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Perspective

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New Insights into the Mechanism of Visible Light Photocatalysis

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ABSTRACT: In recent years, the area of developing visible-light-active photocatalysts based on titanium dioxide has been enormously investigated due to its wide range of applications in energy and environment related fields. Various strategies have been designed to efficiently utilize the solar radiation and to enhance the efficiency of photocatalytic processes. Building on the fundamental strategies to improve the visible light activity of TiO_2-based photocatalysts, this Perspective aims to give an insight into many contemporary developments in the field of visible-light-active photocatalysis. Various examples of advanced TiO_2 composites have been discussed in relation to their visible light induced photoconversion efficiency, dynamics of electron−hole separation, and decomposition of organic and inorganic pollutants, which suggest the critical need for further development of these types of materials for energy conversion and environmental remediation purposes.

Photocatalysis widely refers to the process of using light to activate a substrate (photocatalyst), which modifies or facilitates the kinetics of a chemical reaction but itself remains unconsumed.[1−4] During photocatalysis, a semiconductor metal oxide such as titanium dioxide (TiO_2) or zinc oxide (ZnO) is irradiated with light (where, the energy of the excitation source is higher than the band gap energy of the material), which results in photon absorption and excitation of an electron (e^-) from valence band to the conduction band, thereby generating a positive electron hole (h^+) in the valence band (Figure 1). The electron−hole charge carriers ($h^+_{VB} + e^-_{CB}$) can in turn undergo recombination and dissipate the excess energy through nonradiative mechanisms (eqs 1 and 2)

$$\text{semiconductor} + h\nu \rightarrow h^+_{VB} + e^-_{CB} \quad (1)$$

$$e^-_{CB} + h^+_{VB} \rightarrow \text{energy} \quad (2)$$

This reduces the overall efficiency of the photoinduced process. The charge carriers, which do not undergo charge annihilation, can migrate to the surface of the catalyst and initiate secondary reactions with the surface adsorbed materials. For example, the photoexcited electron in the conduction band can react with oxygen to form superoxide radicals or hydroperoxide radicals and these reactive oxygen species (ROS) can participate in the degradation of organic pollutants, whereas positive holes (h^+) in the valence band can oxidize surface adsorbed water or OH^- and generate hydroxyl radical ($^\bullet OH$), which in turn oxidizes the organic pollutants (Figure 1; eqs 3 and 4).

$$h^+_{VB} + H_2O \rightarrow {}^\bullet OH + H^+ \quad (3)$$

$$e^-_{CB} + O_2 \rightarrow {}^\bullet O_2^- \quad (4)$$

Titanium dioxide (TiO_2)-based materials have received enormous attention in the area of semiconductor photocatalysis. The major breakthrough came in the year 1972, when Fujishima and Honda demonstrated for the first time the

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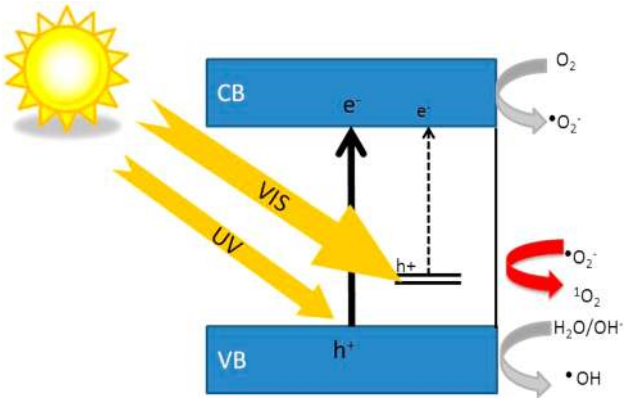

Figure 1. Schematic of semiconductor photocatalysis (adapted from ref 4). Copyright 2013, reprinted with permission from Elsevier.

photoelectrochemical decomposition of water using TiO_2 as an anode and platinum as a counter electrode.[5] TiO_2-based photocatalysts also offer the advantages of high physical and chemical stability, low cost, easy availability, low toxicity, and excellent photoactivity. Titanium dioxide exists in three naturally occurring polymorphic forms such as anatase, rutile, and brookite, where rutile represents the thermodynamically stable form and anatase shows higher kinetic stability. The anatase form of TiO_2 is reported to show higher photocatalytic activity compared to rutile or brookite.[1,3] The major drawbacks

The major drawbacks of TiO_2-based photocatalysts arise from the rapid charge recombination of the electron−hole pairs, thereby suppressing the quantum efficiency, and the wide band gap (3.0 eV for rutile and 3.2 eV for anatase) of the material, which restricts light absorption to only ultraviolet region (wavelength <390 nm) and thus limits the practical applications of TiO_2-based photocatalysts for solar light harvesting.

