Research Article

Probing Photocatalytic Characteristics of Sb-Doped TiO₂ under Visible Light Irradiation

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Received 25 November 2013; Accepted 17 February 2014; Published 6 April 2014

Academic Editor: Necdet Aslan

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Sb-doped TiO₂ nanoparticle with varied dopant concentrations was synthesized using titanium tetrachloride (TiCl₄) and antimony chloride (SbCl₃) as the precursors. The properties of Sb-doped TiO₂ nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), fluorescence spectrophotometer, and Uv-vis spectrophotometer. The absorption edge of TiO₂ nanoparticles could be extended to visible region after doping with antimony, in contrast to the UV absorption of pure TiO₂. The results showed that the photocatalytic activity of Sb-doped TiO₂ nanoparticles was much more active than pure TiO₂. The 0.1% Sb-doped TiO₂ nanoparticles demonstrated the best photocatalytic activity which was better than that of the Degussa P25 under visible light irradiation using terephthalic acid as fluorescent probe. The effects of Sb dopant on the photocatalytic activity and the involved mechanism were extensively investigated in this work as well.

1. Introduction

In the past decade, TiO₂ has become a hot spot of research due to its outstanding photoelectric properties, high chemical stability, low cost, and nontoxicity and can be widely applied on photons device [1], photocatalysis [2], sensor [3], and so forth. Although TiO₂ has many excellent properties, the application is limited due to a relatively wide band gap (3.2 eV for the anatase) and the quick recombination of electron-hole pairs in TiO₂ taking place on a time scale of 10⁻⁹–10⁻¹² s [4]. Therefore, several methods have been attempted to enhance its photocatalytic activity, such as modifying TiO₂ with metals [5–7], nonmetals [8–10], or other semiconductors [11, 12]. In addition, the wide band gap limits the absorption of catalysts to UV light only. It has been reported that the spectral response of TiO₂ photocatalysts can be extended to visible light region through the doping with other elements in order to make a donor or an acceptor level [13, 14] in the forbidden band of TiO₂. The doping level can either capture excited electrons of TiO₂ from valence band or make electrons jump to the conduction band of TiO₂. As a result, the long wave photons can be absorbed and the scope of absorption spectra region is extended to lower

energy [15]. Previously, TiO₂ has been doped with a variety of elements, such as N [16], Fe [17], La [18], and so forth. The effect of Sb element on photocatalytic activity under visible light irradiation has also been studied by several research groups, showing high visible light absorption with UV-vis absorption spectrum measurements [19]. Although catalytic properties of Sb-doped TiO₂ have been found more effective, the photocatalytic mechanisms under visible light are not definitively clarified or elaborated.

In order to further study the catalytic properties of doped TiO₂ under visible light and the contribution of different free radicals in the catalytic reaction. In this work, pure and 0.1%–5% Sb-doped TiO₂ photocatalysts were prepared by coprecipitation method from TiCl₄ and SbCl₃. Moreover, the influence of Sb dopant on the structure of TiO₂, the photoabsorption properties, and catalytic activity of these samples were studied systematically. Sb doping not only expands the absorption spectra of catalysts from UV light to visible light but also improves the catalytic activity of photocatalysts. The obtained results indicate that the catalytic activity of Sb-doped TiO₂ is better than Degussa P25 which absorbs the UV light only [20]. Furthermore, because hydroxyl radicals (OH[•]) and superoxide anion radical (O^{2-•})

can be generated on the surface of pure and Sb-doped TiO_2 under visible light irradiation ($>420\text{ nm}$), the terephthalic acid was employed as the fluorescent probe to evaluate the photocatalytic activity of catalyst [21]. For the understanding of the role of two kinds of free radicals in the catalytic process and the catalytic mechanism involved, scavengers of DMSO and p-benzoquinone are used to eliminate hydroxyl radicals ($\text{OH}^\bullet$) and superoxide anion radical ($\text{O}_2^{\bullet-}$), respectively.

