Limas-Ballesteros, T. Lopez, A. Moreno, R. Gomez,
 O. Novaro and X. Bokhimi, *J. Phys. Chem. B*, 2001, **105**, 9692 9698.
 - 286. H. Miyake and H. Kozuka, J. Phys. Chem. B, 2005, 109, 17951-17956.
 - 287. K. E. Karakitsou and X. E. Verykios, J. Phys. Chem., 1993, 97, 1184-1189.
- 65 288. A. R. Bally, E. N. Korobeinikova, P. E. Schmid, F. Levy and F. Bussy, J. Phys. D-Appl. Phys., 1998, **31**, 1149-1154.
 - 289. R. K. Sharma and M. C. Bhatnagar, Sens. Actuator B-Chem., 1999, 56, 215-219.
- 290. O. Carp, C. L. Huisman and A. Reller, *Prog. Solid State Chem.*, 2004, **32**, 33-177.
- 291. K. Wilke and H. D. Breuer, J. Photochem. Photobiol. A-Chem., 1999, **121**, 49-53.
- 292. M. Grätzel and R. F. Howe, J. Phys. Chem., 1990, 94, 2566-2572.
- 293. H. Kikkawa, B. Oregan and M. A. Anderson, J. Electroanal. Chem.,
 1991, 309, 91-101.
 - 294. M. I. Litter and J. A. Navio, J. Photochem. Photobiol. A-Chem., 1996, **98**, 171-181.
 - 295. K. T. Ranjit and B. Viswanathan, J. Photochem. Photobiol. A-Chem., 1997, **108**, 79-84.
- ⁸⁰ 296. J. A. Navio, G. Colon, M. Trillas, J. Peral, X. Domenech, J. J. Testa, J. Padron, D. Rodriguez and M. I. Litter, *Appl. Catal. B-Environ.*, 1998, **16**, 187-196.
 - 297. J. A. Navio, J. J. Testa, P. Djedjeian, J. R. Padron, D. Rodriguez and M. I. Litter, *Appl. Catal. A-Gen.*, 1999, **178**, 191-203.
- 85 298. Y. Q. Wang, H. M. Cheng, Y. Z. Hao, J. M. Ma, W. H. Li and S. M. Cai, *Thin Solid Films*, 1999, **349**, 120-125.
- 299. M. Iwasaki, M. Hara, H. Kawada, H. Tada and S. Ito, J. Colloid Interface Sci., 2000, 224, 202-204.
- 300. Y. Q. Wang, H. M. Cheng, L. Zhang, Y. Z. Hao, J. M. Ma, B. Xu and W. H. Li, *J. Mol. Catal. A-Chem.*, 2000, **151**, 205-216.
- U. Gesenhues, J. Photochem. Photobiol. A-Chem., 2001, 139, 243-251.
- 302. S. Klosek and D. Raftery, J. Phys. Chem. B, 2001, 105, 2815-2819.
- 303. A. Di Paola, E. Garcia-Lopez, S. Ikeda, G. Marci, B. Ohtani and L. Palmisano, *Catal. Today*, 2002, **75**, 87-93.
- 304. A. W. Xu, Y. Gao and H. Q. Liu, J. Catal., 2002, 207, 151-157.
- 305. J. G. Yu, J. C. Yu, B. Cheng and X. J. Zhao, J. Sol-Gel Sci. Technol., 2002, 24, 39-48.
- 306. Z. H. Yuan, J. H. Jia and L. D. Zhang, *Mater. Chem. Phys.*, 2002, **73**, 323-326.
 - 307. H. L. Zheng, M. F. Tang, Y. K. Gong, X. J. Deng and B. H. Wu, Spectrosc. Spectr. Anal., 2003, 23, 246-248.
- 308. J. Arana, J. M. Dona-Rodriguez, O. Gonzalez-Diaz, E. T. Rendon, J. A. H. Melian, G. Colon, J. A. Navio and J. P. Pena, *J. Mol. Catal.* A-Chem., 2004, 215, 153-160.
 - 309. Y. A. Cao, W. S. Yang, W. F. Zhang, G. Z. Liu and P. L. Yue, New J. Chem., 2004, 28, 218-222.
 - 310. L. Q. Jing, X. J. Sun, B. F. Xin, B. Q. Wang, W. M. Cai and H. G. Fu, J. Solid State Chem., 2004, 177, 3375-3382.