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Chemical modifications of TiO_2 lattice using nonmetals such as C,[18−23] N,[24−26] and S[27−29] appeared as promising strategies to improve visible light responsive photocatalytic activity. In 1986, Sato reported that the incorporation of ammonium hydroxide in a titania precursor sol, followed by a calcination process, resulted in a nitrogen-doped photocatalyst that demonstrated visible light activity.[30] Asahi and co-workers further showed that nitrogen-doped TiO_2 exhibit a substantial enhancement in visible light assisted photocatalytic degradation of methylene blue and acetaldehyde compared to undoped TiO_2.[31] Following this work, various research groups have designed visible-light-active N-doped TiO_2 photocatalysts. Incorporation of nitrogen into TiO_2 lattice is favored due to comparable atomic sizes of nitrogen and oxygen, low ionization potential, and high stability of nitrogen.[25,26,32] Although nonmetal doping (e.g., N, C, F, S, etc.) is found to shift the absorption band of TiO_2 towards the visible region, the chemical nature of the doped species accountable for the visible light activity and the electronic structure of the doped material still remain controversial. In their pioneering work, Asahi and co-workers proposed that substitutional N doping results in band gap narrowing due to efficient mixing of 2p orbitals of N and O. Contrary to this, Serpone and co-workers argued that observations of band gap narrowing through modifications in the energy levels of valence and conduction bands requires high concentrations of dopants and strong interactions among impurity energy states, valence, and conduction bands.[32]

Serpone et al., also suggested that the presence of defects (color centers) associated with oxygen vacancies in doped TiO_2 are responsible for their visible light activity.[32] Di Valentin and co-workers showed the electronic nature of the N-dopant in TiO_2 synthesized through various chemical routes.[33−36] Density functional theory (DFT) predicted that the doped N atoms could occupy substitutional or interstitial sites in the TiO_2 lattice and generate localized energy levels in the band gap. For dopants occupying substitutional positions, a continuum of slightly higher energy levels essentially extends the valence band, whereas an interstitial dopant results in discrete energy levels above the valence band, often referred to as a midgap state (Figure 2A).[35,36] The visible light response in the doped materials arises from the electron transition from the localized N orbitals to the conduction band or to the surface adsorbed O_2.[36] Doping TiO_2 with carbon or sulfur also is found to enhance visible light activated photocatalytic activity.[15,22] The visible light response in these doped materials is thought to arise from the presence of localized energy levels of the dopant lying above the valence band or oxygen vacancies as demonstrated in Figure 2.[23] It was also reported that in case of substitutional doping of TiO_2 by lighter elements such as N, C, and B, the dopant with lower atomic number will appear at higher energy in the band gap due to smaller effective nuclear charge.[33] Visible-light-active, oxygen-rich TiO_2 that exhibits anatase phase stability up to 900 °C, suitable for high temperature applications, has also been developed.[37] The visible light response in the oxygen rich TiO_2 arises from the band gap narrowing of TiO_2 containing oxygen excess defects, which can interact with the lattice oxygen atoms, thereby increasing lattice parameters and consequently decrease the band gap.[37]

In order to improve the visible-light-active photocatalytic efficiency and inhibit charge recombination, several research groups have developed TiO_2 composites codoped with two or more nonmetals such as S−N,[38] B−N,[39] C−N,[40,41] N−F,[42−47] in TiO_2. Hamilton et al. recently reported using photoelectrochemistry in N and F codoped TiO_2 that electrons could be promoted from nitrogen centers (which are located just above the valence band) directly to the conduction band by visible light.[48] It was also showed that the vacant N states thus

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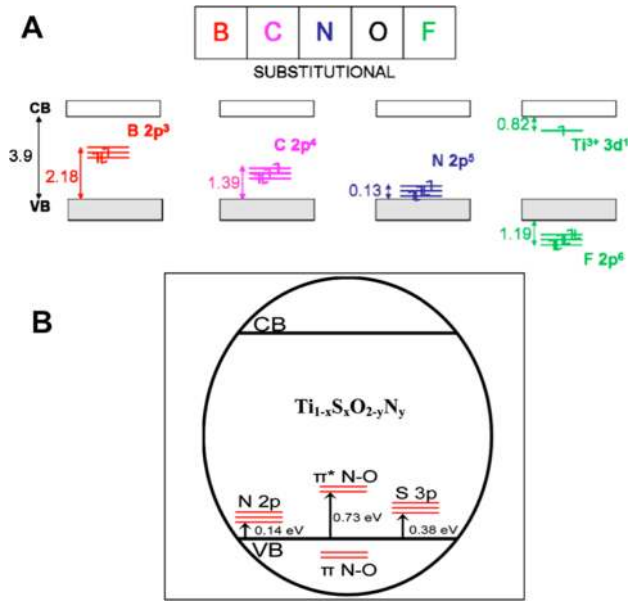

Figure 2. (A) Schematic illustration of localized impurity energy states for the substitutionally doped TiO_2 (adapted from ref 33). Copyright 2013, reprinted with permission from Elsevier. (B) Electronic structure of $Ti_{1-x}S_xO_{2-y}N_y$ showing the presence of localized impurity energy states (adapted from ref 73). Copyright 2012, reprinted from with permission from American Chemical Society.

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produced could be refilled by electron transfer from Ti^{3+} states, which could further accept conduction band electrons. Oxygen vacancies (O_{vac}) situated just above the nitrogen midgap state could also transfer electrons to refill the empty N states. The conduction band electrons can then donate electrons to the oxygen vacancy sites. Therefore, a cycle of events of excited electrons occurs from the N midgap state, to the conduction band, and then to Ti^{3+} or O_{vac} with eventual repopulation of the excited empty nitrogen states as demonstrated in (Figure 3).[48]

In a recent study, Zhao et al. showed that N−F codoped TiO_2 exhibited the best performance to destroy 6-hydroxymethyl uracil (6-HOMU), a model compound for cyanotoxins.[47] Mechanistic investigations carried out in the presence of scavengers for $^{\bullet}O_2^-$, $^1O_2$, $^{\bullet}OH$, and h^+_{vb} have shown that $^{\bullet}O_2^-$