2. Experimental

2.1. Materials and Catalyst Preparation. All reagents used in the experiments were purchased from commercial sources as received, including titanium tetrachloride (TiCl_4 , AR), dimethyl sulfoxide [$(\text{CH}_3)_2\text{SO}$, AR], n-butyl alcohol [$\text{CH}_3(\text{CH}_2)_3\text{OH}$, AR], and p-benzoquinone ($\text{C}_6\text{H}_4\text{O}_2$, CP). The distilled water from Milli-Q system was used in the preparation of materials.

Pure and 0.1%~5% Sb-doped TiO_2 nanoparticles were synthesized by coprecipitation method according to the literature [19], in which the TiCl_4 dissolved in diluted HCl with deionized water and the obtained mixture solution was named Solution A. Dissolving SbCl_3 in HNO_3 at a doping level ranging from 0.1% to 5% nominal atomic against TiCl_4 , we obtained Solution B. Vigorously stirring Solution B until it is completely dissolved and then adding Solution B to Solution A under vigorous stirring at room temperature, titanium hydrous gels were precipitated upon neutralization with NH_4OH at $\text{pH} \sim 8$. The resulting precipitates were repeatedly washed to remove undesirable anions such as Cl^- . The coprecipitated wet gels were treated in a butanol at 100°C for 2 h, followed by drying at 120°C for 10 h. The dried precipitates were calcined at 500°C in air to maintain the anatase phase of TiO_2 and milled with agate mortar in ethanol for 30 min.

2.2. Characterization of Catalyst. X-ray diffraction (XRD, DX-2700) patterns collected from 10° to 80° in 2θ with 0.02° steps/s were used to identify average crystallite sizes and crystallinity of the nanoparticles using a powder X-ray diffractometer ($\lambda = 0.154056\text{ nm}$) with Cu $\text{K}\alpha_1$ radiation from the monochromatized X-ray beam at 40 kV and 40 mA. The optical absorption spectra were measured using a UV-vis spectrophotometer (Shimadzu, UV-2500) equipped with an integrating sphere, a referenced against the compressed BaSO_4 powders. Particle morphologies of samples were examined by scanning electron microscopy (SEM, JSM 6301F) at 15 kV. The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) of the samples was determined by nitrogen adsorption/desorption isotherm measurements at 77 K (ASAP 2010). The fluorescence emission spectrum was recorded at room temperature with excitation at 320 nm on a fluorescence spectrophotometer (Hitachi, F-4500).

2.3. Photocatalytic Activity Test. The fluorescence probe sensitive to the free radicals was applied to detect the photocatalytic activity of pure and 0.1%~5% Sb-doped TiO_2 nanoparticles. Terephthalic acid as the fluorescent probe can readily react with hydroxyl radicals ($\text{OH}^\bullet$) and superoxide anion

SCHEME 1: Reactions of hydroxyl and superoxide anion radicals with terephthalic acid to form the 2-HTA or 4-HBA.

radical ($\text{O}_2^{\bullet-}$) to produce highly fluorescent products [22]. As shown in Scheme 1, the main products of terephthalic acid are 2-hydroxyterephthalic acid (2-HTA) or hydroxybenzoic acid (4-HBA), and only 2-HTA is highly fluorescent and thus can be easily determined by fluorescence spectroscopy [22, 23].

Photoreactivity experiments: 5 mg photocatalysts of P25 TiO_2 ; pure TiO_2 ; and 0.1%, 0.5%, 1%, and 5% Sb-doped TiO_2 were suspended in 20 mL aqueous solution containing 0.01 M NaOH ($\text{pH} \sim 11.5$) and 500 μM terephthalic acid, respectively. Before exposure to visible light, the suspension was stirred in the dark for 30 min. 3 mL of the solution was then taken out after irradiation for 20 min and centrifuged for fluorescence spectroscopy measurement. The emission intensity of the 2-HTA was monitored with the excitation at 320 nm. The photoreactivity in visible region was investigated with the irradiation of light source ($\lambda > 420\text{ nm}$) obtained by the cut-off filter at 420 nm from a 500 W Xe lamp.

