Review

The advancements in sol–gel method of doped-TiO$_2$ photocatalysts

U.G. Akpan, B.H. Hameed *

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

ABSTRACT

A critical review on the advancements in sol–gel method of doping TiO$_2$ photocatalysts is provided. Various sol–gel and related systems of doping were considered, ranging from co-doping, transition metal ions doping, rare earth metal ions doping to other metals and non-metals ions doping of TiO$_2$. The results available showed that doping TiO$_2$ with transition metal ions usually resulted in a hampered efficiency of the TiO$_2$ photocatalyst, though in some few cases, enhancements of the photocatalytic activity of TiO$_2$ were recorded by doping it with some transition metal ions. In most cases, co-doping of TiO$_2$ increases the efficiency of its photocatalytic activity. The review reveals that there are some elemental ions that cannot be used to dope TiO$_2$ because of their negative effects on the photocatalytic activity of the catalyst, while others must be used with caution as their doping will create minimal or no impacts on the TiO$_2$ photocatalytic efficiency.

© 2009 Elsevier B.V. All rights reserved.

Contents

1. Introduction

The advantages derived from TiO$_2$ and doped-TiO$_2$ as photo-catalysts have prompted much research in the field [1–15]. Recently, much interest has been devoted to the use of TiO$_2$-based photocatalysts for the degradation of dyes in aqueous solutions [16–30]. The interests in TiO$_2$-based photocatalysts have also led to the development of several methods of preparing the catalysts for varied usages. TiO$_2$, itself is a versatile material that finds applications in various products, such as pigments, sunscreen lotions, electrochemical electrodes, capacitors, solar cells and even, as a food colouring agent [31] in toothpastes.

Various methods are available for the preparation of TiO$_2$-based photocatalysts, such as electrochemical [32–37], continuous reaction [38], multi-gelation [9,39], supercritical carbon dioxide [40], thin films and spin coating [41–43] and thin film by vacuum arc plasma evaporator [13], combining inverse micelle and plasma treatment [44,45], dip coating [46,47] and SILAR [2], two-step wet chemical [8], precipitation [6,11,48–50], thermal (ethanol thermal, hydrothermal and solvothermal) [7,14,51–55], chemical solvent and chemical vapour decomposition (CSD & CVD) [1,10,56–58], Ultrasonic irradiation [59], extremely low temperature [3,60], and Aerogel and Xerogel [61,62], other methods different from sol–gel [63–66], modified sol–gel [22,67], two-route sol–gel [5,68,69] and methods similar to sol–gel [70], and sol–gel [4,12,15,71–91]. Nevertheless, the benefits derived from preparing TiO$_2$ by sol–gel method (process flow chart shown in Scheme 1), which include synthesis of nanosized crystallized powder of high purity at relatively low temperature, possibility of stoichiometry controlling

* Corresponding author. Tel.: +6045996422; fax: +6045941013.
  E-mail address: chbassim@eng.usm.my (B.H. Hameed).
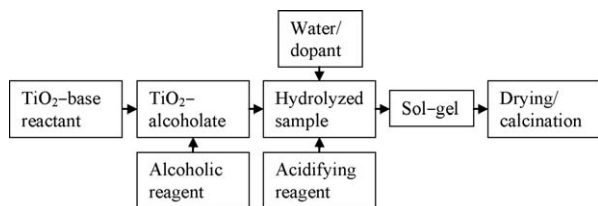
Scheme 1. Process flow chart for the preparation of TiO_2-based photocatalysts by sol–gel method.

process, preparation of composite materials, and production of homogeneous materials have driven many researchers to the use of the method in preparing TiO_2-based photocatalysts. This crusade of researches on sol–gel preparation methods of TiO_2-based photocatalysts has provided the push for the present study.

Sol–gel technology has been in existence as from as long ago as the mid-1800s [92], and was used almost a century later by Schott Glass Company (Jena, Germany) [92]. Sol–gel technology finds applications in the development of new materials for catalysis [93–95], chemical sensors [96,97], membranes [98–101], fibers [102–104], optical gain media [105], photochronic applications [106], and solid state electrochemical devices [107,108], and in a diverse range of scientific and engineering fields, such as ceramic industry [92], nuclear industry [92] and electronic industry [109].

Sol–gel is one of the most exploited methods; it is used mainly to produce thin film and powder catalysts. Many studies revealed that different variants and modifications of the process have been used to produce pure thin films or powders in large homogeneous concentration and under stoichiometry-control [110–119]. Han et al. [120] recently undertook a review on 'Tailored titanium dioxide photocatalysts for the degradation of organic dyes in wastewater treatment'. As good as the review is, it was a kind of generalized approach (which covered many methods of modifications of TiO_2) that was employed. This may not provide enough depth for various methods available for it, but the present review focuses on sol–gel and sol–gel related methods of preparing TiO_2-based photocatalysts. Therefore, the main target of the present review is on sol–gel and sol–gel related methods of doping TiO_2 photocatalysts, with emphasis on the efficiency of the catalysts prepared by the method in any considered photocatalytic activity. This has been considered important, as numerous researches are currently going on in this field. It is therefore becoming compelling to put previous information available on this method together with the merits and demerits in one volume so that newcomers to the field can conserve time and resources as they embark on their researches.

2. Doped-TiO_2 photocatalysts by sol–gel method and evaluation of their photocatalytic activity

In this section, we discuss various sol–gel and sol–gel related systems of doping TiO_2, which include co-doping, transition metal doping, rare earth metal doping, other metals and non-metals doping, and their photocatalytic performance in degradation of pollutants in aqueous solutions.

2.1. Co-doping of TiO_2 by sol–gel method

Gombac et al. [76] described a two route (the second being subsequent to the first) method of co-doping TiO_2 with boron and nitrogen. The full experimental details are as follows.

Typically, 17 g of $Ti(OBu)_4$ was dissolved in 40 ml of anhydrous ethanol at room temperature (r.t.) under argon flow to prepare solution A. Meanwhile, 3.0 ml of concentrated HNO_3 was mixed with 35 ml of anhydrous ethanol and 15 ml of water to prepare

solution B. Solution A was subsequently added dropwise to solution B under vigorous stirring in argon flow, within 20 min. The solution was subsequently stirred for further 30–60 min and aged for at least 24 h at r.t. As-prepared TiO_2 gels were dried at 120 °C for 12 h. The obtained solids were ground and finally calcined at 450 °C for 6 h (heating rate = 3 °C/min).

Boron-doped TiO_2 was synthesized using a similar preparation method. An appropriate amount of H_3BO_3 was dissolved in 10 ml of water (solution C) and rapidly added to the mixture of solutions A and B. The subsequent treatments were identical to those described above for the undoped-TiO_2.

For the N-doped and B/N-co-doped TiO_2, an impregnation method was used. Exactly two gram of the prepared and calcined TiO_2 powder was suspended in 2 ml aqueous solution of guanidine carbonate with the appropriate concentration and stirred at r.t. for 1 h. The suspension was kept in the dark for 16 h and then evaporated to dryness at 120 °C to yield a white powder which was calcined in air at 450 °C for 1 h (heating rate = 3 °C/min). After calcination, the powder particles were washed with diluted sulphuric acid (0.2 M) and then with water up to neutral pH, and dried under vacuum to obtain the N-doped TiO_2 samples.

For the preparation of B-N-TiO_2 specimens, the boron doped samples, synthesized as previously described, were impregnated with the proper guanidine carbonate solution according to the above procedure, dried and subjected to an additional calcination at 450 °C for 1 h (heating rate = 3 °C/min). The doped samples were denoted as TiO_2-Xn-Ym, where 'X' and 'Y' denote the doping element (N or B) and the corresponding nominal dopant molar percentage m and n.

The developed catalysts were used in the degradation of methyl orange (MO). The results of their findings were found to be consistent with previous observations [58,109], which indicated B- and N-doping enhancement of TiO_2 photodegradation activity, especially when both dopants are present together. The TiO_2-B9-N5 system was found to be the most active, and during the first 2 h of irradiation, the MO degradation proceeded with a rate constant $k_1 = 1.24 \times 10^{-2}$/min that subsequently increased to $k_2 = 3.03 \times 10^{-2}$/min, indicating a decolorization rate (in the second half of the experiment) more than twice as faster as the initial one. On comparison to all the systems described above, the TiO_2-"B9-N5 system was found to be the best.

Zhang and Liu [15] also prepared B-Ni-Ce-co-doped TiO_2 via sol–gel method, with some modifications. In their case, 0.062 g H_3BO_3, 0.29 g $Ni(NO_3)_2 \cdot 6H_2O$, and 0.43 g $Ce(NO_3)_3 \cdot 6H_2O$ were dissolved in a mixture of 10 ml of deionized water, 8 ml of glacial acetic acid and 30 ml of ethanol to obtain solution A. 34.0 g tetrabutyl titanate was dissolved in 50 ml of anhydrous ethanol to gain solution B. Then, the solution B was added into the solution A within 30 min, keeping the reaction mixture vigorously magnetically stirred to form the sol. The sol was stirred continuously for 2 h and aged for 72 h to prepare the gel. The gel was dried for 12 h at 100 °C under reduced pressure to gain the xerogel, which was milled and annealed at the desired temperatures for 2 h to prepare the ternary co-doped photocatalyst. The as-prepared sample was labeled as BNiCeTiO$_2$(t), where B, Ni, and Ce represented doping with B, Ni, and Ce, respectively, and t was the annealing temperature (°C).

The developed catalysts were employed in the visible light degradation of phenol; the results are presented in Fig. 1. It is clear from the results that TiO_2-doped with the three metal ions shows the highest degradation potentials. A critical analysis of the results revealed that boron has a very high impact on the efficiency of the co-doped TiO_2, and might be the greatest contributor to the high degradation by the co-doped TiO_2.