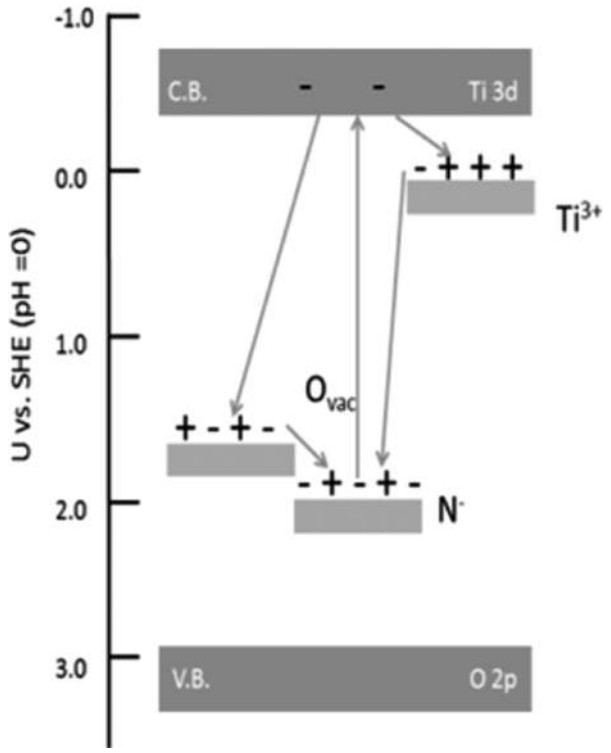

Figure 3. Visible light excitation of N−F codoped TiO_2 and refilling of empty N states by electron transfer from either Ti^{3+} or O_{vac} (adapted from ref 48). Copyright 2014, reprinted with permission from American Chemical Society.

is the prime ROS leading to the photoassisted degradation of 6-HOMU (Figure 4). This study has contributed to the better basic understanding of different roles of ROS in doped and codoped visible-light-active titanium dioxide photocatalysts.[47] Pulgarin and co-workers suggested that for N,S codoped TiO_2, photogenerated holes formed under visible light irradiation do not possess suitable reduction potential to generate $^{\bullet}OH$ radical by the oxidation of H_2O.[49,50] It has also been reported that under visible light irradiation, less oxidative superoxide radical anion $^{\bullet}O_2^-$, and singlet oxygen $^1O_2$ species (Figure 1) are predominantly responsible for the photocatalytic bacterial inactivation.[49,50] However, under UV light excitation, highly oxidizing $^{\bullet}OH$ radicals are produced, which play active roles toward photocatalytic activity.[49,50]

Based on the first principle calculations (DFT), Huang and co-workers demonstrated that the presence of doping agents result in surface distortions in a {101} surface of TiO_2, which promotes transfer of photogenerated electrons from the bulk/subsurface atomic layer to the outer surface region, thereby facilitating the photocatalytic reactions and also improving quantum efficiency of photocatalytic processes by increasing the separation of photogenerated electrons and holes.[51] A gel combustion method has been recently developed to synthesize nanostructured modified TiO_2 (m-TiO_2) that involved calcination of a mixture of urea with an acidified solution of titanium alkoxide at temperatures 350−500 °C.[52] The hybrid inorganic/organic materials show unique physicochemical properties and remarkably high rate for visible light induced photocatalytic decomposition of methylene blue dye compared to the reference material Degussa (Evonik) P25. The significantly high visible light assisted photocatalytic activity of m-TiO_2 materials with a core−shell morphology arises from

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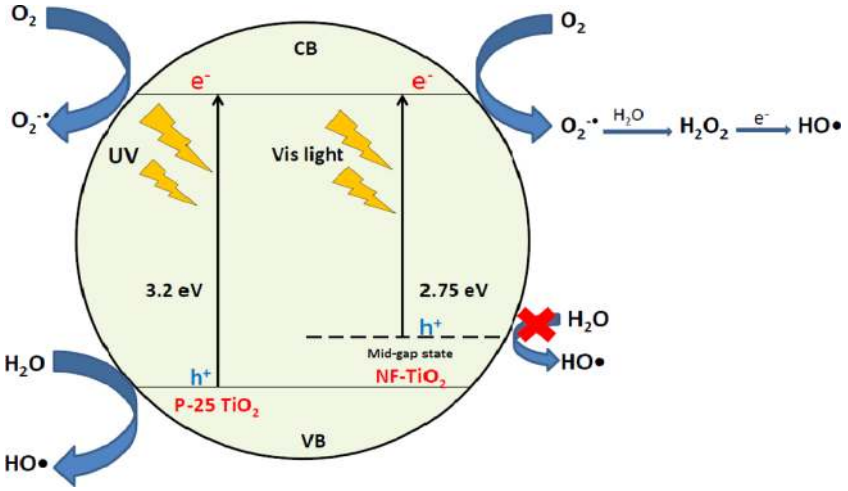

Figure 4. Production of different ROS during the visible-light-active photocatalytic processes for the destruction of 6-hydroxymethyl uracil (adapted from ref 47). Copyright 2014, reprinted with permission from Elsevier.

the sensitization of the TiO_2 by a thin porous layer of carbonaceous species, which also favors charge separation and impede charge recombination at the inorganic/organic heterojunction.[52]