- 110 311. Y. M. Wang, S. W. Liu, M. K. Lu, S. F. Wang, F. Gu, X. Z. Gai, X. P. Cui and J. Pan, *J. Mol. Catal. A-Chem.*, 2004, **215**, 137-142.

- 312. Y. Yang, X. J. Li, J. T. Chen and L. Y. Wang, J. Photochem. Photobiol. A-Chem., 2004, 163, 517-522.
- 313. D. W. Jing, Y. J. Zhang and L. J. Guo, *Chem. Phys. Lett.*, 2005, 415, 74-78.
- 5 314. S. Kim, S. J. Hwang and W. Y. Choi, J. Phys. Chem. B, 2005, 109, 24260-24267.
- 315. C. Sahoo, A. K. Gupta and A. Pal, *Dyes Pigment.*, 2005, **66**, 189-196.
- 316. M. Bettinelli, A. Speghini, D. Falcomer, M. Daldosso, V. Dallacasa
 and L. Romano, J. Phys.-Condes. Matter, 2006, 18, S2149-S2160.
- 317. J. C. Colmenares, M. A. Aramendia, A. Marinas, J. M. Marinas and F. J. Urbano, *Appl. Catal. A-Gen.*, 2006, **306**, 120-127.
- 318. G. Colon, M. Maicu, M. C. Hidalgo and J. A. Navio, *Appl. Catal. B-Environ.*, 2006, 67, 41-51.
- 15 319. M. G. Ha, E. D. Jeong, M. S. Won, H. G. Kim, H. K. Pak, J. H. Jung, B. H. Shon, S. W. Bae and J. S. Lee, *Journal of the Korean Physical Society*, 2006, **49**, S675-S679.
- 320. D. H. Kim, K. S. Lee, Y. S. Kim, Y. C. Chung and S. J. Kim, J. Am. Ceram. Soc., 2006, 89, 515-518.
- 20 321. K. Lee, N. H. Leea, S. H. Shin, H. G. Lee and S. J. Kim, *Mater. Sci. Eng. B-Solid State Mater. Adv. Technol.*, 2006, **129**, 109-115.
- 322. M. M. Mohamed and M. M. Al-Esaimi, J. Mol. Catal. A-Chem., 2006, 255, 53-61.
- 323. T. Ohno, Z. Miyamoto, K. Nishijima, H. Kanemitsu and X. Y. Feng,
 Appl. Catal. A-Gen., 2006, **302**, 62-68.
- 324. Y. Tsuge, K. Inokuchi, K. Onozuka, O. Shingo, S. Sugi, M. Yoshikawa and S. Shiratori, *Thin Solid Films*, 2006, **499**, 396-401.
- 325. J. G. Yu, H. G. Yu, C. H. Ao, S. C. Lee, J. C. Yu and W. K. Ho, *Thin Solid Films*, 2006, **496**, 273-280.
- 30 326. T. Umebayashi, T. Yamaki, T. Sumita, S. Yamamoto, S. Tanaka and K. Asai, Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms, 2003, 206, 264-267.
- 327. J. Osterwalder, T. Droubay, T. Kaspar, J. Williams, C. M. Wang
- and S. A. Chambers, *Thin Solid Films*, 2005, **484**, 289-298.
- 328. S. M. Karvinen, Ind. Eng. Chem. Res., 2003, 42, 1035-1043.
- 329. J. F. Zhu, Z. G. Deng, F. Chen, J. L. Zhang, H. J. Chen, M. Anpo, J. Z. Huang and L. Z. Zhang, *Appl. Catal. B-Environ.*, 2006, **62**, 329-335.
- 40 330. T. C. Lu, Y. Z. Liu, L. B. Lin, X. T. Zu, J. M. Zhu and L. P. Wu, J. Inorg. Mater., 2001, 16, 373-376.
 - 331. A. Ghicov, B. Schmidt, J. Kunze and P. Schmuki, *Chem. Phys. Lett.*, 2007, 433, 323-326.
- 332. T. A. Egerton, E. Harris, E. J. Lawson, B. Mile and C. C. Rowlands,
 Phys. Chem. Chem. Phys., 2001, 3, 497-504.
- 333. C. Y. Wang, D. W. Bahnemann and J. K. Dohrmann, *Chemical Communications*, 2000, 1539-1540.
- 334. H. Yamashita, M. Harada, J. Misaka, M. Takeuchi, B. Neppolian and M. Anpo, *Catal. Today*, 2003, 84, 191-196.