Huang et al. [79] used sol–gel-solvothermal method to prepare N-F-codoped-TiO_2 photocatalysts as follows: 20 ml of tetrabutyl
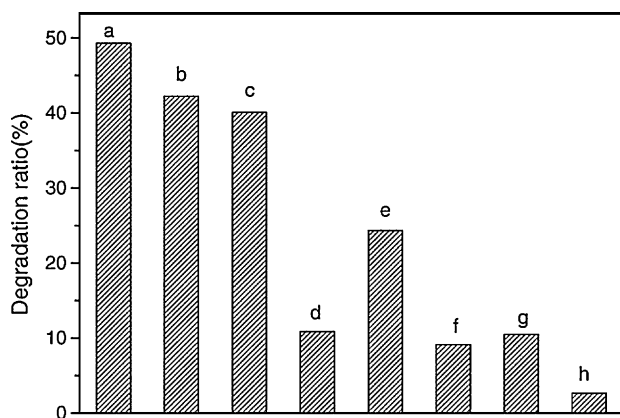
Fig. 1. Under visible light illumination after reaction for 3 h the degradation phenol ratios of (a) BNiCeTiO$_2$(500), (b) BNiTiO$_2$(500), (c) BCeTiO$_2$(500), (d) NiCeTiO$_2$(500), (e) BTiO$_2$(500), (f) NiTiO$_2$(500), (g) CeTiO$_2$(500), and (h) TiO$_2$(500) [15].

titanate, 10 ml of ethanol and 5.0 ml of acetic acid were mixed in a 200 ml flask with stirring for 30 min to form solution A. About 0.15 g ammonium fluoride, 6 ml of ultrapure deionized water, 4 ml of triethylamine, 3.0 ml of nitric acid and 80.0 ml of ethanol were mixed with stirring for 10 min to form solution B. Secondly, solution B was added drop by drop into solution A under vigorous stirring. Then, the solution was slowly stirred until a transparent immobile gel was formed. The gel obtained was dispersed in a solvent to form a sol mixture. Finally, the sol mixture was transferred to a Teflon tube and placed in a 300 cm^3 stainless steel autoclave. An additional 30 ml of solvent and a limited amount of hexamethylenetetramine were added into the gap between the test tube and the autoclave wall. The autoclave was heated in an oven and kept at 140 °C for 10 h. The powder product was separated by centrifugation, dried at 60 °C in vacuum overnight and calcined at 320 °C for 6 h in air.

To evaluate the performance of the prepared co-doped photocatalysts, they considered the degradation of p-chlorophenol under filtered irradiation (400–500 nm) of a 150 W tungsten halogen lamp, and under irradiation (350–400 nm) of a 150 W high pressure UV mercury lamp. The co-doped sample performed better than both Degussa P25 and just N- or F-doping under the two light sources. Nevertheless, only 17.8% degradation was achieved with the co-doped sample under the visible light irradiation for 12 h. In contrast to this, 43.1% degradation was achieved with the same sample under UV light irradiation for the same irradiation time. This shows that the degradation of p-chlorophenol by N-F-co-doped TiO$_2$ is better undertaken under the UV light irradiation.

B-Ce-codoped TiO$_2$ had been prepared by Wei et al. [121]. The TiO$_2$ nanoparticle colloidal solutions were prepared using the controlled hydrolysis of tetrabutyl titanate and titanous trichloride [122]. A calculated amount of boric acid and cerous nitrate were dissolved in 50 ml of anhydrous ethanol. After 1 h of vigorous magnetic stirring, 2.5 ml of tetrabutyl titanate and 2.5 ml of titanous trichloride were added with vigorous magnetic stirring under anaerobic conditions (purged with N$_2$). Sodium hydroxide solution (1 mol/l) was then slowly added to the solution, surrounded by an ice bath. The clear solution was stirred at room temperature for 2d. Subsequently, the gel that was formed was dried at 100 °C. Finally, the prepared samples were calcined at desired temperatures (300, 500, 700, or 900 °C) for 5 h. Pure, boron-doped and cerium-doped TiO$_2$ were prepared without adding boric acid and cerous nitrate under identical conditions, respectively. The prepared photocatalysts were named B$_m$Ce$_n$-TiO$_2$, where m and n denoted the atomic ratios of B/Ti and Ce/Ti, respectively.

The photocatalytic activities of TiO$_2$ doped with different dosages of boron and cerium were measured by monitoring the degradation of Acid Red B (ARB). The percentage degradations of ARB were 94.2, 95.7, 96.0, 86.6 and 77.1 over B$_{1.6}$Ce$_{0.0}$-TiO$_2$, B$_{1.6}$Ce$_{0.1}$-TiO$_2$, B$_{1.6}$Ce$_{0.5}$-TiO$_2$, B$_{1.6}$Ce$_{1.0}$-TiO$_2$, and Degussa P25, respectively, after 10 min UV irradiation. These results indicated that the photocatalytic activity of the photocatalysts increased slightly with increase in cerium dopant, when the atomic ratio of Ce/Ti was ≤0.5. However, for greater atomic ratios of Ce/Ti, the photocatalytic activity showed a decrease. It can be deduced from the results that co-doping of TiO$_2$ with B and Ce at the specified ratios enhances its photocatalytic efficiency.

Liu et al. [67] prepared an N-Ce co-doped TiO$_2$ via modified sol–gel process. Briefly, a varied amount of Ce(NO$_3$)$_3$ together with a constant amount of urea (atomic ratio of urea to tetrabutyl titanate = 0.5) were dissolved in anhydrous ethanol according to the doping ratio of Ce/Ti of 0, 0.1, 0.3, 1.0, 3.0 or 10.0 at%, respectively. The resulting solution was added dropwise into a tetrabutyl titanate solution with anhydrous ethanol as solvent at room temperature under vigorous stirring condition to obtain a sol–gel. The resultant gel was dried at 110 °C for 8 h in air, and thereafter calcined at 500 °C for 2 h.

The as-prepared catalysts were used to degrade methyl orange, MO under visible light irradiation for 2 h. The percentage degradation was found to increase with the increase in molar ratio of Ce/Ti from 0 to 0.3%, thereafter it decreased to exert detrimental effect on the activity of TiO$_2$ at 3% Ce/Ti. Nevertheless, there was an increase recorded at 10% Ce/Ti up to 92% degradation. However, since about 90% degradation of MO is attained at 0.3% Ce/Ti, so the increase to about 92% at 10% Ce/Ti may be termed negligible. Therefore, having 10% Ce/Ti doping may appear to be a wasteful exercise, noting that no significant % degradation is obtained better than 0.3% Ce/Ti.

Fe^{3+} and Ho^{3+} co-doped TiO$_2$ has been reported [80]. Sol–gel method was used in the preparation of the catalysts. The results revealed that, within the first 9 min of UV light irradiation of MO, the degradation rates of MO were in the order Fe$_{0.05}$Ho$_{0.5}$-TiO$_2$ > Ho$_{0.5}$TiO$_2$ > TiO$_2$ > Fe$_{0.05}$TiO$_2$. Nevertheless, beyond 9 min irradiation, all the doped photocatalysts performed better than the undoped TiO$_2$, though they all, including the undoped TiO$_2$, ended up at the same point at the 21st minute of the irradiation. As long as there is no distinct advantage at the 21st minute of the irradiation, these might not be considered to be better photocatalysts than the undoped TiO$_2$.

Srinivasan et al. [73] considered the effects of sulfation and codoping of TiO$_2$ with Fe and Zn on the visible light photocatalysis of TiO$_2$. Fe^{3+}/Zn^{2+} codoped TiO$_2$ was obtained by sol–gel method; thereafter, it was impregnated with SO$_4^{2-}$ by immersing the Fe^{3+}/Zn^{2+} codoped sample in 1 M H$_2$SO$_4$ solution for 1 h. Controlled hydrolysis of a Ti-alkoxide was achieved with the molar ratio of Ti(OBu)$_4$:C$_2$H$_5$OH:H$_2$O:HNO$_3$ equivalent to 1:20:6:0.8–0.45. 13.5 mol of anhydrous ethanol was mixed with 1 mol of Ti(OBu)$_4$ and stirred for 10 min at room temperature. 0.8 mol of HNO$_3$ was then added dropwise to the solution to stabilize the Ti precursor so that immediate hydrolysis would not occur upon the addition of H$_2$O. A separate solution of 6.5 mol of ethanol and 1 mol of de-ionized H$_2$O was vigorously stirred and added drop by drop to the parent solution to prepare pure TiO$_2$.

For the Fe^{3+}/Zn^{2+} co-doped TiO$_2$, Fe(NO$_3$)$_3$·9H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O were mixed with the pure TiO$_2$ solution in a Fe:Zn molar ratio of 2:1. The final pH values of doped and undoped solutions were maintained at 0.85, which allows the gelation time of approximately 12 h for all samples. The resultant dispersion of colloidal particles defined as the sol, was then aged followed by gelation at room temperature for 48 h. The resulting sol–gel was heated at 100 °C for 12 h to remove the residual solvents. The

obtained amorphous Fe^{3+}/Zn^{2+} co-doped TiO_2 particles were then impregnated in a 1 M H_2SO_4 solution for 1 h using 50 ml of solvent per gram of catalyst. The as-prepared sulfated and co-doped TiO_2 nanoparticles were then filtered and dried at 100 °C for 3 h. These particles were slowly heated up to 145 °C to surpass the exothermic reaction of $Ti(OBu)_4$ precursors. The sulfated particles were further filtered, dried, and calcined at 500 °C under flowing air.

In the degradation of phenol, a reduced activity of TiO_2 due to the codoped Fe^{3+}/Zn^{2+}-TiO_2 was observed under UV–vis light irradiation. However, a little enhancement with maximum degradation of 8.55% was noticed under visible light irradiation. The UV–vis photocatalytic activities of the sulfated (impregnated) and non-sulfated (non-impregnated) were found to be roughly the same. Though codoped, this reflects on the negative impact of some transition metal ions doping of TiO_2.

Co-doping of TiO_2 was generally found to enhance the photocatalytic activity of the catalyst, though there are a few cases which are detrimental. The observation is quite true for any B-codoped TiO_2. Boron has been found to contribute positively to the photocatalytic activity of TiO_2. The photocatalytic degradation of p-chlorophenol by N-F-codoped TiO_2 is better undertaken under UV light than under visible light irradiation. On the other hand, Fe^{3+} and Ho^{3+} co-doped TiO_2 in 21 min UV light irradiation for the degradation of MO does not display any distinction over the undoped TiO_2, thus the material may not be considered a better photocatalyst than the undoped TiO_2. Also Fe^{3+}/Zn^{2+}-TiO_2 was not found to be much better than the undoped TiO_2 for the degradation of phenol under visible light irradiation, and the undoped TiO_2 was better than the Fe^{3+}/Zn^{2+}-TiO_2 under UV light irradiation for the degradation of the same substance.

2.2. Transition metals doping of TiO_2 by sol–gel method

Wilke and Breuer [82] studied the influence of transition metal (Cr^{3+} and Mo^{3+}) doping on the physical and photocatalytic properties of titania. 6.95 ml (6.7 g, 23.55 mmol) tetra-isopropy-lorthotitanate was diluted in 30 g (0.6 mol) isopropanol. For stabilization purposes, 9 g (8.77 ml, 68.85 mmol) ethyl acetonate and 1 ml (1.4 g, 14.44 mmol) nitric acid were added to the solution, which was then stirred for 24 h at room temperature. In case of doped titania, the synthesis started with the dissolving of the respective amount of chromium (III) nitrate or molybdenum (V) nitrate. For the preparation of the powders, the sol was evaporated to dryness at 100 °C and calcined at 400 °C for 24 h. By this procedure powders with dopant concentrations from 0.1 to 10 at% were obtained.