Chemical modifications of TiO_2 with 3d transition metal ions,[10,53] lanthanides,[13,14] and noble metals[54−56] have also been found to improve the visible light response of TiO_2. It was shown that the addition of increased amounts of Ag up to 5 mol % facilitates visible light absorbance.[57] Many different explanations have been proposed to account for the enhanced visible light activity of such doped TiO_2, including band gap narrowing, formation of impurity energy levels within the band gap of TiO_2, and formation of intrinsic defects (such as oxygen vacancies, interstitial Ti). However, addition of metal ion impurities can also induce recombination of charge carriers and lower the overall efficiency of photocatalysis. TiO_2 photocatalyst surface modified with Rh^{3+} has displayed very high activity for mineralization of volatile organic compounds (VOC) under visible light irradiation compared to conventional metal doped TiO_2.[58] The enhanced activity of Rh^{3+}modified TiO_2 has been attributed to the bifunctional role of Rh^{3+} as an electron injector as well as a promoter for multielectron reduction of O_2 under visible light irradiation. Electron transfer occurs from the *d* orbital of Rh^{3+} to the conduction band of TiO_2 under visible light irradiation, thereby forming Rh^{4+}, which in turn participates in degradation of organic substrate and undergoes reduction to Rh^{3+} species (Figure 5). Electrons in the conduction band of TiO_2 can be transferred to O_2 to form $^{\bullet}O_2^-$ through one electron reduction mechanism. Alternatively, Rh^{3+} can function as a conduction band electron acceptor to yield unstable Rh^{2+}, which rapidly forms Rh^+, a species capable of reducing O_2 to H_2O_2 through two electron transfer reduction and thus acts as a promoter for O_2 reduction.

In recent years incorporation of plasmonic noble metal nanostructures appear as an attractive approach to enhance the visible light absorption due to direct excitation of the surface plasmon resonance (SPR) band of the nanoparticles.[59,60] Plasmonic nanostructures are being increasingly used to enhance the light harvesting efficiency of photovoltaic devices.[61−64] For example, Kamat and co-workers demonstrated that the photocurrent generation of nanostructured TiO_2 films increases several times in the presence of surface deposited gold nanoparticles, which promote charge transfer process in the composite systems.[62,63] In the presence of photoexcited plasmonic nanoforms, electron injection occurs from the nanosurface to the conduction band of TiO_2 in femtosecond time scale (Figure 6).[65] The positive hole formed on the nanosurface oxidizes the substrate, whereas the electron in the conduction band of TiO_2 reacts further with O_2. However, the rapid back electron transfer and consequent charge recombination limit the efficiency of the photocatalytic processes. The size and shape of the metallic nanoparticles have significant effect on the overall efficiency of the process. Kamat and co-workers demonstrated that small sized nanoparticles shift the energy of the Fermi level of the TiO_2-nanocomposite toward more negative value and affect the photocatalytic process due to direct changes in the energetics of the composite systems.[64] Various mechanisms have been proposed to account

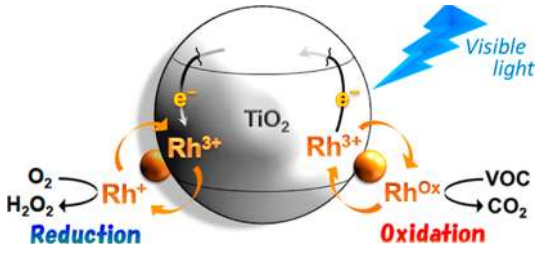

Figure 5. Schematic representation showing the dual role of Rh^{3+} in Rh modified TiO_2 as an electron injector as well as a promoter for two electron reduction of O_2 (ref 58). Copyright 2013, reprinted with permission from American Chemical Society.

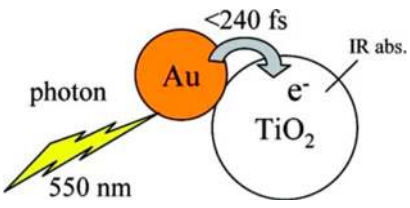

Figure 6. Schematic presentation showing electron injection from photoexcited Au to the conduction band of TiO_2 in response to visible light absorption (ref 65). Copyright 2007, reprinted with permission from American Chemical Society.

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for the improved photocatalytic efficiency of TiO_2−SPR nanostructures, including enhanced light absorption by the surface plasmons, improved charge separation efficiency, and changes in the energetics of the Fermi level in the composite system arising from the electron storage effects.[66] Alloying noble metal Cu with Pt (Pt−Cu) supported on anatase TiO_2 has resulted in a lower work function of metallic platinum, which in turn facilitates the efficient electron injection from the photoexcited platinum nanoparticles to the conduction band of TiO_2 due to lowering the height of Schottky barrier at the interface.[67] The Pt−Cu/TiO_2 catalyst exhibited high rate of alcohol oxidation under sunlight irradiation compared to Pt/TiO_2 composite.

Formation of TiO_2 with oxygen vacancy along with deposition of noble metal nanoparticle on such TiO_2 has been found to boost the photocatalytic performance.[68] Degussa (Evonik) P25 with oxygen vacancies was prepared through a photocatalytic reaction utilizing the oxidation of benzyl alcohol on TiO_2 surface, which creates oxygen vacancies. This was followed by the deposition of noble metal nanoparticles (Ag, Pt, Pd) on Degussa (Evonik) P25 with oxygen vacancy. The oxygen vacancy sites facilitate visible light absorption and electron−hole pair formation, whereas the metal nanoparticles can act as electron acceptors and promote interfacial charge separation and increase the lifetime of the charge separated species.