- ⁵⁰ 335. L. H. Jeong, J. H. Ahn, B. H. Kim, Y. S. Jeon, K. O. Jeon and K. S. Hwang, *Journal of the Korean Physical Society*, 2005, 46, 559-561.
- 336. M. H. Zhou, J. G. Yu and B. Cheng, J. Hazard. Mater., 2006, 137, 1838-1847.
- 337. X. W. Zhang, M. H. Zhou and L. C. Lei, Catal. Commun., 2006, 7,
- 55 427-431.

- 338. X. H. Wang, J. G. Li, H. Kamiyama, Y. Moriyoshi and T. Ishigaki, J. Phys. Chem. B, 2006, 110, 6804-6809.
- 339. S. Nahar, K. Hasegawa and S. Kagaya, *Chemosphere*, 2006, **65**, 1976-1982.
- 60 340. W. Y. Teoh, R. Amal, L. Madler and S. E. Pratsinis, *Catal. Today*, 2007, **120**, 203-213.
 - 341. D. Dvoranova, V. Brezova, M. Mazur and M. A. Malati, *Appl. Catal. B-Environ.*, 2002, **37**, 91-105.
- 342. F. Gracia, J. P. Holgado, A. Caballero and A. R. Gonzalez-Elipe, J.
 Phys. Chem. B, 2004, 108, 17466-17476.
 - 343. L. Zang, C. Lange, I. Abraham, S. Storck, W. F. Maier and H. Kisch, J. Phys. Chem. B, 1998, 102, 10765-10771.
 - 344. W. Macyk, G. Burgeth and H. Kisch, *Photochem. Photobiol. Sci.*, 2003, 2, 322-328.
- 70 345. A. Fuerte, M. D. Hernandez-Alonso, A. J. Maira, A. Martinez-Arias, M. Fernandez-Garcia, J. C. Conesa and J. Soria, *Chem. Commun.*, 2001, 2718-2719.
 - 346. M. Gratzel and R. F. Howe, J. Phys. Chem., 1990, 94, 2566-2572.
- 347. S. Sakthivel, M. V. Shankar, M. Palanichamy, B. Arabindoo, D. W.
 ⁷⁵ Bahnemann and V. Murugesan, *Water Res.*, 2004, **38**, 3001-3008.
 - 348. M. Radecka, M. Wierzbicka, S. Komornicki and M. Rekas, *Physica B*, 2004, **348**, 160-168.
 - 349. J. G. Yu, M. H. Zhou, H. G. Yu, Q. J. Zhang and Y. Yu, *Mater. Chem. Phys.*, 2005, 95, 193-196.
- 80 350. E. Arpac, F. Sayilkan, M. Asilturk, P. Tatar, N. Kiraz and H. Sayilkan, J. Hazard. Mater., 2007, 140, 69-74.
 - 351. H. Tada, T. Mitsui, T. Kiyonaga, T. Akita and K. Tanaka, *Nat. Mater.*, 2006, 5, 782-786.
- 352. T. Kiyonaga, T. Mitsui, M. Torikoshi, M. Takekawa, T. Soejima and H. Tada, *J. Phys. Chem. B*, 2006, **110**, 10771-10778.
- 353. A. Kudo, K. Omori and H. Kato, J. Am. Chem. Soc., 1999, **121**, 11459-11467.
- 354. Z. G. Zou, J. H. Ye and H. Arakawa, *Chem. Phys. Lett.*, 2000, **332**, 271-277.
- 90 355. Z. G. Zou, J. H. Ye, K. Sayama and H. Arakawa, *Nature*, 2001, **414**, 625-627.
- 356. Z. G. Zou and H. Arakawa, J. Photochem. Photobiol. A-Chem., 2003, **158**, 145-162.
- 357. M. K. Tian, W. F. Shangguan, J. Yuan, L. Jiang, M. X. Chen, J. W.
 Shi, Z. Y. Ouyang and S. J. Wang, *Appl. Catal. A-Gen.*, 2006, 309, 76-84.
 - 358. J. H. Ye and Z. G. Zou, J. Phys. Chem. Solids, 2005, 66, 266-273.
 - 359. H. Irie and K. Hashimoto, J. Am. Ceram. Soc., 2005, 88, 3137-3142.
- 360. D. F. Wang, Z. G. Zou and J. H. Ye, *Chem. Mat.*, 2005, **17**, 3255-3261.
 - 361. Z. B. Lei, W. S. You, M. Y. Liu, G. H. Zhou, T. Takata, M. Hara, K. Domen and C. Li, *Chem. Commun.*, 2003, 2142-2143.