The performance of the as-prepared catalysts was tested by the photocatalytic degradation of Rhodamine B under UV light irradiation. The results of 60 min irradiation showed that neither the Cr^{3+}- nor the Mo^{5+}-doped TiO_2 enhanced the phocatalytic activity of the undoped TiO_2 produced via the same method. However, a marked difference was noticed between the two dopants. For both ions, photocatalytic activity decreases at low dopant concentrations. While for Cr^{3+}, the activity remained low (about 20% of the initial value), there was an increase of activity for Mo^{3+} at higher concentrations. However, even at the highest Mo^{5+} concentration, there was no improvement compared to undoped titania.

Recently, TiO_2 was doped with Cr [77]. To prepare the Cr-doped TiO_2, the researchers added 0.01 mol of titanium tetrachloride to a solution containing 1 g of pluronic P123 and 10 g of ethanol. To this solution, 1×10^{-5}, 5×10^{-5} and 1×10^{-4} mol $Cr(NO_3)_3$ was added for the synthesis of mesoporous Cr-doped TiO_2, respectively. The resulting sol was gelled in an open petri dish at 50 °C in air for 4 days. The as-made bulk samples were then calcined at 400 °C for

3 h in air at the heating rate of 1 °C/min to remove the surfactant. The calcined samples were labeled according to the Cr-doping content (the pure mesoporous TiO_2 is denoted as MT-0, the mesoporous Cr-doped TiO_2 is denoted as MT-0.1 and so on). The synthesis of the nonporous 0.1 mol% Cr-doped TiO_2 labeled as Cr-TiO_2-0.1 was similarly conducted but without the surfactant of P123.

The photocatalytic activities of the prepared samples were evaluated by the oxidation of acetaldehyde in air at room temperature. The results of the photocatalytic degradation of acetaldehyde in 15 min under UV light, and for three hours under visible light are presented in Figs. 2 and 3. From the results, it is clear that the undoped TiO_2, MT-O and P25 under UV light irradiation outperformed all the doped catalysts. Nevertheless, under visible light irradiation, a minimal enhancement of all the doped mesoporous Cr-TiO_2 was noticed with the highest being 1×10^{-5} mol $Cr(NO_3)_3$. But that of the non-porous Cr-TiO_2(0.1) was still less than that of the undoped TiO_2. It must be noted that the level of degradation under visible light by MT-0.1 is far less than the level of degradation by the undoped TiO_2 under UV light for 15 min. Then, researchers must seriously consider whether TiO_2 must be doped with Cr at all, since a
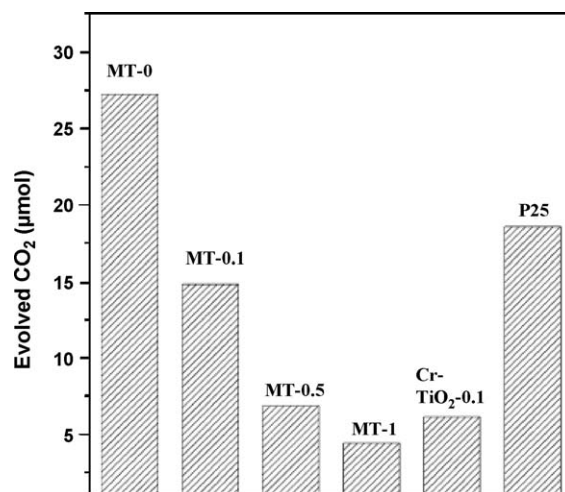
Fig. 2. The photocatalytic activities of samples under UV-light (full arc of 300 W Xe lamp) irradiation for 15 min [77].
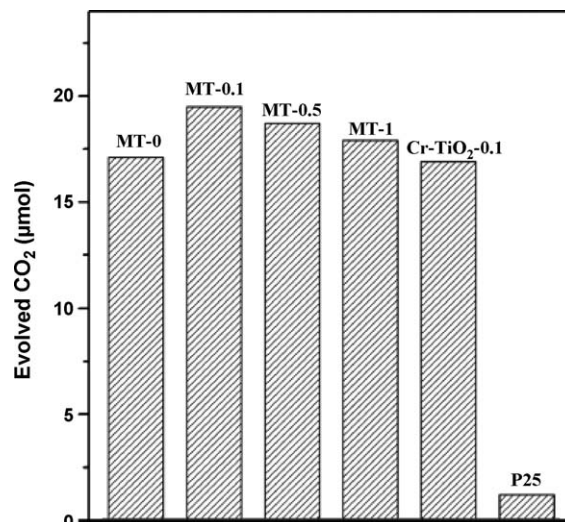
Fig. 3. The photocatalytic activities of samples under visible light irradiation ($\lambda > 440$ nm) for 3 h [77].

higher level of degradation can be attained by the undoped sample than the doped.

Liu et al. [81] reported on preparing Zn^{2+}-TiO_2 by two methods: sol–gel and solid phase reaction (SPR). For the sol–gel, a solution was made from tetrabutyl titanate and isopropanol in an appropriate proportion and its pH was adjusted to about 3 with HCl. Subsequently, zinc nitrate was added dropwise to the above solution during vigorous stirring, and the molar ratio of tetrabutyl titanate:isopropanol:deionized water:zinc nitrate was controlled as 1:22:4:0.005. Then a translucent sol was obtained; it was left to gel for a few minutes. The gel was dried at 80 °C until a dry gel was obtained, and then the dry gel was calcined at 500 °C for 2 h in air to form powders. In the SPR method, various mol% (0.1, 0.3, 0.5, 0.8, 1.0, 1.5, 2.0) ZnO were mixed with the undoped TiO_2, ground and sieved through #120 mesh. Subsequently, the powder was calcined at 500 °C for 2 h. The prepared catalysts were used for the degradation of Rhodamine B under UV light. The results revealed that Zn^{2+} doping in the sol–gel method had little or no influence on the photocatalytic activity of TiO_2, as the two had the same end point after 60 min irradiation. But Zn^{2+} doping by SPR method enhanced the photocatalytic activity of TiO_2, as it brought about a complete degradation of Rhodamine B within 50 min.

Liao et al. [12] prepared TiO_2 and TiO_2/ZnO composite nanoparticles through the sol–gel method with the introduction of surfactants. The detailed preparation method is as follows: $Ti(OBu)_4$ was dissolved in ethanol with a $Ti(OBu)_4$/ethanol molar ratio of 1:10. The pH of the solution was adjusted to 2.0 with HCl. Surfactant (DBS or SDS) was dissolved in ethanol according to a set molar ratio and fed into the $Ti(OBu)_4$ solution slowly at a rate of 0.5 ml/min. In this study, the molar ratio of surfactant to $Ti(OBu)_4$ was fixed at 0.02:1 for SDS and 5:1 for DBS, respectively. These molar ratios were used because of the very high photocatalytic activity obtained with these molar ratios in a previous study [89]. One mole per liter of $Zn(NO_3)_3 \cdot 6H_2O$ solution was added into the $Ti(OBu)_4$/surfactant mixture slowly with a set molar ratio (0.1:1 to 0.5:1) of Zn to $Ti(OBu)_4$. After that, the $Ti(OBu)_4$/surfactant mixture was fed into a mixture of deionized water/ethanol ($Ti(OBu)_4$:water:ethanol molar ratio of 1:4:10) at 0.5 ml/min. Hydrolysis reactions and polymerization took place in this mixture and TiO_2 sol was formed. After gelation for 24 h, the gel was dried at 70 °C in an oven until yellow crystals were obtained. After the sample was calcined in a muffle furnace at a high temperature (600–800 °C), white TiO_2 nanoparticles were obtained.

The effectiveness of the prepared photocatalysts was tested on the photocatalytic decomposition of methyl orange MO under UV light irradiation. The results showed that all the doped samples showed improved photocatalytic activity over the undoped TiO_2, with the highest kinetic rate constant ($k = 1.81$/h) obtained at 600 °C, Zn/Ti ratio of 0.25:1, and sodium dodecyl benzene sulfonate (surfactant). The results of improved photocatalytic activity of TiO_2 nanoparticles through formation of composites with ZnO are consistent with the findings of Yang et al. [91].

Xin et al. [123] prepared Cu-TiO_2 photocatalysts by sol–gel method. 7.6 ml of tetrabutyl titanate was slowly added into 8 ml of ethanol under vigorous stirring to form solution A. Then a certain amount of $Cu(NO_3)_2$ dissolved in 2 ml of ethanol was added dropwise to the solution A. Finally the mixed solution was continuously stirred until the gel was formed. The gel was dried at 100 °C, calcined at 400 °C, and ground to obtain the Cu-TiO_2 nanoparticles. The Cu concentrations in the samples were 0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 1 and 3 mol%, respectively.

Photocatalytic degradation of Rhodamine B (RhB) under UV light irradiation was considered to test the performance of the prepared catalysts. The results showed that the photocatalytic activity of TiO_2 in 4 h irradiation of RhB increased from about 62%

degradation over the undoped TiO_2 to about 68% as the Cu dopant content slowly increased to 0.06 mol% Cu-TiO_2. This is about 9.68% enhancement. At high Cu dopant level (>0.06 mol%), the doping became detrimental to the process, because the excessive oxygen vacancies and Cu species can become the recombination centers of photoinduced electrons and holes, hence reducing the photocatalytic efficiency of the catalyst.

Huang et al. [68] described a method of Pt modified TiO_2 loading on natural zeolite (the complete procedure is provided). Pt-modified TiO_2 loaded on natural zeolite was prepared by sol–gel process and photoreductive deposition method. The precursor solution composites consist of tetra-n-butyl titanate, n-butyl alcohol, chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) and nitric acid. The nitric acid was used as catalyst to control the hydrolysis process. The typical steps are as follows:

(1) A given amount of tetrabutyl titanate was dissolved in pure ethanol with a volume ratio of 1:3 of tetrabutyl titanate to ethanol, and then nitric acid solution was added drop by drop into the solution to readjust the pH value to 4. During these procedures, the solution was stirred vigorously to avoid precipitation. After stirring for 8 h, weak yellow and clear TiO_2 sol was obtained. Subsequently, a requisite amount of natural zeolite, which was preheated at 450 °C for 4 h, was mixed with the TiO_2 sol with vigorous stirring, and a mixed suspension formed. After being stirred for 6 h, a mixture of ethanol and distilled water was added gradually into the mixed suspension and it became gel. It was then dried at 80 °C for 6 h, ground to fine powder in an agate mortar, and moved to an oven to be further calcined at different temperatures (110 °C, 200 °C, 300 °C, and 500 °C) for 4 h. By this procedure, TiO_2 loaded on natural zeolite was prepared; it will be denoted as TiO_2/zeolite.
(2) Pt modified TiO_2/zeolite was prepared by a photochemical reduction process [69]: a certain amount of chloroplatinic acid was dissolved in the mixture solution of distilled water and methanol, and then a weighed amount of TiO_2/zeolite was put into the solution. The mixture solution was irradiated by UV light for 5 h, followed by washing and drying at 80 °C for 6 h. Pt modified TiO_2/zeolite composite was achieved; it will be denoted as Pt-TiO_2/zeolite. Previous investigation revealed that the decolorization rate increased with the amount of TiO_2 loading and then decreased with further increase of TiO_2 loading. The decolorization rate was about 66.9% with 25% TiO_2 loading heated at 200 °C at 30 min irradiation time [78].