Formation of photocatalytic heterostructures based on TiO_2 with other semiconductor/noble metal has emerged as an important strategy to increase the separation of charge carriers and suppress the recombination rate of photoinduced electron−hole pair, resulting in improved photocatalytic efficiency.

In recent years, formation of photocatalytic heterostructures based on TiO_2 with other semiconductor/noble metal has emerged as an important strategy to increase the separation of charge carriers and suppress the recombination rate of photoinduced electron−hole pair, resulting in improved photocatalytic efficiency (Figure 7).[69−74] Additionally, the synergistic effects induced by the components in the heterostructure also result in an increased photostability and photocatalytic efficiency. Over the past decade, heterojunctions based on ZnO/TiO_2 nanocomposites,[69] anatase−rutile TiO_2 heterojunctions,[70−73] and Ag/TiO_2 nanofibers[74] have been developed for the degradation of organic pollutants and water splitting under UV−vis irradiation. Metallic oxides with oxygen vacancies such as $W_{18}O_{49}$ are gaining huge interest in the field of visible light driven photocatalysis as they exhibit wide absorption tail in Near-Infrared (NIR) region arising from oxygen defects. Therefore, combination of TiO_2 with $W_{18}O_{49}$ can result in a hybrid photocatalyst covering both UV and visible region.[75] Additionally such hybrid structures also favor enhanced photoinduced charge separation and inhibit charge recombination. It was found that simultaneous modification of TiO_2 with a nonmetal boron and nickel oxide (Ni_2O_3)

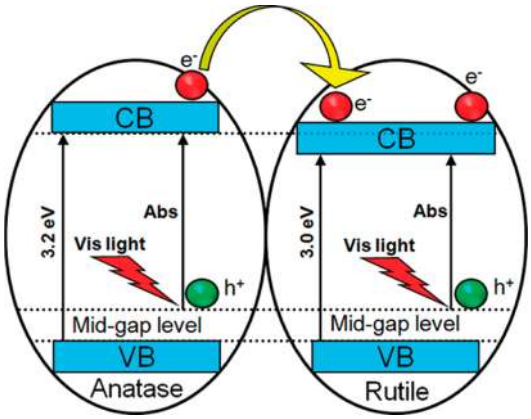

Figure 7. Electron transfer mechanism of anatase−rutile heterojunctions in visible light photocatalysts (ref 73). Copyright 2012, reprinted with permission from American Chemical Society.

significantly enhanced the photocatalytic activity of TiO_2 in the visible region and resulted in an efficient degradation of organic pollutants such as sodium benzoate, trichlorophenol, and 2,4-dichlorophenol.[76] Visible light irradiation of the modified photocatalyst using a Nd:YAG laser (λ = 532 nm), generated long-lived charge carriers that can react with surface adsorbed O_2/H_2O to produce $^{\bullet}OH$ and $^{\bullet}O_2^-$ radicals, and promote mineralization of organic pollutants.[76] It has been proposed that Ni_2O_3 loaded on the surface of B-doped TiO_2 acts as an electron trap and promotes charge separation.

Near-infrared light active core−shell TiO_2 nanoparticles were synthesized, where upconverting luminescent material (YF_3 codoped with Yb^{3+}/Tm^{3+} codoped) is used as the core and TiO_2 as the shell.[77,78] During the photoexcitation process, Yb^{3+} absorbs NIR radiation and transfer the energy to Tm^{3+}, which emits UV radiation and in turn excites TiO_2 to generate photoexcited electrons and holes. To further enhance the photocatalytic efficiency of these systems, nanocrystals of TiO_2 and a narrow-band semiconductor such as CdS were linked with $NaYF_4$ codoped with Yb^{3+} and Tm^{3+}.[78] Upon NIR excitation, Yb^{3+} acts as a sensitizer and transfers the energy to Tm^{3+}, which in turn activates CdS or TiO_2 by Förster resonance energy transfer or photon reabsorption mechanism and generates photoinduced electron and hole required for mineralization of organic chemicals. The presence of CdS/TiO_2 heterojunction further enhances the photocatalytic efficiency by facilitating the separation and migration of charge carriers at the interface.

Advanced nanostructured photocatalytic materials have been synthesized by combining TiO_2 nanoparticles with reduced graphene oxide (r-GO)[79−83] and carbon nanotube (CNT)[80] using liquid phase deposition method followed by thermal reduction at different temperatures. VLA nanocatalysts and composite materials were immobilized onto hybrid ultra/nanofiltration membranes (with improved permeability and low energy consumption) and incorporated into state of the art photocatalytic reactors, where the nanocomposites were systematically evaluated for their ability to degrade a number of pollutants under both UV and visible light irradiation.[81−83]

Dye sensitization is also considered to be a promising strategy to induce visible light activated photocatalysis by TiO_2.[6−8] The process involves light absorption (mainly visible light) by a transition metal complex or an organic dye (or a colored pollutant) known as sensitizer followed by electron