 - 362. I. Tsuji, H. Kato and A. Kudo, Chem. Mat., 2006, 18, 1969-1975.
- 363. G. J. Liu, L. Zhao, L. J. Ma and L. J. Guo, *Catal. Commun.*, 2008, 9, 105
 126-130.
 - G. Hitoki, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi and K. Domen, *Chem. Commun.*, 2002, 1698-1699.
 - 365. T. Mishima, M. Matsuda and M. Miyake, *Appl. Catal. A-Gen.*, 2007, **324**, 77-82.

- 366. M. Y. Liu, W. S. You, Z. B. Lei, G. H. Zhou, J. J. Yang, G. P. Wu, G. J. Ma, G. Y. Luan, T. Takata, M. Hara, K. Domen and L. Can, *Chem. Commun.*, 2004, 2192-2193.
- 367. K. G. Kanade, J. O. Baeg, B. B. Kale, S. M. Lee, S. J. Moon and K.
- J. Kong, Int. J. Hydrog. Energy, 2007, 32, 4678-4684.
- 368. X. P. Lin, T. Huang, F. Q. Huang, W. D. Wang and J. L. Shi, J. Mater. Chem., 2007, 17, 2145-2150.
- 369. W. D. Wang, F. Q. Huang, X. P. Lin and J. H. Yang, Catal. Commun., 2008, 9, 8-12.
- 10 370. J. W. Tang, Z. G. Zou and J. H. Ye, J. Phys. Chem. C, 2007, 111, 12779-12785.
 - 371. H. B. Fu, L. W. Zhang, W. Q. Yao and Y. F. Zhu, Appl. Catal. B-Environ., 2006, 66, 100-110.
- 372. Y. Maruyama, H. Irie and K. Hashimoto, J. Phys. Chem. B, 2006,
 110, 23274-23278.
 - 373. X. Zhang, Z. H. Ai, F. L. Jia, L. Z. Zhang, X. X. Fan and Z. G. Zou, *Mater. Chem. Phys.*, 2007, **103**, 162-167.
- 374. K. Sayama, A. Nomura, Z. G. Zou, R. Abe, Y. Abe and H. Arakawa, *Chem. Commun.*, 2003, 2908-2909.
- 20 375. J. W. Tang, Z. G. Zou and J. H. Ye, Angew. Chem.-Int. Edit., 2004, 43, 4463-4466.
 - 376. T. Kako, Z. G. Zou, M. Katagiri and J. H. Ye, *Chem. Mat.*, 2007, 19, 198-202.
- 377. S. X. Ouyang, Z. S. Li, Z. Ouyang, T. Yu, J. H. Ye and Z. G. Zou, *J. Phys. Chem. C*, 2008, **112**, 3134-3141.
- 378. J. W. Tang, Z. G. Zou and J. H. Ye, J. Phys. Chem. B, 2003, 107, 14265-14269.
- 379. H. Kato, H. Kobayashi and A. Kudo, J. Phys. Chem. B, 2002, 106, 12441-12447.
- 30 380. H. G. Kim, D. W. Hwang and J. S. Lee, J. Am. Chem. Soc., 2004, 126, 8912-8913.
 - 381. D. F. Wang, Z. G. Zou and J. H. Ye, *Catal. Today*, 2004, **93-95**, 891-894.
- 382. D. F. Wang, Z. G. Zou and J. H. Ye, *Chem. Phys. Lett.*, 2005, **411**, 25 285-290.
 - 383. W. F. Yao and J. H. Ye, J. Phys. Chem. B, 2006, 110, 11188-11195.
 - 384. G. Q. Li, T. Kako, D. F. Wang, Z. G. Zou and J. Ye, J. Solid State Chem., 2007, 180, 2845-2850.
- 385. Z. G. Yi and J. H. Ye, *Appl. Phys. Lett.*, 2007, **91**, 254108 (254101-254103).
- 386. D. F. Wang, T. Kako and J. H. Ye, J. Am. Chem. Soc., 2008, 130, 2724-2725.
- 387. S. X. Ouyang, H. T. Zhang, D. F. Li, T. Yu, J. H. Ye and Z. G. Zou, *J. Phys. Chem. B*, 2006, **110**, 11677-11682.
- 45 388. H. M. Liu, R. Nakamura and Y. Nakato, J. Electrochem. Soc., 2005, 152, G856-G861.