110 °C is the best calcination temperature of the prepared catalysts that yielded 73.0% and 87.8% decolorization for the undoped TiO_2/zeolite and 1.5% Pt-TiO_2/zeolite, under UV light irradiation for the same irradiation time. Increasing the calcination temperature will accelerate the formation of TiO_2 anatase phase, which is beneficial to the improvement of photocatalytic efficiency, but in this case, it will also cause conglomeration of catalyst particles, which reduces the specific surface areas of samples, resulting in the decrease of photocatalytic efficiency; hence, catalysts calcined at lower temperature had higher photocatalytic activity. The results revealed that 1.5 wt% Pt-TiO_2 loaded on natural zeolite provided a better enhancement for the TiO_2, but anything more than 1.5 wt% Pt-TiO_2 may be detrimental to the process.

Li et al. [84] prepared WO_x-TiO_2 and used it in the photocatalytic degradation of MB under visible light irradiation. A 0.05 mol TiO_2 transparent sol was first prepared using $Ti(O-Bu)_4$, 120 ml absolute ethanol, 15 ml acetic acid, and 5 ml doubly distilled water, and this sol was aged for 1 day. Then 3.0 ml aqueous solution of ammonium tungstate $(NH_4)_{10}H_2W_{12}O_{42} \cdot 4H_2O$

was added dropwise to the sol under vigorous stirring for 2 h until WO_x-TiO_2 gel formed. WO_x-TiO_2 sample was obtained in a doping level of 1.5% after being aged, dried, ground and sintered at 973 K for 2 h; it is labeled as 1.5% WO_x-TiO_2. Similarly, 3, 4, 5, and 10% WO_x-TiO_2 samples were also prepared according to the above procedure.

The pseudo-first-order kinetic rate constant, evaluated within 40 min reaction, showed that all the WO_x-TiO_2 samples had higher degradation rates for the photocatalytic degradation of MB under visible light irradiation than the undoped TiO_2. The rate increased with dopant content from 0 to 3.0% WO_x-TiO_2 and thereafter started to decline rapidly. This shows that 3.0% WO_x is the optimum doping amount of TiO_2; this combination can produce the best photocatalyst for the degradation of MB.

Colmenares et al. [3] prepared transition metals (Ag, Fe, Pd, Pt, Zn, and Zr) doped TiO_2 by sol–gel method under extremely low temperature. The preparation temperature of the precursor was 0–5 °C. When the metal salts were added, the sol–samples were left under vigorous stirring at 0 °C for 3 h. Subsequently, the pH of the prepared samples was increased up to 9 with 5N NH_4OH to form a gel, which was divided into two parts. One part was magnetically stirred (ST) for 24 h, whereas the other was treated with ultrasonic (US) irradiation, operated in the continuous mode. In the latter case, the mixture was kept at 5 °C to avoid solvent evaporation. The resulting gels were filtered under vacuum and washed with an aqueous solution of NH_4OH at pH 9, then dried at 110 °C for 24 h, ground and sifted to fine powders (particle diameter below 0.149 mm), and calcined at 500 °C for 6 h in the air. The doping was on individual metal particles.

The prepared and calcined catalysts were used to study their photocatalytic activities on the selective oxidation of propan-2-ol for 5 h under UV light irradiation (see Fig. 4). The commercial TiO_2-Degussa P25 was used alongside with the doped catalysts for comparison. In the molar conversion of propan-2-ol, Degussa P25 out-performed all the doped and undoped TiO_2 samples. Nevertheless, the best results were obtained with Pd-, Pt-, and Ag-containing systems with TiO_2-US and TiO_2-Zn-US. On the other hand, Fe- and Zr-containing catalysts exhibited the lowest conversion values (below 20%), whereas TiO_2-St and TiO_2-Zn-St occupied a medium position in the conversion-scale (conversions ca. 33% and 29%, respectively). It is very clear from Fig. 4 that a detrimental effect existed in doping TiO_2 with Fe or Zr, since their performances were far lower than that of pure TiO_2 prepared under

Fig. 4. Results obtained for gas-phase selective photo-oxidation of 2-propanol with all the systems synthesized in the present study in terms of molar conversion (%), selectivity to acetone (%) and selectivity to CO_2 (%) for a time-on-stream of 5 h. For the sake of comparison, results obtained with Degussa P25 have also been included [3].
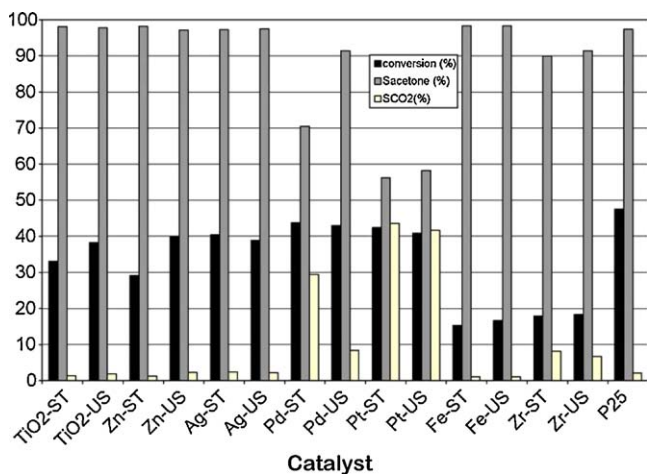
the same experimental conditions. No distinct differences were noticed in the methods of stirring the prepared samples for Ag-, Pd-, Pt-, Zr-, and Fe-doped catalysts, as their conversions are almost the same for their respective US and ST samples. Though it has been reported that doping with Zn is detrimental to the photocatalytic activity of TiO_2 [124], which is true for TiO_2-Zn-St system, TiO_2-Zn-US exhibited slightly higher photocatalytic ability than TiO_2-US.

Apart from the above described method of preparing Ag-doped TiO_2 catalyst, Stir et al. [72], and Rengaraj and Li [87] reported using ultrasonic assisted sol–gel for the same purpose with their respective modifications. Stir et al. [72] dissolved 30 ml titanium tetraisopropoxide in 100 ml ethanol under vigorous stirring for about 15 min. Then distilled water and HNO_3 (5 ml, 0.1N) were added to complete the hydrolysis reaction in an ultrasonic bath. The amount of water varied between 15 ml and 36 ml, corresponding to hydrolysis ratios [H_2O]/[TTIP] between 8 and 20. Then, a prepared $AgNO_3$ solution of 4 ml was added and the solutions were further homogenized for a few hours with a magnetic stirrer, and then aged at room temperature. There was no photocatalytic activity on the prepared catalyst.

On the other hand, Rengaraj and Li [87] dissolved 21 ml of Ti(O-Bu)$_4$ in 80 ml of absolute ethanol under stirring. The resulting solution was stirred in an ice bath; 2 ml of water and 0.2 ml of HNO_3 (50%) were added into another 80 ml of ethanol to make an ethanol–water–HNO_3 solution, which was slowly added to the Ti(O-Bu)$_4$–ethanol solution under stirring and cooling with ice. When the resulting mixture turned to sol, the $AgNO_3$ solution was dripped into it; the dispersion was placed in a supersonic bath, stirred vigorously with a glass-stirring rod, and kept at 25 °C throughout the whole process. After sonification for 30 min, 1–2 ml of water was dripped into the dispersion at a rate of 0.5 ml/min until gel was formed. The gel was placed for 24 h at room temperature and dried at 70 °C under vacuum condition, and then ground. The resulting powder was calcined at 500 °C for 4 h for further studies. A pure TiO_2 sample was also prepared by the above procedure, but without addition of $AgNO_3$ solution. The prepared photocatalysts (Ag-TiO_2) were used for the photocatalytic degradation of bisphenol A (BPA). A great enhancement was noticed in the photocatalytic activity of the doped catalyst, especially at 1.0% Ag-TiO_2 when compared to the as-prepared TiO_2.

If one compares to the results obtained by Colmenares et al. [3], the results obtained by the Rengaraj and Li [87] method appear to be better; it provided almost 100% degradation of BPA in 2 h irradiation, while about 40% degradation of propan-2-ol was obtained in 5 h irradiation by Colmenares, though with different degrading substances and probably different concentrations. In this case, a final conclusion cannot be drawn since the works degraded different substances.

Some levels of improvements on the photocatalytic activity of TiO_2 have been noticed when it was doped with some transition metal ions, but with some, whether under UV light or visible light irradiation, however, doping TiO_2 with some of them is detrimental to, or has almost no enhancement on the photocatalytic activity of the catalyst. Precisely, from the results of the works presented in this paper, doping TiO_2 with any of Cr, Fe, Zr, Mo is detrimental to the photocatalytic activity of TiO_2. This observed trend leads to the question of why this is so. This could be as a result of the high electron density about the nucleus, resulting in repulsion of any further electrons trying to come into it. For instance, Cr has 6 available electrons and the same atomic radius of 140 pm as Ti; Fe has 8 available electrons and the same atomic radius as Ti; Zr is next to Ti in the same homologous series with atomic radius of 155 pm, Mo is next in the same homologous series to Cr and has atomic radius of 145 pm. The concentration of these electrons about the nucleus provides more shielding of other electrons from

the nucleus, and will therefore not permit a good interaction with Ti, but rather will set repulsive forces. A very minute enhancement (about 9.68% of the undoped TiO_2) was noticed at the optimum dopant level of 0.06 mol% $Cu-TiO_2$. This trend calls for a serious consideration of whether TiO_2 should be doped at all with Cu, as no distinct effect was noticed in its performance over the undoped TiO_2. Sol–gel method of doping TiO_2 with Zn has little or no influence on the photocatalytic activity of TiO_2, but a great deal of improvement was achieved by solid phase reaction doping of TiO_2 by Zn. Again, when TiO_2 is doped with Zn, with addition of surfactant, improvement is expected in the photocatalytic performance of TiO_2. On the other hand, Pt and WO_x proved to be beneficial to the improvement of TiO_2 photocatalytic activity.