To study the reactivity of $\text{OH}^\bullet$ radicals formed from trapped holes solely, p-benzoquinone (0.05 mM) was used to quench $\text{O}_2^{\bullet-}$ radicals. Similarly, for the study of $\text{O}_2^{\bullet-}$ anion radicals, dimethyl sulfoxide (DMSO) (1 mM) was used to quench $\text{OH}^\bullet$ radicals formed on the Sb-doped TiO_2 surface. Scavenger of DMSO can react with $\text{OH}^\bullet$ to generate methyl sulfinic acid (CH_3SOOH) and methyl radical ($\text{CH}_3^\bullet$) [24]. Detailed methods were performed as follows: 5 mg P25 TiO_2 ; pure TiO_2 ; and 0.1%, 0.5%, 1%, and 5% Sb-doped TiO_2 were suspended in 20 mL aqueous solution containing 0.01 M NaOH, 500 μM terephthalic acid, and (1) without scavenger, (2) 1 mM DMSO, (3) 0.01 mM p-benzoquinone, respectively. Measurement method of fluorescence spectrum is the same as photoreactivity experiments except that the irradiation time is 10 min.

In this way, we were thus able to study separately the reactivity of two radicals $\text{h}^+/\text{OH}^\bullet$ and $\text{e}^-/\text{O}_2^{\bullet-}$ on the surface of Sb-doped TiO_2 by observing the fluorescent spectra of products.

3. Results and Discussion

For pure TiO_2 , the absorption edge is in UV region and the bandgap is around 3.2 eV. With the Sb doping, new dopant level was formed in the forbidden band of TiO_2 (Figure 1). When TiO_2 is exposed to light of energy greater

FIGURE 1: The generation of photogenerated electron-hole pairs and the formation process of two kinds of radicals on the surface of Sb-doped TiO_2 catalyst.

than the bandgap energy, electrons are excited from its valence band into the conduction band to form spatially separated electron-hole (e^-/h^+) pairs by light absorption. The photogenerated charge carriers can be transferred to the surface of the catalyst and react with electron donors or acceptors adsorbed on the surface of the photocatalyst to generate reactive oxygen species such as $\text{OH}^\bullet$ and $\text{O}_2^{\bullet-}$. As shown in Figure 1, in an aqueous environment, the photogenerated electrons are trapped by adsorbed oxygen to generate radicals ($\text{O}_2^{\bullet-}$), and photogenerated holes are trapped by adsorbed water or hydroxyl bound superoxide anion (OH^-) to generate bound hydroxyl radicals ($\text{OH}^\bullet$) [25].

Figure 2(A) shows the UV-vis absorption spectra of pure and 0.1%~5% Sb-doped TiO_2 prepared by coprecipitation method. The pure TiO_2 had strong absorption only in the UV region corresponding to its band gap energy, while Sb-doped TiO_2 exhibited a new absorption band in the short wavelength region of visible light. The visible light absorption was enhanced by the dopant of pure TiO_2 and increased with Sb dopant. The color of the prepared catalysts changed from yellowish-white to yellow with the increasing dopant concentration of Sb.

Figure 2(B) shows X-ray diffraction patterns of TiO_2 with different Sb doping concentration; the anatase is the crystal phase of samples prepared by coprecipitation method. The average crystallite sizes of TiO_2 can be estimated from XRD spectra by using the Scherrer equation [26]:

$$D = \frac{k\lambda}{\beta \cos \theta}, \quad (1)$$

where D is the crystallite size (nm), k is the Scherrer constant ($k = 0.89$), λ is the wavelength of the X-ray radiation source ($\lambda = 0.154056 \text{ nm}$ in this case), β is the full width at half maximum intensity (radians), and θ is the angle between the incident and diffracted beams. The average crystallite sizes of TiO_2 are presented in Table 1. It is found that the average crystal sizes of TiO_2 with different Sb doping concentration

TABLE 1: Crystalline properties of the prepared TiO_2 photocatalysts.