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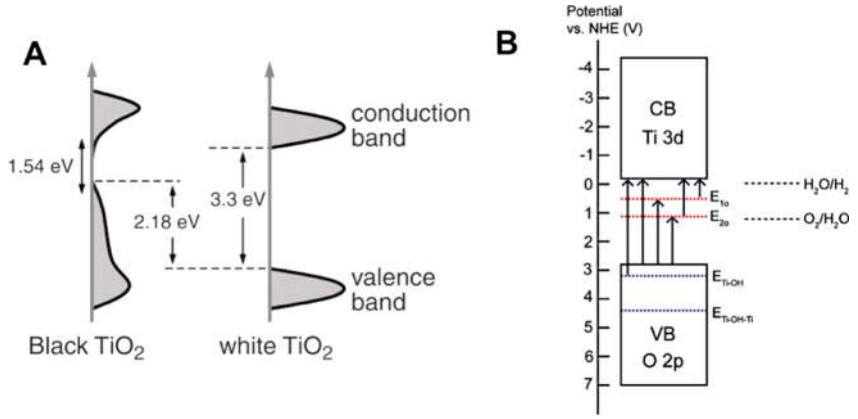

Figure 8. (A) Schematic representation showing the density of states of black TiO_2 and white TiO_2 nanocrystals (ref 90). Copyright 2011, reprinted with permission from Science. (B) Energy diagram of reduced TiO_2 nanowires, where E_{1o} and E_{2o} shown in red dashed lines refer to the oxygen vacancies located at 0.73 and 1.18 eV below the TiO_2 conduction band. Arrows represent electronic transitions between different energy levels (ref 91). Copyright 2011, reprinted with permission from American Chemical Society.

injection from the excited sensitizer molecule into the conduction band of semiconductor material. The resulting radical cations can lead to a number of oxidative processes and the formation of ROS leading to the degradation of target compounds such as various organic pollutants.[84−86] Zhao and co-workers developed a dye-sensitized TiO_2 composite incorporating alizarin red as the visible light absorbing dye and the nitrosyl radical TEMPO.[87] The combination of dye sensitized TiO_2 and TEMPO produced an efficient photocatalytic system for selective oxidation of alcohol under visible light irradiation at ambient condition. Visible light irradiation of the dye anchored on TiO_2 surface produces excited dye molecules, which in turn injects electrons to the conduction band of TiO_2 and generates dye radical cation. The dye radical cation can in turn oxidize TEMPO to regenerate the dye and $TEMPO^+$. The oxidized $TEMPO^+$ can further oxidize various alcohols to the corresponding aldehydes and regenerates the nitroxyl radical TEMPO.[87] The sensitization principle also finds important applications in the development of dye-sensitized solar cells (DSSC), which are third generation photovoltaics based on nanocrystalline large band gap semiconductors and highly efficient light harvesting molecular antennas.[85] In fact, metal-porphyrins[7] and Ru(II) polypyridyl[9] complexes have gained considerable attention in this context due to the presence of extensive delocalized π-electron system and strong absorption band in the visible region. Recently, Lin and co-workers have reported the development of a series of porphyrins for the application in DSSC containing anthracene in combination with pyrene or 4-dimethylaminophenyl group that show absorption in the NIR region.[88,89] The rapid electron injection and regeneration steps are crucial for the optimal activity of the system. Thus, the use of a porphyrin sensitizer (SM315) with the cobalt (II/III) redox couple led to the current 13% power conversion efficiency record.[89]

In a recent investigation, Chen et al. developed an alternative approach to enhance the visible light response of TiO_2 by introducing disorders using hydrogenation in the surface layers of nanophase TiO_2, resulting in TiO_2 particles absorbing in the visible and NIR wavelength region (Figure 8).[90] The unique photophysics of these "black TiO_2" presumably results from the presence of energy states corresponding to the disorder above valence band as well as fast exchange of hydrogens.[90] It has also been suggested that hydrogenation of TiO_2 nanowires generates a high degree of oxygen vacancies that act as electron donor states lying about 0.75 and 1.18 eV below the conduction band of hydrogenated rutile TiO_2.[91] The visible and NIR absorption of "black TiO_2" can be assigned to the transitions from TiO_2 valence band to the oxygen vacancy levels or from the oxygen vacancy states to the TiO_2 conduction band (as shown in Figure 8B).

Core−shell structured "black TiO_2" nanoparticles with a rutile core and sulfide shell have been developed that showed significantly enhanced photocatalytic activity and efficient photochemical water splitting compared to pristine rutile TiO_2.[92] Synthesis of such "black TiO_2" through reduction of TiO_2 using molten aluminum creates a disordered surface layer with a large amount of Ti^{3+} and oxygen vacancies. These defects create localized energy states in the band gap and account for the visible and NIR light activity of these nanoparticles. Furthermore, the S^{2-} ions from the outer sulfide shell can occupy the oxygen vacancy sites and contributes to the further narrowing of the band gap.

In an attempt to enhance the visible and infrared light activity, gray TiO_2 consisting of a TiO_{2-x} (core)/TiO_2 (shell) nanowires using metallic aluminum as the reducing agent has also been synthesized.[93] These nanowires of TiO_2 showed significantly higher solar-light driven photocatalytic efficiency than the standard Degussa (Evonik) P25. The activity under dark and visible light irradiated conditions enhanced strongly with an increase in reaction temperature. Photoluminescence studies revealed that annealing of TiO_2 at elevated temperatures under reducing atmosphere generates oxygen vacancies, which act as electron traps and lower the recombination of photoinduced electrons and holes and result in a quenching of luminescence intensity.