2.3. Rare earth (RE) metal doping of TiO_2

Rare earth (La^{3+}, Ce^{3+}, Er^{3+}, Pr^{3+}, Gd^{3+}, Nd^{3+}, Sm^{3+})/TiO_2 photocatalysts have been prepared by Xu et al. [71]. In the molar ratio $Ti(OBu)_4$:C_2H_5OH:H_2O:HNO_3 = 1:20:6:0.8, 12.5 ml $Ti(OBu)_4$ (C.P.) was dissolved in 33.3 ml ethanol with stirring for 10 min; then 0.25 ml HNO_3 was added dropwise to the above solution under stirring for 30 min. Another solution containing 16.7 ml ethanol, 1.5 ml H_2O, and rare earth metal salts ($La(NO_3)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, $Er(NO_3)_3 \cdot 5H_2O$, $Pr(NO_3)_3 \cdot 5H_2O$, $Gd(NO_3)_3 \cdot 5H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$, and $Sm(NO_3)_3 \cdot 5H_2O$) in the required stoichiometry was slowly added into the above solution; the mixture was hydrolyzed at room temperature for 40 min under vigorous stirring and finally the transparent sol was obtained. The gel was prepared by aging the sol for 48 h at room temperature. The derived gel was dried at 100 °C for 24 h to remove the solvents and then fired in air at 500 °C for 3 h and milled into powders for use. Pure TiO_2 was prepared in the same way.

The evaluation of the photocatalytic activity of the prepared catalysts was carried out on the degradation of nitrite (NO_2^-) under UV light irradiation. The results showed that all the doped photocatalysts performed better than the undoped TiO_2. Nevertheless, Degussa P25 had a better photocatalytic performance than all the doped catalysts during the first 35 min irradiation, thereafter; TiO_2-doped with 1.0% and 0.5% Gd^{3+} out performed the P25, the best being 0.5% Gd^{3+} at 60 min irradiation. From the results obtained with the other RE, except for Gd^{3+} at 60 min irradiation, it is clear that the performance of P25 was better than theirs. Rather, the disappearance of NO_2^- was independent of NO_2^- concentration, indicating a zero order kinetic dependence for all the RE except for Gd^{3+}. This behaviour was explained on the basis of a high electron-hole recombination rate which was facilitated by the considered metal ions.

Saif and Abdel-Mottaleb [74] also prepared TiO_2 doped with lanthanide ions of Tb, Eu and Sm, and studied their performance on the photocatalytic degradation of Remazol Red RB-133 (RR RB-133) dye under UV–vis light irradiation. TTIP (8.5 ml) was dissolved in 40 ml absolute ethanol and the TTIP solution was added dropwise under vigorous stirring into 57 ml of a mixture solution containing 41.5 ml of 95% ethanol, 0.5 ml of 0.1 M Ln(III)($Tb(NO_3)_3(6H_2O)$ or $EuCl_3(6H_2O)$ or $SmCl_3$) and 15 ml of acetic acid. The resulting transparent colloidal suspension was stirred for 2 h and aged for 2 days until the formation of gel. The gel was dried at 80 °C and then ground. The powder was calcined at 500 °C for 3 h and eventually the Ln(III)-TiO_2 nanocrystals were obtained in a nominal atomic doping level of 0.2% abbreviated as 0.2% Ln(III)-TiO_2. Other lanthanide ion-doped TiO_2 samples were prepared according to the above procedure with the dosage of 0.7%, 1.3% and 2.0%, respectively. In the meantime, pure TiO_2 was also prepared in the same way without doping.

The results of the photocatalytic degradation of RR RB-133 under UV–vis light irradiation by the TiO_2 doped with the Ln

Table 1
The conventional parameter characterization of photo-oxidation of Remazol Red RB-133 using undoped and doped TiO_2 [74].

Catalyst	k (/min) $\times 10^{-3} \pm$ error limit $\times 10^{-4}$	Coefficient of determination, R^2
Pure TiO_2	2.62 ± 2.70	0.984
0.2% Tb^{3+}-TiO_2	8.28 ± 12.4	0.958
0.7% Tb^{3+}-TiO_2	15.8 ± 24.2	0.961
1.3% Tb^{3+}-TiO_2	12.8 ± 19.7	0.966
2.0% Tb^{3+}-TiO_2	3.76 ± 2.06	0.995
0.2% Eu^{3+}-TiO_2	20.4 ± 36.0	0.956
0.7% Eu^{3+}-TiO_2	22.4 ± 35.1	0.965
1.3% Eu^{3+}-TiO_2	23.2 ± 31.6	0.973
2.0% Eu^{3+}-TiO_2	15.3 ± 24.5	0.963
0.2% Sm^{3+}-TiO_2	4.26 ± 3.66	0.981
0.7% Sm^{3+}-TiO_2	14.6 ± 24.4	0.966
1.3% Sm^{3+}-TiO_2	10.5 ± 10.1	0.972
2.0% Sm^{3+}-TiO_2	5.54 ± 8.29	0.975

showed that all the doped samples had faster rates of degradation than the undoped TiO_2. The summary of results is given in Table 1. The results obtained here are consistent with the report of Xu et al. [71] that all the doped rare earths used in their study performed better than the undoped TiO_2. Nevertheless, Saif and Abdel-Mottaleb [74] did not validate their results with Degussa P25 to really evaluate whether the TiO_2-doped Ln had better performance than the Degussa P25. However, at present, among all the rare-earth metal ions doping TiO_2, Gd^{3+} appears to be more effective than Degussa P25 at 60 min irradiation under UV light in the photocatalytic degradation of NO_2^-. Though Degussa P25 performed better than rare earth (La^{3+}, Ce^{3+}, Er^{3+}, Pr^{3+}, Gd^{3+}, Nd^{3+}, Sm^{3+}) doped TiO_2, more investigations should be carried out to obtain an optimum operating condition which will give a better degradation than Degussa P25, since all the doped samples performed better than the undoped ones.

2.4. Doping TiO_2 with alkaline earth metal

The effect of doping TiO_2 with alkaline earth metal ions on its photocatalytic activity had been studied [83]. Undoped TiO_2 was prepared by dissolving 5 ml $Ti(OBu)_4$ in 20 ml ethanol under stirring and then 0.5 ml HNO_3 solution ($VHNO_3$:VH_2O = 1:1) and 1 ml H_2O were added dropwisely to the above solution. The mixture was vigorously stirred at room temperature for 30 min to obtain a transparent sol. The gel was obtained after aging the sol for 24 h at room temperature. Pure TiO_2 was prepared by drying the gel at 100 °C for 24 h and calcining it in air at 400 °C for 1 h.

The alkaline-earth metal ion doped-TiO_2 photocatalysts were prepared by two methods. For the co-precipitation synthesis of M^{2+}-TiO_2 photocatalysts (denoted as M^{2+}-CP-TiO_2; M = Be, Mg, Ca, Sr, Ba) the same procedure was adopted as for the pure TiO_2 except that an aqueous MCl_2(M = Be, Mg, Ca, Sr, Ba) solution was used instead of H_2O. For the impregnation synthesis of M^{2+}-TiO_2 photocatalysts (denoted as M^{2+}-IP-TiO_2, M = Be, Mg, Ca, Sr, Ba), the required amount of pure TiO_2 powder was added into a given concentration of MCl_2 (M = Be, Mg, Cr, Sr, Ba) solution. Each mixture was dispersed in an ultrasonic bath for 10 min. After impregnation for 1 h, the mixture was kept at 110 °C to remove water by evaporation. Except when studying the photocatalytic activity vs. calcination temperature and time, the samples were treated at 400 °C in air for 1 h.

The photocatalytic activity of the produced catalysts was studied on the production of hydrogen. Using the same irradiation time, and testing for varying doping (by impregnation) ion contents, at%, Be-TiO_2 at 1.25 at% turned out to produce the best result, followed by Ca-TiO_2 at 2.25 at%, then others. Comparing the results from the catalysts doped by co-precipitation method with

the results from the undoped TiO_2 for the production of H_2, it was found that the undoped TiO_2 performed better than those doped by the alkaline earth metal ions via co-precipitation. The results obtained showed that TiO_2 alkaline earth metal-doped by impregnation method enhances the efficiency of TiO_2 for the photocatalytic production of hydrogen under UV light irradiation, while co-precipitation reduces its activity.

2.5. Doping TiO_2 with other metals and non-metals ions

Boron and vanadium doped TiO_2 has been reported [24]. The description of the doping process is as follows: For the V-doped samples, 30.0 ml of ethanol, 0.8 ml of HCl, and 6.0 ml of $Ti(OBu)_4$ were mixed together under stirring. The vanadium alkoxide was added at different times: after 1 min, 5 min, 30 min, 1 h and the samples were denoted as TV1m, TV5m, TV30m, or TV1h, respectively. The solvent was evaporated at 60 °C until the xerogels were formed. The xerogels were annealed in air at 500 °C for 5 h and yellow-brown powders were obtained. In all cases, the nominal molar ratio between titanium and vanadium was 99:1. For the sake of comparison, an undoped titania sample, labeled as $TiO_2(I)$, was also prepared using the same procedure.

For B-doped samples, 17.0 g of $Ti(OBu)_4$ were dissolved at 25 °C in 40.0 ml of anhydrous ethanol under argon atmosphere to form the solution 1. Meanwhile, 3.0 ml of concentrated HNO_3 were mixed with 35.0 ml of anhydrous ethanol and 15.0 ml of water to prepare the solution 2. Then solution 1 was added dropwisely into solution 2, under argon atmosphere, within 20 min under vigorous stirring. Appropriate amounts of H_3BO_3 were dissolved in 10.0 ml of bi-distilled water, and rapidly added dropwisely to the resulting solution. Each solution was continuously stirred for 30–60 min until the formation of TiO_2 gel. After aging for at least 24 h at room temperature, the as-prepared TiO_2 gel was dried at 120 °C for 12 h. The obtained solid was ground and annealed at 450 °C for 6 h with a heating rate of 3 °C/min.