Samples	Different Sb doping concentration (%)				
	0%	0.1%	0.5%	1%	5%
Crystallite size (nm)	14.5	19.2	14.7	16.4	13.6
Surface area (m^2/g)	56.281	57.822	69.220	49.691	40.606

are about 13.6~19.2 nm. The Sb^{5+} species are formed in the calcination step through oxidation of the incorporated Sb^{3+} (0.0760 nm) to Sb^{5+} [27]. The ionic radii of Ti^{4+} and Sb^{5+} are 0.0600 and 0.0605 nm, respectively [28], and the ionic radius of Sb^{5+} is similar to that of Ti^{4+} . It is suggested that Sb^{5+} ions are likely to be substituted at Ti^{4+} sites within TiO_2 . Sb^{5+} ions partially replace Ti^{4+} until the solubility limit is reached.

Figures 2(C) and 2(D) show the SEM images of pure and 1% Sb-doped TiO_2 , respectively. They indicate that the surface morphologies of pure and 1% Sb-doped TiO_2 are almost undifferentiated. All samples are irregular in shape, and the size of particles is in the range of 25~40 nm. The particle sizes of 1% Sb-doped TiO_2 are almost the same as that of pure TiO_2 due to the small amount of Sb [29]. There is a slight difference between the results of SEM and Scherrer formula, probably arising from aggregated particles. In addition, the specific surface area of the samples was obtained using the BET surface area measuring apparatus at the boiling point of liquid nitrogen. The specific surface area (S_{BET}) of catalyst is among 40.606~69.220 m^2/g (as shown in Table 1).

Here, on the basis of the fact that both of these radicals $h^+/\text{OH}^\bullet$ and $e^-/\text{O}_2^{\bullet-}$ can react oxidatively with nonfluorescent probe terephthalic acid to generate product 2-HTA (highly fluorescent) or 4-HBA (Scheme 1), the catalytic activities can be monitored by fluorescence spectroscopy. Figure 3(a) shows fluorescence spectrum of terephthalic acid solution with P25, pure, and 0.1%~5% Sb-doped TiO_2 , respectively. The results indicate that the samples of 0.1%~1% Sb-doped TiO_2 have better photocatalytic activity compared with pure and Degussa P25 TiO_2 in visible light region, and 0.1% Sb-doped TiO_2 demonstrated the best photocatalytic activity. It could be suggested that Sb dopant acts as electron traps retarding electron-hole recombination and enhancing interfacial charge carriers transfer to the surface of the particles; however, the recombination rate will increase when the dopant concentration of Sb is too high [30]. Upon excitation with visible light, electrons are excited from oxygen atoms in the conduction band, probably to the Ti 3d orbitals, and are further trapped by adsorbed O_2 to produce $\text{O}_2^{\bullet-}$ radicals. The photogenerated holes are trapped by adsorbed H_2O or OH^- to produce $\text{OH}^\bullet$ radicals bound to the surface [25]. These trapped electrons ($e^-/\text{O}_2^{\bullet-}$) or holes ($h^+/\text{OH}^\bullet$) react with the nearby adsorbed molecules, as shown in Figure 1.

It is known that the photocatalytic process will generate two kinds of free radical, $e^-/\text{O}_2^{\bullet-}$ and $h^+/\text{OH}^\bullet$, to drive the subsequent chemical reaction. Here, on the basis of that $e^-/\text{O}_2^{\bullet-}$ and $h^+/\text{OH}^\bullet$ can be quenched by scavengers of p-benzoquinone and DMSO, respectively; it is expected to get more insight into the catalytic mechanism of pure and Sb-doped TiO_2 by adding scavengers. As shown in Figure 3(b),

FIGURE 2: (A) UV-vis absorption spectra of pure TiO_2 and 0.1%~5% Sb-doped TiO_2 ; (B) X-Ray diffraction spectra of catalysts with different Sb-doped percentage calculated at 500°C for 2 h: (a) 0%, (b) 0.1%, (c) 0.5%, (d) 1%, and (e) 5%; (C) SEM image of pure TiO_2 ; (D) SEM image of 1% Sb-doped TiO_2 .