 - 389. L. Zhou, W. Z. Wang, S. W. Liu, L. S. Zhang, H. L. Xu and W. Zhu, J. Mol. Catal. A-Chem., 2006, 252, 120-124.
 - 390. L. Z. Zhang, I. Djerdj, M. H. Cao, M. Antonietti and M. Niederberger, *Adv. Mater.*, 2007, **19**, 2083-2086.
 - 391. X. Li and J. H. Ye, J. Phys. Chem. C, 2007, 111, 13109-13116.
 - 392. L. Zhou, W. Z. Wang and L. S. Zhang, J. Mol. Catal. A-Chem., 2007, 268, 195-200.
 - 393. S. C. Zhang, C. Zhang, H. P. Yang and Y. F. Zhu, J. Solid State Chem., 2006, 179, 873-882.
- 394. J. Orenstein, Nature, 1999, 401, 333-334.

- 395. K. Maeda, N. Saito, D. L. Lu, Y. Inoue and K. Domen, J. Phys. Chem. C, 2007, 111, 4749-4755.
- 396. J. Choi, S. Y. Ryu, W. Balcerski, T. K. Lee and M. R. Hoffmann, J.
 Mater. Chem., 2008, 18, 2371-2378.
 - 397. K. Maeda, T. Takata, M. Hara, N. Saito, Y. Inoue, H. Kobayashi and K. Domen, J. Am. Chem. Soc., 2005, **127**, 8286-8287.
- 398. K. Maeda, K. Teramura, T. Takata, M. Hara, N. Saito, K. Toda, Y. Inoue, H. Kobayashi and K. Domen, *J. Phys. Chem. B*, 2005, 109, 20504-20510.
- 399. K. Maeda, K. Teramura, D. L. Lu, T. Takata, N. Saito, Y. Inoue and K. Domen, *Nature*, 2006, **440**, 295-295.
- 400. K. Maeda, K. Teramura, D. L. Lu, N. Saito, Y. Inoue and K. Domen, Angew. Chem.-Int. Edit., 2006, 45, 7806-7809.
- 70 401. J. Yin, Z. G. Zou and J. H. Ye, J. Phys. Chem. B, 2003, 107, 61-65.
 - 402. J. H. Ye, Z. G. Zou, M. Oshikiri, A. Matsushita, M. Shimoda, M. Imai and T. Shishido, *Chem. Phys. Lett.*, 2002, **356**, 221-226.
 - 403. Y. S. Hu, A. Kleiman-Shwarsctein, A. J. Forman, D. Hazen, J. N. Park and E. W. McFarland, *Chem. Mat.*, 2008, **20**, 3803-3805.
- 75 404. K. Rajeshwar, J. Appl. Electrochem., 2007, 37, 765-787.
- 405. D. F. Wang, J. H. Ye, H. Kitazawa and T. Kimura, *J. Phys. Chem. C*, 2007, **111**, 12848-12854.
- 406. J. W. Tang, Z. G. Zou, J. Yin and J. Ye, *Chem. Phys. Lett.*, 2003, **382**, 175-179.
- 80 407. J. W. Tang, Z. G. Zou, M. Katagiri, T. Kako and J. H. Ye, *Catal. Today*, 2004, **93-95**, 885-889.
- 408. Y. Y. Jiang, J. G. Li, X. T. Sui, G. L. Ning, C. Y. Wang and X. M. Gu, J. Sol-Gel Sci. Technol., 2007, 42, 41-45.
- 409. H. B. Fu, C. S. Pan, W. Q. Yao and Y. F. Zhu, *J. Phys. Chem. B*, 2005, **109**, 22432-22439.
- 410. X. Zhao, T. G. Xu, W. Q. Yao, C. Zhang and Y. F. Zhu, *Appl. Catal. B-Environ.*, 2007, **72**, 92-97.
- 411. J. W. Tang and J. Ye, Chem. Phys. Lett., 2005, 410, 104-107.
- 412. X. K. Li, T. Kako and J. H. Ye, Appl. Catal. A-Gen., 2007, 326, 1-7.
- 90 413. J. W. Tang, Z. G. Zou and J. H. Ye, *Chem. Mat.*, 2004, 16, 1644-1649.
 - 414. X. P. Lin, T. Huang, F. Q. Huang, W. D. Wang and J. L. Shi, *J. Phys. Chem. B*, 2006, **110**, 24629-24634.
- 415. X. Zhao, J. H. Qu, H. J. Liu and C. Hu, *Environ. Sci. Technol.*, 95 2007, **41**, 6802-6807.