In the V-doped TiO_2, differences were noticed in the doping mode, and this was reflected in the doping timing. The results indicated that the sample of TiO_2 which was doped with vanadium (VI) 1 min after $Ti(OBu)_4$ was poured into the reactor showed a little better enhancement than the undoped TiO_2 for the photodegradation of methylene blue, MB under a 450 W medium pressure mercury lamp (model 7825-34, ACE GLASS Inc., USA) irradiation. About 55% degradation was obtained for the VI as against 50% degradation by the undoped TiO_2 in 4 h irradiation. All others had activities less than that of the undoped TiO_2. On the other hand, B-TiO_2 appeared to generally enhance the TiO_2 photocatalytic degradation of MB, except for 2 mol% B-TiO_2. Nine mol% B-doped TiO_2 had a faster rate of degradation than the 18 mol% B-TiO_2 for the first 3 h, but all ended up at the same point at 4 h irradiation. Distinct enhancement in the performance of TiO_2 was observed here; the optimum dopant content should be fixed at about 9 mol% B.

Yu et al. [125] prepared N-doped TiO_2 catalysts and tested the catalysts' performance on photocatalytic degradation of MB under UV light irradiation and of 4-chlorophenol under visible light irradiation. The method employed for the preparation of the N-doped TiO_2 catalysts was completely different from that used by Gombac et al. [76]. In the case of Yu et al. [125], tetra-butyl titanate was dissolved in 95 ml anhydrous alcohol. Into the solution of $Ti(OBu)_4$, was added 5 ml NH_4Cl (1 mol/l) dropwisely under stirring to carry out hydrolysis. The pH of the solution with NH_4Cl was controlled at a certain value. The gel was left for aging for one day at room temperature and subsequently dried at 70 °C for several hours. Finally, the dried material was calcined at different temperatures to obtain N-doped TiO_2 nanoparticle catalyst with different doping level of nitrogen. The results showed that the

doped photocatalysts prepared at pH 3.0 and calcined at 500 °C exhibited the highest ability for the degradation of MB under UV irradiation with about 97% degradation at 100 min irradiation. Only about 63% degradation of 4-chlorophenol under 6 h visible light irradiation was noticed. Although degraded substances were not used in the visible light and the UV light irradiation, the results appears to favour UV light irradiation of N-doped TiO_2 prepared by this method.

Zaleska et al. [78] reported on the preparation and photocatalytic activity of B-modified TiO_2 under UV and visible light irradiations. Two methods were adopted in the preparation of the catalysts; one was the sol–gel method and the second was a modification of the TiO_2 prepared by the sol–gel and TiO_2 (ST-01) obtained from Ishihara Sangyo, Japan. The complete process description is as follows: In the sol–gel method, B-doped TiO_2 catalysts were prepared as follows: A sample of 10 cm^3 of titanium (IV) isopropoxide solution in isopropanol (3.74 ml) was mixed with 0.073 g or 1.46 g of boric acid (0.5 or 10%B) or with 0.2, 0.4, 1, and 2 ml of boric acid triethyl ester (0.5, 1, 5 or 10%B), 2.35 ml of deionized water were added dropwisely into each solution. The solution was stirred for 1 h and subsequently kept at room temperature for 2 weeks until white powder was obtained. The resulting powders were dried for 96 h at 80 °C and then calcined at 450 °C for 1 h at a heating rate of 15 °C/min.

In the second procedure boron-modified TiO_2 powders were prepared by grinding 3 g of ST-01 in an agate mortar with 0.084 g or 1.69 g of boric acid and 0.23 ml or 4.7 ml of boric acid triethyl ester, respectively. Obtained powders were dried for 24 h at 80 °C and calcined at 450 °C. The resulting powders were labeled as B-E for boric acid triethyl ester and B-A for boric acid as boron precursors.

The activity of the prepared B-TiO_2 catalysts was evaluated by the photocatalytic degradation of phenol under UV and visible light irradiation. Under UV light irradiation, all powders prepared by sol–gel with boric acid triethyl ester exhibited lower photocatalytic activity than the undoped TiO_2, prepared by sol–gel, while both photocatalysts prepared by grinding with boric acid triethyl ester revealed similar photoactivity with respect to the pure TiO_2 ST-01. These results suggest that doping of B atoms into TiO_2 particles does not improve the photocatalytic activity of TiO_2 for the oxidation of phenol under UV light irradiation. All photocatalysts prepared by hydrolysis of TIP in the presence of boric acid triethyl ester revealed the same photoactivity under visible light comparable to that of pure TiO_2. Better photoactivity under visible light was observed only for B-TiO_2 prepared by grinding of ST-01 with boric acid triethyl ester. 62% and 46% degradation of phenol were attained after 60 min irradiation with 0.5 wt% and 10 wt% B-TiO_2, respectively. Comparing the best results obtained with the 0.5 wt% B-TiO_2 (62% degradation) under visible light irradiation in 60 min with the prepared undoped TiO_2 (about 80% degradation) under UV light irradiation in 60 min, it is clear that the doping of TiO_2 with B via the method used here only succeeded in pushing the reaction from UV-region to the visible region, but did not provide a better degradation alternative to the undoped TiO_2.

Rengaraj and Li [87] and Rengaraj and Li [86] prepared Bi^{3+}-doped TiO_2 and studied the photocatalytic activity of the prepared catalysts by the photodegradation of methylparathion and photocatalytic reduction of nitrate, respectively. In the two cases, the same procedure as described below was used for the preparation of the photocatalysts. The Bi^{3+}-doped TiO_2 samples were prepared by sol–gel method, in which 21 ml of $Ti(O-Bu)_4$ was dissolved in 80 ml of absolute ethanol, and the resulting solution was stirred vigorously. Then 2 ml of water and 0.5 ml of acetic acid (50%) were added to another 80 ml of ethanol to make an ethanol–water–acetic acid solution. The latter solution was slowly added to the $Ti(O-Bu)_4$-ethanol solution under vigorous

Table 2
The composition of starting solutions and experimental conditions for undoped and S-doped sol–gel TiO_2 films preparation [4].

Sample	The composition of solution	Molar ratio
Un-doped TiO_2 Titanium source: $Ti(OC_2H_5)_4$	$[C_2H_5OH]:[Ti(OC_2H_5)_4]$	55
	$[H_2O]:[Ti(OC_2H_5)_4]$	1.5
	$[HNO_3]:[Ti(OC_2H_5)_4]$	0.258 (pH 3.5)
	Gelling time (h)	216
S-doped TiO_2 sulfur source: thiourea (H_2NCSNH_2) $S^{2-} = 2$ wt%	$[C_2H_5OH]:[Ti(OC_2H_5)_4]$	55
	$[H_2O]:[Ti(OC_2H_5)_4]$	1.5
	$[HNO_3]:[Ti(OC_2H_5)_4]$	0.212 (pH 3)
	$[S^{2-}]:[Ti(OC_2H_5)_4]$	0.051
	Gelling time (h)	228
Sulfur source: thiourea (H_2NCSNH_2) $S^{2-} = 5$ wt%	$[C_2H_5OH]:[Ti(OC_2H_5)_4]$	55
	$[H_2O]:[Ti(OC_2H_5)_4]$	1.5
	$[HNO_3]:[Ti(OC_2H_5)_4]$	0.212 (pH 3)
	$[S^{2-}]:[Ti(OC_2H_5)_4]$	0.128
	Gelling time (h)	216
Experimental conditions		
Reaction time (min)/reaction temperature (°C)		60/50
Withdrawal speed (cm/min)/withdrawal temperature (°C)		5/20
Number of coatings		1; 2
Thermal treatment of the film		
Temperature (°C)/time (h)		300, 400, 500/1 with a heating rate of 1 °C/min

stirring. When the resulting mixture turned into a sol, the bismuth nitrate solution was added drop-by-drop. The resulting transparent colloidal suspension was stirred for 1 h and then aged for 2d until the formation of a gel. The gel was dried at 70 °C in vacuum and then ground. The resulting powder was calcined at 500 °C for 4 h. A TiO_2 sample was also prepared by the above same procedure without the addition of the bismuth nitrate solution, and this is subsequently referred to as *neat* TiO_2. The doping concentrations of Bi^{3+} are expressed as wt%.

The results of the degradation of methylparathion under UV-A irradiation demonstrated that methylparathion was degraded by more than 95% within 120 min by all the catalysts, including undoped TiO_2. However, the $Bi-TiO_2$ catalysts attained faster degradation rates than the undoped TiO_2. For example, the experiment using 1.5% $Bi-TiO_2$ achieved a complete degradation of methylparathion at 90 min. In the case of nitrate reduction, formic acid, as hole-scavenger was added to all the reaction mixtures, and varying doping contents were considered to understudy their effects on the reduction of nitrate. The results revealed that, at about 60 min reaction time, all the doped catalysts performed better than the undoped TiO_2 for the photocatalytic reduction of nitrate under UV light irradiation, the best being 1.5% $Bi-TiO_2$ which had 83% reduction of nitrate compared to about 45% by the undoped TiO_2. If one compares the results obtained in the two cases; methylparathion degradation and nitrate reduction by $Bi-TiO_2$, the likely optimum dopant level for $Bi-TiO_2$ is 1.5%.

Crisan et al. [4] prepared S-doped TiO_2 by sol–gel method. The experimental details are presented in Table 2. The doped materials were obtained by simultaneous gelation of both precursors in the sol–gel process. The hydrolysis reaction was carried out in a closed system in nitrogen atmosphere under vigorous stirring. Supported TiO_2 based vitreous films were obtained by dip coating on microscopic slide substrates. The un-supported porous materials resulted from the gelling of the starting solutions at room temperature were dried at 80 °C and then thermally treated at 300, 400, 500 °C/h according to DTA/TGA results. The densification of the films was realized at the same temperatures. The second layer was deposited after the densification of the first one at 300 °C.

The photocatalytic performances of the films prepared by this method were tested by the photocatalytic removal of chlorobenzene from water at neutral pH under UV light irradiation (the results are presented in Table 3). From these results, though the highest efficiency of the removal of chlorobenzene was noticed with TiO_2 doped with 2%S in all cases, the difference between it and the undoped TiO_2 is minimal. Therefore, under this condition, considering the financial implications that may be involved in doping TiO_2 with 2%S and having double layers coating, and obtaining a difference of 4% only, it may not actually be economical to embark on such a process.

Most of the other metals and non-metals ions-doped TiO_2 showed enhanced activity of TiO_2 photocatalyst in some degradation reactions, some did not. Though Zaleska et al. [78] reported a lower activity of $B-TiO_2$ than the undoped TiO_2, most reports showed that $B-TiO_2$ has higher photocatalytic activity than the undoped TiO_2. The lower efficiency of $B-TiO_2$ reported by Zaleska et al. [78] will not be dissociated from the method used in the preparation of the catalyst. The boric acid triethyl ester added might have contributed to this negative effect on the catalyst. It must be noted here that, though a majority of the other metals and non-metals ions

Table 3
Chlorobenzene removal from water by photodegradation in UV/TiO_2 system at pH 7 [4].