DMSO inhibited the activity of catalysts obviously, because DMSO can react with $\text{OH}^\bullet$ and reduce the concentration of $\text{OH}^\bullet$. The result indicates the existence of $\text{OH}^\bullet$ in solution and participation in the catalytic reaction of fluorescent probe. Similarly, the activity of catalysts had been also inhibited with $\text{O}_2^{\bullet-}$ scavenger by p-benzoquinone, showing the existence of $\text{O}_2^{\bullet-}$ and its involvement in the catalytic reaction at the same time. With the comparison of different Sb doping concentration, it was demonstrated that the scavengers can inhibit the photocatalytic activity of all the catalysts.

Doped TiO_2 demonstrates that doping Sb in TiO_2 can improve the photocatalytic activity of Sb-doped TiO_2 . The XRD results indicate that the crystalline structure of the Sb-doped TiO_2 is anatase with a small mean diameter. It is accepted that the anatase phase and small mean diameter are very beneficial for photocatalytic reaction [31, 32]. The Sb atoms may be substituted at some of Ti sites in TiO_2 and forming a narrow Sb band under the conduction band, which was determined to be responsible for visible light sensitivity. The reactive oxygen species such as $\text{OH}^\bullet$ and $\text{O}_2^{\bullet-}$ on the surface of catalysts are considered beneficial for the photocatalytic process. On one hand, when the $\text{OH}^\bullet$ or

H_2O species accept h^+ under light irradiation, they might be oxidized to form $\text{OH}^\bullet$. On the other hand, the surface hydroxyl groups can also act as absorption centers for O_2 molecules. The e^- from the conduction band can be captured by O_2 molecules to produce $\text{O}_2^{\bullet-}$. It is $\text{OH}^\bullet$ and $\text{O}_2^{\bullet-}$, which possess high oxidizability, that oxidize terephthalic acid.

4. Conclusion

The pure and Sb-doped TiO_2 photocatalysts have been prepared by a coprecipitation method using TiCl_4 and SbCl_3 as precursor. The influence of Sb doping concentration on the catalytic property, using terephthalic acid as fluorescent probe, has been studied in this work. Sb ions can be isomorphously substituted into the TiO_2 lattice to generate a new doping energy level and change the electron transition way of TiO_2 from valence band to conduction band. In this case, it extends the scope of TiO_2 absorption spectrum to the visible light region and improves photocatalytic activity of catalysts. The obtained results show that the photocatalytic activity of 0.1%~1% Sb-doped TiO_2 is higher than pure TiO_2 , and 0.1% Sb-doped TiO_2 presents the best photocatalytic

FIGURE 3: (a) Plots of the fluorescence spectral for the 500 μM terephthalic acid on P25 TiO_2 and pure and 0.1%–5% Sb-doped TiO_2 catalysts after visible light irradiation for 20 min. (b) The fluorescence intensity at 426 nm after irradiation 10 min for terephthalic acid on the pure and 0.1%–5% Sb-doped TiO_2 , without scavenger (red), with DMSO (blue) and p-benzoquinone (green), respectively.

activity, which is much better than Degussa P25. This superior catalytic activity mainly arises from the fact that the Sb-doped TiO_2 generates a new level in the forbidden band of TiO_2 and contributes to the capture of carriers as well as improving the separation of photogenerated electron hole. As for the catalytic mechanism of $\text{OH}^\bullet$ and $\text{O}_2^{\bullet-}$ in the fluorescence probe method, it can be attributed to the product fluorescence bursts from the oxidation of terephthalic acid to form 2-HTA by either one of these two radicals.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This work was partially supported by the National Science Foundation of China (21173068) and the Program for Innovative Research Team (Science and Technology) at the University of Henan Province (13IRTSTHN017).