Important developments have recently been made in the field of perovskite materials ($^{XII}A^{2+VI}B^{4+}X^{2-}_3$), a class of compounds that have the same type of crystal structure as calcium titanate ($CaTiO_3$).[94−96] In recent years, several perovskite related materials have been developed that showed enhanced visible light driven H_2 production and decomposition of organic pollutants.[96−98] Both cationic and anionic dopants have been introduced into the layered perovskite-based metal oxide structure to tune the band gap positions required for visible-light-active photocatalysts.[99−102] The presence of anionic or cationic monodopants in perovskite-structure-based photo-

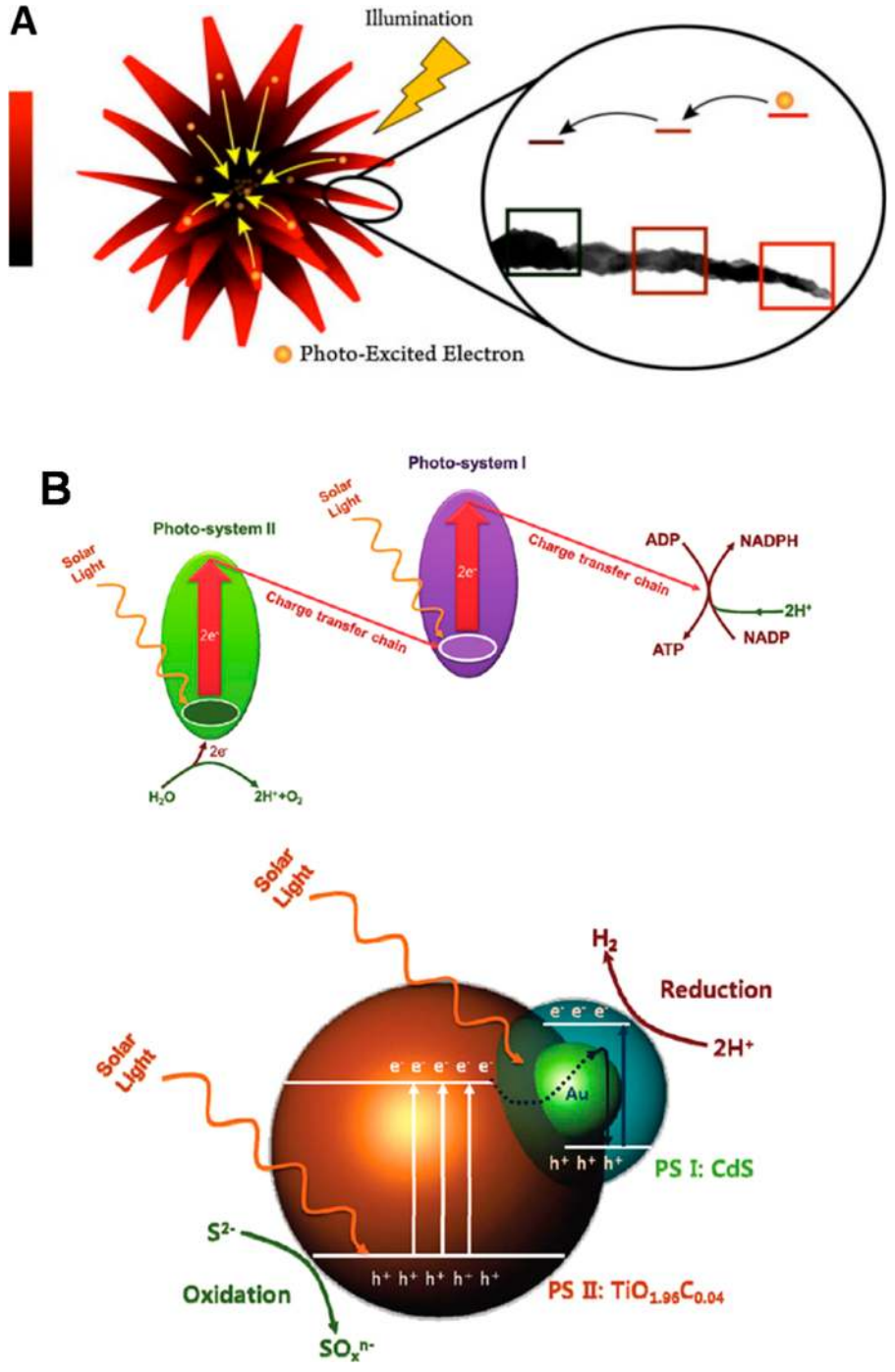

Figure 9. (A) The schematic illustration showing cascade of electron transfer in a nano/macro hierarchically structured TiO_2 upon illumination (ref 105). Copyright 2013, reprinted with permission from Elsevier. (B) Proposed Z-scheme mechanisms of the photosynthesis system: in natural photosynthesis system (top) and artificial CdS/Au/$TiO_{1.96}C_{0.04}$ photosynthesis system (bottom) (ref 107). Copyright 2011, reprinted with permission from American Chemical Society.

catalysts such as $Sr_2Ta_2O_7$ and $La_2Ti_2O_7$ creates additional impurity energy levels in the band gap and reduces the effective band gap.[100,101] However, these energy states also act as electron−hole recombination centers and decreases the photocatalytic efficiency, which can be overcome by systemically designing cationic−anionic codoped systems.[100,101] Chen and co-workers reported the synthesis of Cr-doped $SrTi_{1-x}Cr_xO_3$ and $Bi_4Ti_{3-x}Cr_xO_{12}$ that showed enhanced photocatalytic H_2 production activity under visible light illumination (λ > 420 nm). DFT calculations suggested that doping with Cr generates Cr 3d energy states in the band gap and the visible light absorption arises from the charge transfer from Cr 3d orbitals to Cr 3d + Ti 3d hybrid upon photoexcitation of the doped material.[102] Very recently, perovskite solar cells have emerged as cost-effective, high-efficiency systems for solar energy conversion to electricity. In fact, photovoltaic devices based on organic−inorganic [e.g., $CH_3NH_3PbI_3$][94−96] or inorganic [e.g., p-type $CsSnI_3$][94] perovskite structured semiconductors achieved power conversion efficiencies higher than 16% and were included in the "Science's Top 10 Breakthroughs of