Photocatalyst type	Number of layers	Irradiation time (h)	Remanent chlorobenzene (mg/l)	Chlorobenzene removal yield (%)
TiO_2	1	0.5	2.7	75
$TiO_2 + 2\%S$			2.37	78
$TiO_2 + 5\%S$			2.48	77
TiO_2		1	1.19	89
$TiO_2 + 2\%S$			0.62	94.3
$TiO_2 + 5\%S$			0.76	93
TiO_2	2	0.5	2.59	76
$TiO_2 + 2\%S$			1.95	82
$TiO_2 + 5\%S$			2.32	78.5
TiO_2		1	0.76	93
$TiO_2 + 2\%S$			0.32	97
$TiO_2 + 5\%S$			0.49	95.5

doped TiO$_2$ enhanced the photocatalytic activity of TiO$_2$, an increase in the activity of TiO$_2$ was noticed with S-doped TiO$_2$.

3. Conclusion

Various sol–gel and sol–gel related systems of doping TiO$_2$ (codoping, transition metal ions, rare earth metal ions, alkaline earth metal ions, other metal and non-metal ions) were investigated. From the results available, it can be concluded that co-doping of TiO$_2$ generally enhances the photocatalytic efficiency of the catalyst. On the contrary, doping TiO$_2$ with transition metals is detrimental to the photocatalytic efficiency of the catalyst, except in some very few cases. Doping TiO$_2$ with alkaline earth metals by impregnation method provided added efficiency to the TiO$_2$ for the photocatalytic generation of hydrogen; the results were better than those for TiO$_2$ doped with alkaline earth metals by co-precipitation. Degussa P25 performed better than any rare earth metal (RE)-doped TiO$_2$ in the first 35 min of the photocatalytic degradation of nitrite under UV light irradiation, but Gd^{3+}-TiO$_2$ became better than P25 after 35 min of reaction. Addition of surfactants is found to enhance the photocatalytic activity of doped TiO$_2$. Therefore, caution must be exercised in the choice of ions considered for doping of TiO$_2$ if an enhancement is expected in its performance.

Acknowledgement

References

[1] P. Babelon, A.S. Dequiedt, H. Mostefa-Sba, S. Bourgeois, P. Sibillot, M. Sacilotti, Thin Solid Films 322 (1998) 63–67.
[2] H.M. Pathan, S.-K. Min, J.D. Desai, K.-D. Jung, O.-S. Joo, Mater. Chem. Phys. 97 (2006) 5–9.
[3] J.C. Colmenares, M.A. Aramendia, A. Marinas, J.M. Marinas, F.J. Urbano, Appl. Catal. A: Gen. 306 (2006) 120–127.
[4] M. Crisan, A. Braileanu, M. Raileanu, M. Zaharescu, D. Crisan, N. Dragan, M. Anastasescu, A. Ianculescu, I. Nitoi, V.E. Marinescu, S.M. Hodorogea, J. Non-Cryst. Solids 354 (2008) 705–711.
[5] X. Ding, T. An, G. Li, S. Zhang, J. Chen, J. Yuan, H. Zhao, H. Chen, G. Sheng, J. Fu, J. Colloid Interface Sci. 320 (2) (2008) 501–507.
[6] D. Dvoranova, V. Brezova, M. Mazur, M.A. Malati, Appl. Catal. B: Environ. 37 (2002) 91–105.
[7] X. Feng, Q. Wang, G. Wang, F. Qiu, Chin. J. Catal. 27 (3) (2006) 195–196.
[8] J.-E. Gu, B.-C. Yang, Y.-D. Hu, Catal. Commun. 9 (2008) 1472–1476.
[9] S. Inoue, A. Muto, H. Kudou, T. Ono, Appl. Catal. A: Gen. 269 (2004) 7–12.
[10] B.-H. Kim, J.-Y. Lee, Y.-H. Choa, M. Higuchi, N. Mizutani, Mater. Sci. Eng. B107 (2004) 289–294.
[11] A.-C. Lee, R.-H. Lin, C.-Y. Yang, M.-H. Lin, W.-Y. Wang, Mater. Chem. Phys. 109 (2–3) (2007) 275–280.
[12] D.L. Liao, C.A. Badour, B.Q. Liao, J. Photochem. Photobiol. A: Chem. 194 (1) (2008) 11–19.
[13] T. Miyata, S. Tsukada, T. Minami, Thin Solid Films 496 (2006) 136–140.
[14] J. Zhu, Z. Deng, F. Chen, J. Zhang, H. Chen, M. Anpo, J. Huang, L. Zhang, Appl. Catal. B: Environ. 62 (2006) 329–335.
[15] X. Zhang, Q. Liu, Mater. Lett. 62 (2008) 2589–2592.
[16] J. Sun, L. Qiao, S. Sun, G. Wang, J. Hazard. Mater. 155 (1–2) (2008) 312–319.
[17] A.-C. Lee, R.-H. Lin, C.-Y. Yang, M.-H. Lin, W.-Y. Wang, Mater. Chem. Phys. 109 (2008) 275–280.
[18] V. Stengl, S. Bakardjieva, N. Murafa, Mater. Chem. Phys. 114 (2009) 217–226.
[19] H.-L. Qin, G.-B. Gu, S. Liu, Mater. Chem. Phys. 112 (2008) 346–352.
[20] L. Mi, P. Xu, H. Shen, P.-N. Wang, J. Photochem. Photobiol. A: Chem. 193 (2008) 222–227.
[21] J. Zita, J. Krysa, A. Mills, J. Photochem. Photobiol. A: Chem. 203 (2009) 119–124.
[22] L. Andronic, A. Duta, Mater. Chem. Phys. 112 (2008) 1078–1082.
[23] Y. Yang, H. Wang, X. Li, C. Wang, Mater. Lett. 63 (2009) 331–333.
[24] S. Song, L. Xu, Z. He, H. Ying, J. Chen, X. Xiao, B. Yan, J. Hazard. Mater. 152 (3) (2008) 1301–1308.
[25] S. Erdemoglu, S.K. Aksu, F. Sayılkan, B. Izgi, M. Asilturk, H. Sayılkan, F. Frimmel, S. Guçer, J. Hazard. Mater. 155 (3) (2008) 469–476.
[26] S. Kaewgun, C.A. Nolph, B.I. Lee, L.-Q. Wang, Mater. Chem. Phys. 114 (2009) 439–445.
[27] R. Jain, M. Shrivastava, J. Hazard. Mater. 152 (1) (2008) 216–220.
[28] B. Mounir, M.N. Pons, O. Zahraa, A. Yaacoubi, A. Benhammou, J. Hazard. Mater. 148 (3) (2007) 513–520.
[29] X. Zhang, D.D. Sun, G. Li, Y. Wang, J. Photochem. Photobiol. A: Chem. 199 (2008) 311–315.
[30] M.M. Mohamed, I. Othman, R.M. Mohamed, J. Photochem. Photobiol. A: Chem. 191 (2007) 153–161.
[31] P. Pichat, Chemical Degradation Methods for Wastes and Pollutants: Environmental and Industrial Applications, Marcel Dekker Inc., N.Y., Basel, 2003 pp. 77–119.
[32] W. Song, W. Xiaohong, Q. Wei, J. Zhaohua, Electrochim. Acta 53 (2007) 1883–1889.
[33] X.H. Wu, Z.H. Jiang, H.L. Liu, X.D. Li, X.G. Hu, Mater. Chem. Phys. 80 (2003) 39–43.
[34] S. Karuppuchamy, N. Suzuki, S. Ito, T. Endo, Curr. Appl. Phys. 9 (1) (2009) 243–248.
[35] L. Fan, N. Ichikuni, S. Shimazu, T. Uematsu, Appl. Catal. A: Gen. 246 (2003) 87–95.
[36] J. Chen, J. Zhang, Y. Xian, X. Ying, M. Liu, L. Jin, Water Res. 39 (2005) 1340–1346.
[37] M. Takahashi, K. Tsukigi, T. Uchino, T. Yoko, Thin Solid Films 388 (2001) 231–236.
[38] K.D. Kim, H.T. Kim, Colloids Surf. A: Physicochem. Eng. Aspects 207 (2002) 263–269.
[39] Y. Shiroto, T. Ono, S. Asaoka, M. Nakamura, USP 4,422,960.
[40] C.-I. Wu, J.-W. Huang, Y.-L. Wen, S.-B. Wen, Y.-H. Shen, M.-Y. Yeh, Mater. Lett. 62 (2008) 1923–1926.
[41] K.R. Patil, S.D. Sathaye, Y.B. Khollam, S.B. Deshpande, N.R. Pawaskar, A.B. Mandale, Mater. Lett. 57 (2003) 1775–1780.
[42] F. Cheng, Z. Peng, C. Liao, Z. Xu, S. Gao, C. Yan, D. Wang, J. Wang, Solid State Commun. 107 (9) (1998) 471–476.
[43] S. Prasad, A. Vijayalakshmi, N.S. Gajbhiye, Therm. Anal. Calorim. 52 (1998) 595–607.
[44] N. Arimitsu, A. Nakajima, Y. Kameshima, Y. Shibayama, H. Ohsaki, K. Okada, Mater. Lett. 61 (2007) 2173–2177.
[45] X.M. Lin, C.N. Sorensen, K.J. Klabunde, G.C. Hadjipanayis, Langmuir 14 (25) (1998) 7140–7146.
[46] P. Kluson, H. Luskova, T. Cajthaml, O. Solcov, Thin Solid Films 495 (2006) 18–23.
[47] J. Sun, X. Wang, J. Sun, R. Sun, S. Sun, L. Qiao, J. Mol. Catal. A: Chem. 260 (2006) 241–246.
[48] Y. Li, G.P. Demopoulos, Hydrometallurgy 90 (2008) 26–33.
[49] J. Sun, L. Qiao, S. Sun, G. Wang, J. Hazard. Mater. 155 (2008) 312–319.
[50] T. Ohno, T. Akiyoshi, T. Umebayashi, K. Asai, T. Mitsui, M. Matsumura, Appl. Catal. A: Gen. 265 (2004) 115–121.
[51] W. Zhiyu, C. Haifeng, T. Peisong, M. Weiping, Z. Fuan, Q. Guodong, F. Xianping, Colloids Surf. A: Physicochem. Eng. Aspects 289 (2006) 207–211.
[52] F. Wang, Z. Shi, F. Gong, J. Jiu, M. Adachi, Chin. J. Chem. Eng. 15 (5) (2007) 754–759.
[53] F. Peng, L. Cai, L. Huang, H. Yu, H. Wang, J. Phys. Chem. Solids 69 (7) (2008) 1657–1664.
[54] X. Zhao, M. Liu, Y. Zhu, Thin Solid Films 515 (2007) 7127–7134.
[55] G. Li, L. Chen, N.M. Dimitrijevic, K.A. Gray, Chem. Phys. Lett. 451 (2008) 75–79.
[56] T.K. Ghorai, D. Dhak, S.K. Biswas, S. Dalai, P. Pramanik, J. Mol. Catal. A: Chem. 273 (2007) 224–229.
[57] X. Zhang, M. Zhou, L. Lei, Appl. Catal. A: Gen. 282 (2005) 285–293.
[58] X. Zhang, L. Lei, Mater. Lett. 62 (2008) 895–897.
[59] F. Peng, L. Cai, H. Yu, H. Wang, J. Yang, J. Solid State Chem. 181 (2008) 130–136.
[60] M.S. Jeon, W.S. Yoon, H. Joo, T.K. Lee, H. Lee, Appl. Surf. Sci. 165 (2000) 209–216.
[61] T. Horikawa, M. Katoh, T. Tomida, Micropor. Mesopor. Mater. 110 (2008) 397–404.
[62] M. Zhou, J. Yu, J. Hazard. Mater. 152 (2008) 1229–1236.
[63] W. Ren, Z. Ai, F. Jia, L. Zhang, X. Fan, Z. Zou, Appl. Catal. B: Environ. 69 (2007) 138–144.
[64] C. Shifu, C. Gengyu, Surf. Coat. Technol. 200 (2006) 3637–3643.
[65] J.-C. Xu, Y.-L. Shi, J.-E. Huang, B. Wang, H.-L. Li, J. Mol. Catal. A: Chem. 219 (2004) 351–355.
[66] G. Zhang, X. Ding, F. He, X. Yu, J. Zhou, Y. Hu, J. Xie, J. Phys. Chem. Solids 69 (5–6) (2008) 1102–1106.
[67] C. Liu, X. Tang, C. Mo, Z. Qiang, J. Solid State Chem. 181 (4) (2008) 913–919.
[68] M. Huang, C. Xu, Z. Wu, Y. Huang, J. Lin, J. Wu, Dyes Pigments 77 (2008) 327–334.
[69] F.B. Li, X.Z. Li, Chemosphere 48 (2002) 1103–1111.
[70] L.-C. Chen, C.-M. Huang, F.-R. Tsai, J. Mol. Catal. A: Chem. 265 (2007) 133–140.
[71] A.-W. Xu, Y. Gao, H.-Q. Liu, J. Catal. 207 (2002) 151–157.
[72] M. Stir, R. Nicula, E. Burkel, J. Eur. Ceram. Soc. 26 (2006) 1547–1553.
[73] S.S. Srinivasan, J. Wade, E.K. Stefanakos, Y. Goswami, J. Alloys Compd. 424 (2006) 322–326.
[74] M. Saif, M.S.A. Abdel-Mottaleb, Inorg. Chim. Acta 360 (2007) 2863–2874.
[75] F.B. Li, X.Z. Li, C.H. Ao, S.C. Lee, M.F. Hou, Chemosphere 59 (6) (2005) 787–800.
[76] V. Gombac, L.D. Rogatis, A. Gasparotto, G. Vicario, T. Montini, D. Barreca, G. Balducci, P. Fornasiero, E. Tondello, M. Graziani, Chem. Phys. 339 (2007) 111–123.
[77] X. Fan, X. Chen, S. Zhu, Z. Li, T. Yu, J. Ye, Z. Zou, J. Mol. Catal. A: Chem. 284 (2008) 155–160.
[78] A. Zaleska, J.W. Sobczak, E. Grabowska, J. Hupka, Appl. Catal. B: Environ. 78 (2008) 92–100.
[79] D.-G. Huang, S.-J. Liao, J.-M. Liu, Z. Dang, L. Petrik, J. Photochem. Photobiol. A: Chem. 184 (2006) 282–288.
[80] J.-W. Shi, J.-T. Zheng, Y. Hu, Y.-C. Zhao, Mater. Chem. Phys. 106 (2007) 247–249.
[81] G. Liu, X. Zhang, Y. Xu, X. Niu, L. Zheng, X. Ding, Chemosphere 59 (2005) 1367–1371.
[82] K. Wilke, H.D. Breuer, J. Photochem. Photobiol. A: Chem. 121 (1999) 49–53.