References

- [1] T. L. Thompson and J. T. Yates Jr., "Surface science studies of the photoactivation of TiO_2 —new photochemical processes," *Chemical Reviews*, vol. 106, no. 10, pp. 4428–4453, 2006.
- [2] A. Kudo and Y. Miseki, "Heterogeneous photocatalyst materials for water splitting," *Chemical Society Reviews*, vol. 38, no. 1, pp. 253–278, 2009.
- [3] M. Liu, L. Piao, and W. Wang, "Fabrication and characteristics of three-dimensional flower-like titanate nanostructures," *Journal of Nanoscience and Nanotechnology*, vol. 10, no. 11, pp. 7469–7472, 2010.
- [4] M. Szostak and J. Aubé, "Chemistry of bridged lactams and related heterocycles," *Chemical Reviews*, vol. 113, no. 8, pp. 5701–5765, 2013.
- [5] A. Di Paola, G. Marci, L. Palmisano et al., "Preparation of polycrystalline TiO_2 photocatalysts impregnated with various transition metal ions: characterization and photocatalytic activity for the degradation of 4-nitrophenol," *Journal of Physical Chemistry B*, vol. 106, no. 3, pp. 637–645, 2002.
- [6] W. Xue, G. Zhang, X. Xu, X. Yang, C. Liu, and Y. Xu, "Preparation of titania nanotubes doped with cerium and their photocatalytic activity for glyphosate," *Chemical Engineering Journal*, vol. 167, no. 1, pp. 397–402, 2011.
- [7] T. Morikawa, Y. Irokawa, and T. Ohwaki, "Enhanced photocatalytic activity of TiO_2 -xNx loaded with copper ions under visible light irradiation," *Applied Catalysis A: General*, vol. 314, no. 1, pp. 123–127, 2006.
- [8] J. Y. Shi, W. H. Leng, W. C. Zhu, J. Q. Zhang, and C. N. Cao, "Electrochemically assisted photocatalytic oxidation of nitrite over Cr-Doped TiO_2 under visible light," *Chemical Engineering and Technology*, vol. 29, no. 1, pp. 146–154, 2006.
- [9] S. Klosek and D. Raftery, "Visible light driven V-doped TiO_2 photocatalyst and its photooxidation of ethanol," *Journal of Physical Chemistry B*, vol. 105, no. 14, pp. 2815–2819, 2002.
- [10] M. Sathish, B. Viswanathan, R. P. Viswanath, and C. S. Gopinath, "Synthesis, characterization, electronic structure, and photocatalytic activity of nitrogen-doped TiO_2 nanocatalyst," *Chemistry of Materials*, vol. 17, no. 25, pp. 6349–6353, 2005.
- [11] T. Yamaki, T. Sumita, and S. Yamamoto, "Formation of TiO_2 -xNx compounds in fluorine-implanted TiO_2 ," *Journal of Materials Science Letters*, vol. 21, no. 1, pp. 33–35, 2002.
- [12] B. Mahltig, E. Gutmann, and D. C. Meyer, "Solvochemical preparation of nanocrystalline anatase containing TiO_2 and