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2013".[94] Moreover, current research on perovskites solar cells has proved the possibility of fine-tuning the optoelectronic properties (including energy gap and charge mobility) of materials, leading to increased light absorption, low charge recombination, and lasing ability,[103] properties that could be further optimized and exploited in the field of VLA photocatalysis.

There has been an exponential growth in research on development of visible-light-active TiO_2 photocatalysis over the last few decades after the discovery of VLA of N-doped TiO_2. The field of solar light driven photocatalysis of TiO_2 is still expanding due to its wide range of applications in various fields including photoelectrochemical water splitting, reduction of CO_2, and environmental remediation. In addition to dye sensitization, doping with metals and nonmetals, formation of heterojunctions have been widely used to enhance the visible light response of TiO_2 materials. Recently, perovskite-based layered metal oxides have also received tremendous attention for their applications in photoinduced processes, including their use in solar cells and as photocatalytic materials for removal of environmental pollutants. In recent years, quantum dots are appearing as excellent candidates for sensitization of TiO_2 for applications in photocatalysis and photovoltaics because of their interesting photophysical properties (high extinction coefficient, and quantum yield of emission), ease of synthesis, and the possibility to tune band gap.[104] However, a key factor in obtaining high efficiency of the photoconversion process is to facilitate the migration and separation of the charge carriers and increase the lifetime of the charge-separated species. Therefore, it is of critical importance to understand the excited state dynamics of the semiconductor material upon photoexcitation, which can shed light on the mechanistic aspects of the process as well as proves crucial in developing new materials with enhanced process efficiency. The importance of structural hierarchy in promoting charge migration and separation has been recently elucidated using chrysanthemum-like (ornamental-flower-like structure) TiO_2 structures with leafy branches.[105] The grain sizes in the branches increase gradually from nanoscale to microscale range along the direction of tip of the branches toward the center. The gradual size variation resulted in a series of heterojunctions between grains of different sizes, where the energy decreases gradually with increasing grain size. Thus, irradiation of this structure results excitation of electrons at the tip followed by a cascade of electron transfer as demonstrated in Figure 9A toward the central matrix leading to an efficient separation of charge carriers and improved photocatalytic properties.

To replicate the structural hierarchy and light harvesting ability of green leaves, *morph*-structured TiO_2 composites have been synthesized based on green leaves as templates.[106] Green leaves were initially treated with acid followed by $TiCl_3$ solution to substitute the Mg^{2+} in chloroplast by Ti^{3+} ions to generate the Ti-substituted layered nanostructure of thylakoid membrane. This was followed by reaction with $Ti(OBu)_4$ to generate the porous TiO_2 network replicating the vascular structure of green leaves. The *morph* structured TiO_2 derived from green leaf templates were doped with nitrogen from green leaves, and the N content was shown to depend on the leaf source. The high photocatalytic activity exhibited by the *morph*-TiO_2 composites has been assigned to the higher light harvesting ability of the porous and layered nanostructure and enhanced visible light absorption due to doping of nitrogen atoms from green leaves.

Several research groups have developed heterojunction structures derived from TiO_2 to promote directional electron transfer and facilitate charge carrier separation to mimic the so-called Z-scheme of electron transport occurring in green leaves during photosynthesis.[107,108] Yun et al. reported the synthesis of carbon-doped titania ($TiO_{2-x}C_x$) acting as photosystem II (PSII) combined with a Au/CdS core−shell structure, functioning as photosystem I (PSI).[107] Upon visible light irradiation, the photoexcited electrons from the conduction band of $TiO_{2-x}C_x$ move to CdS (PSI) through the Au core and combine with the photogenerated holes at the valence band of CdS (Figure 9B). These vectorial electron transports consequently increase the lifetime of conduction band electrons at the CdS (PSI) site, which can efficiently generate H_2 via the photocatalytic reduction of H_2O. Tada and co-workers reported development of a similar nanoheterojuntion consisting of CdS(PSI)/Au/TiO_2(PSII) that exhibited very high activity for photocatalytic reduction of methyl viologen.[108] The enhanced photocatalytic activity has been attributed to the simultaneous excitation of both CdS and TiO_2 centers and vectorial electron transfer from the conduction band of TiO_2 to CdS via Au core.

The results obtained to date strongly indicate the critical necessity for further development of these groups of photocatalytic materials driven by solar light by combining the visible light activity with structural modification to achieve long-lived charge carriers, for applications in energy conversion, and environmental remediation purposes.

The results obtained to date strongly indicate the critical necessity for further development of these groups of photocatalytic materials driven by solar light by combining the visible light activity with structural modification to achieve long-lived charge carriers, for applications in energy conversion, and environmental remediation purposes. Important developments in the field are also expected for the use of VLA materials in tandem PEC-DSC cells for self-driven solar water splitting and CO_2 photocatalytic conversion (reduction path) to hydrocarbons.

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