[83] Y. Li, S. Peng, F. Jiang, G. Lu, S. Li, J. Serb. Chem. Soc. 72 (4) (2007) 393–402.
[84] X.Z. Li, F.B. Li, C.L. Yang, W.K. Ge, J. Photochem. Photobiol. A: Chem. 141 (2001) 209–217.
[85] S. Rengaraj, X.Z. Li, P.A. Tanner, Z.F. Pan, G.K.H. Pang, J. Mol. Catal. A: Chem. 247 (2006) 36–43.
[86] S. Rengaraj, X.Z. Li, Chemosphere 66 (2007) 930–938.
[87] S. Rengaraj, X.Z. Li, Int. J. Environ. Pollut. 27 (1/2/3) (2006) 20–37.
[88] C. Su, B.-Y. Hong, C.-M. Tseng, Catal. Today 96 (2004) 119–126.
[89] D.L. Liao, B.Q. Liao, Int. J. Chem. Reactor Eng. 5 (A24) (2007) 1–17.
[90] S. Liu, J.-H. Yang, J.-H. Choy, J. Photochem. Photobiol. A: Chem. 179 (2006) 75–80.
[91] Y. Yang, X.-J. Li, J.-T. Chen, L.-Y. Wang, J. Photochem. Photobiol. A: Chem. 163 (2004) 517–522.
[92] C.J. Brinker, G.W. Scherer, Sol-gel Science: The Physics and Chemistry of Sol-gel Processing, Academic Press, Boston, MA, 1990.
[93] G. Oye, W.R. Glomm, T. Vralstad, S. Volden, H. Magnusson, M. Stocker, J. Sjoblom, Adv. Colloid. Interface Sci. 123–126 (2006) 17–32.
[94] L. Arnelao, D. Barreca, B. Moraru, J. Non-Crystal. Solids 316 (2–3) (2003) 364–371.
[95] M.A. Aegerter, Sol. Energy Mater. Sol. Cells 68 (3–4) (2001) 401–422.
[96] N. Carmona, E. Herrero, J. Llopis, M.A. Villegas, Sensors Actuators B 126 (2007) 455–460.
[97] G. Maduraiveeran, R. Ramaraj, Electrochem. Commun. 9 (8) (2007) 2051–2055.
[98] C.J. Brinker, N.K. Raman, M.N. Logan, R. Sehgal, R.A. Assink, D.W. Hua, T.L. Waed, J. Sol-gel Sci. Technol. 4 (2) (1995) 117–133.
[99] M. Pakizeh, M.R. Omidkhah, A. Zarringhalam, Int. J. Hydrogen Energy 32 (12) (2007) 1825–1836.
[100] S.H. Park, J.-S. Park, S.-D. Yim, S.-H. Park, Y.-M. Lee, C.-S. Kim, J. Power Sources 181 (2) (2008) 259–266.
[101] Y. Yang, P. Wang, Polymer 47 (8) (2006) 2683–2688.
[102] X.J. Li, Z.R. Zeng, S.Z. Gao, J. Chromatogr. A 1023 (1) (2004) 15–25.
[103] L. Yun, Anal. Chim. Acta 486 (1) (2003) 63–72.
[104] Z.R. Zeng, W.L. Qiu, Z.F. Huang, Anal. Chem. 73 (11) (2001) 2429.
[105] P.C.A. Jeronimo, A.N. Araujo, M. Conceica, B.S.M. Montenegro, Talanta 72 (2007) 13–27.
[106] M. Volkan, D.L. Stokes, T. Vo-Dinh, Sensors Actuators B: Chem. 106 (2) (2005) 660–667.
[107] B. Dunn, G.C. Farrington, B. Katz, Solid State Ionics 70–71 (1994) 3–10.
[108] S. Skaarup, K. West, B. Zachau-Christiansen, M. Popal, J. Kappel, J. Kron, G. Eichinger, G. Semrau, Electrochim. Acta 43 (10–11) (1998) 1589–1592.
[109] A.R. Phani, M. Passacantando, S. Santucci, J. Non-Crystal. Solids 353 (5–7) (2007) 663–669.
[110] S. Bu, Z. Jin, X. Liu, T. Yin, Z. Cheng, J. Mater. Sci. 41 (7) (2006) 2067–2073.
[111] R. Campostrini, M. Ischia, L. Palmisano, J. Therm. Anal. Calorim. 71 (3) (2003) 997–1009.
[112] R. Campostrini, M. Ischia, L. Palmisano, Therm. Anal. Calorim. 71 (3) (2003) 1011–1021.
[113] R. Campostrini, M. Ischia, L. Palmisano, J. Therm. Anal. Calorim. 75 (3) (2004) 13–24.
[114] R. Campostrini, M. Ischia, L. Palmisano, J. Therm. Anal. Calorim. 75 (1) (2004) 25–34.
[115] Y. Li, T.J. White, S.H. Lim, J. Solid State Chem. 177 (4–5) (2004) 1372–1381.
[116] A. Peng, E. Xie, C. Jia, R. Jiang, H. Lin, Mater. Lett. 59 (29–30) (2005) 3866–3869.
[117] S. Sivakumar, P.P. Krishna, P. Makundan, K.G.K. Warrier, Mater. Lett. 57 (2) (2002) 330–335.
[118] S.S. Watson, D. Beydoun, J.A. Scott, R. Amal, Chem. Eng. J. 95 (1) (2003) 213–220.
[119] W. Xu, W. Hu, M. Li, C. Wen, Mater. Lett. 60 (13–14) (2006) 1575–1578.
[120] F. Han, V.S.R. Kambala, M. Srinivasan, D. Rajarathnam, R. Naidu, Appl. Catal. A: Gen. 359 (2009) 25–40.
[121] C.-H. Wei, X.-H. Tang, J.-R. Liang, S.-Y. Tan, J. Environ. Sci. 19 (2007) 90–96.
[122] W. Zhao, W.H. Ma, C.C. Chen, J. Am. Chem. Soc. 126 (15) (2004) 4782–4783.
[123] B. Xin, P. Wang, D. Ding, J. Liu, Z. Ren, H. Fu, Appl. Surf. Sci. 254 (2008) 2569–2574.
[124] Y. Ma, X.-T. Zhang, Z.-S. Guan, Y.-A. Cao, J.-N. Yao, J. Mater. Res. 16 (10) (2001) 2928–2933.
[125] H. Yu, X. Zheng, Z. Yin, F. Tao, B. Fang, K. Hou, Chin. J. Chem. Eng. 15 (6) (2007) 802–807.