- TiO₂/SiO₂ coating agents for application of photocatalytic treatments," *Materials Chemistry and Physics*, vol. 127, no. 1-2, pp. 285–291, 2011.
- [13] D. Chen, H. Zhang, S. Hu, and J. Li, "Preparation and enhanced photoelectrochemical performance of coupled bicomponent ZnO-TiO₂ nanocomposites," *Journal of Physical Chemistry C*, vol. 112, no. 1, pp. 117–122, 2008.
- [14] S. Stoyanov, D. Mladenova, and C. Dushkin, "Photocatalytic properties of mixed TiO₂/V₂O₅ films in water purification at varying pH," *Reaction Kinetics and Catalysis Letters*, vol. 88, no. 2, pp. 277–283, 2006.
- [15] W. Choi, A. Termin, and M. R. Hoffmann, "The role of metal ion dopants in quantum-sized TiO₂: correlation between photoreactivity and charge carrier recombination dynamics," *Journal of Physical Chemistry*, vol. 98, no. 51, pp. 13669–13679, 1994.
- [16] H.-C. Wu, S.-W. Lin, and J.-S. Wu, "Effects of nitrogen concentration on N-doped anatase TiO₂: density functional theory and Hubbard U analysis," *Journal of Alloys and Compounds*, vol. 522, pp. 46–50, 2012.
- [17] M.-C. Wang, H.-J. Lin, C.-H. Wang, and H.-C. Wu, "Effects of annealing temperature on the photocatalytic activity of N-doped TiO₂ thin films," *Ceramics International*, vol. 38, no. 1, pp. 195–200, 2012.
- [18] W. Chen, P. Yuan, S. Zhang, Q. Sun, E. Liang, and Y. Jia, "Electronic properties of anatase TiO₂ doped by lanthanides: a DFTU study," *Physica B: Condensed Matter*, vol. 407, no. 6, pp. 1038–1043, 2012.
- [19] J. Moon, H. Takagi, Y. Fujishiro, and M. Awano, "Preparation and characterization of the Sb-doped TiO₂ photocatalysts," *Journal of Materials Science*, vol. 36, no. 4, pp. 949–955, 2001.
- [20] Y. He, Y. Wu, H. Guo, T. Sheng, and X. Wu, "Visible light photodegradation of organics over VYO composite catalyst," *Journal of Hazardous Materials*, vol. 169, no. 1-3, pp. 855–860, 2009.
- [21] K.-I. Ishibashi, A. Fujishima, T. Watanabe, and K. Hashimoto, "Detection of active oxidative species in TiO₂ photocatalysis using the fluorescence technique," *Electrochemistry Communications*, vol. 2, no. 3, pp. 207–210, 2000.
- [22] K. Bubacz, E. Kusiak-Nejman, B. Tryba, and A. W. Morawski, "Investigation of OH radicals formation on the surface of TiO₂/N photocatalyst at the presence of terephthalic acid solution. Estimation of optimal conditions," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 261, pp. 7–11, 2013.
- [23] U. Černigoj, M. Kete, and U. L. Štangar, "Development of a fluorescence-based method for evaluation of self-cleaning properties of photocatalytic layers," *Catalysis Today*, vol. 151, no. 1-2, pp. 46–52, 2010.
- [24] M. K. Eberhardt and R. Colina, "The reaction of OH radicals with dimethyl sulfoxide. A comparative study of Fenton's reagent and the radiolysis of aqueous dimethyl sulfoxide solutions," *Journal of Organic Chemistry*, vol. 53, no. 5, pp. 1071–1074, 1988.
- [25] W. Xu, P. K. Jain, B. J. Beberwyck, and A. P. Alivisatos, "Probing redox photocatalysis of trapped electrons and holes on single Sb-doped titania nanorod surfaces," *Journal of the American Chemical Society*, vol. 134, no. 9, pp. 3946–3949, 2012.
- [26] Q. Zhang, J.-B. Joo, Z. Lu et al., "Self-assembly and photocatalysis of mesoporous TiO₂ nanocrystal clusters," *Nano Research*, vol. 4, no. 1, pp. 103–114, 2011.
- [27] E. Redel, E. Arsenault, P. G. O'Brien, N. P. Kherani, and G. A. Ozin, "Growth of metal nanocrystals on nanostructured metal oxides-dramatic effect of antimony doping," *Chemistry of Materials*, vol. 23, no. 6, pp. 1353–1355, 2011.
- [28] R. D. Shannon, "Revised effective Ionic-RadII and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica Section A*, vol. 32, pp. 751–767, 1976.
- [29] D. N. Liu, G. H. He, L. Zhu, W. Y. Zhou, and Y. H. Xu, "Enhancement of photocatalytic activity of TiO₂ nanoparticles by coupling Sb₂O₃," *Applied Surface Science*, vol. 258, no. 20, pp. 8055–8060, 2012.
- [30] T. Ikeda, T. Nomoto, K. Eda et al., "Photoinduced dynamics of TiO₂ doped with Cr and Sb," *Journal of Physical Chemistry C*, vol. 112, no. 4, pp. 1167–1173, 2008.
- [31] H. Choi, E. Stathatos, and D. D. Dionysiou, "Sol-gel preparation of mesoporous photocatalytic TiO₂ films and TiO₂/Al₂O₃ composite membranes for environmental applications," *Applied Catalysis B: Environmental*, vol. 63, no. 1-2, pp. 60–67, 2006.
- [32] C. He, B. Tian, and J. Zhang, "Thermally stable SiO₂-doped mesoporous anatase TiO₂ with large surface area and excellent photocatalytic activity," *Journal of Colloid and Interface Science*, vol. 344, no. 2, pp. 382–389, 2010.