

## Editorial

# Environmental Photocatalysis

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In recent years, semiconductor photocatalytic technology has been demonstrated to be one of the "green" and effective strategies for solving environmental pollution problems. Therefore, environmental photocatalysis, including water disinfection, hazardous waste remediation, air and water purification, deodorization, antibacterial, and self-cleaning, has caused more and more attention in recent years (see the work of J. G. Yu et al. "*TiO<sub>2</sub> photocatalytic materials*" [1–9]). However, owing to low photocatalytic efficiency and activity of photocatalytic materials, the environmental applications of various photocatalytic technologies and materials are still very limited. Thus, more investigations are highly required from the viewpoint of practical use and commerce.

This special issue contains eighteen papers, which mainly deal with environmental photocatalysis. Among them eight papers are related to preparation, characterization, and photocatalytic performance of photocatalytic materials including CeO<sub>2</sub>-SiO<sub>2</sub>, BiVO<sub>4</sub>, mesoporous TiO<sub>2</sub>, Bi<sub>2</sub>WO<sub>6</sub>, Bi<sub>2</sub>O<sub>3</sub>-Bi<sub>2</sub>CrO<sub>6</sub>, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/SiO<sub>2</sub>, Mn-C-codoped TiO<sub>2</sub>, ZnO, and N-doped TiO<sub>2</sub>, three papers, are devoted to decolorization and treatment of industrial wastewater, three papers present photocatalytic degradation of dyes, one paper reports on indoor air purification, two papers are related to photo-Fenton and photoelectron-Fenton reactions, and the remaining one deals with photocatalytic degradation of nitrobenzene. Furthermore, in this special issue, 16 papers are research articles and two papers are review articles. We

wish to express our thanks to all the authors who have made this special issue possible. A brief summary of all eighteen papers is presented below.

The article entitled "*Comparison between solar and artificial photocatalytic decolorization of textile industrial wastewater*" mainly reported the photocatalytic decolorization of industrial wastewater by using TiO<sub>2</sub> and ZnO photocatalysts. Heterogeneous photocatalysis applied under natural weathering conditions, in the presence of solar radiation, shows a promising degradation capability. The complete removal of color was achieved in a relatively short time of about 20 minutes when ZnO was used, and about 100 minutes when TiO<sub>2</sub> was used under solar irradiation. The results indicated that the photocatalytic decolorization of textile industrial wastewater was obviously influenced by different factors including mass and type of catalyst, reactor, dye concentration, and temperature.

In the article entitled "*Synthesis and characterization of CeO<sub>2</sub>-SiO<sub>2</sub> nanoparticles by microwave-assisted irradiation method for photocatalytic oxidation of methylene blue dye*," CeO<sub>2</sub>-SiO<sub>2</sub> nanoparticles were prepared for the first time by a facile microwave-assisted irradiation process. The photocatalytic activities were evaluated by the decomposition of methylene blue dye under UV light irradiations. The results showed that all solid samples exhibited mesoporous textures with high specific surface areas, relatively small pore size diameters, and large pore volume. The sample prepared by 30 min microwave irradiation time exhibited the best

photocatalytic activity. The photocatalytic activity of  $\text{CeO}_2$ - $\text{SiO}_2$  nanoparticles prepared by 30 min irradiation times was found to have better performance than commercial reference P25.

In the paper entitled “*Electrochemical techniques in textile processes and wastewater treatment*,” the authors review the electrochemical techniques applied to textile industry. In particular, they are an efficient method to remove color of textile effluents. The reuse of the discolored effluent is possible, which implies an important saving of salt and water (i.e., by means of the “UVEC Cell”). Electrochemical reduction reactions are mostly used in sulfur and vat dyeing, but, in some cases, they are applied to effluents discoloration. However, the main applications of electrochemical treatments in the textile sector are based on oxidation reactions. Most of electrochemical oxidation processes involve indirect reactions which imply the generation of hypochlorite or hydroxyl radical in situ. These electrogenerated species are able to bleach indigo-dyed denim fabrics and to degrade dyes in wastewater in order to achieve the effluent color removal.

In the paper entitled “*Impact of preparative pH on the morphology and photocatalytic activity of  $\text{BiVO}_4$* ,” single-crystalline  $\text{BiVO}_4$  was prepared using aqueous-phase precipitation method by adjusting pH. The effects of pH on structure, surface morphology, visible-light photocatalytic activity, and light absorption performance of  $\text{BiVO}_4$  were explored and discussed. The highest photocatalytic performance on the degradation of a methylene blue solution was observed under  $\text{pH} = 7.0$  for  $\text{BiVO}_4$  in monoclinic scheelite, which is attributed to its small grain size and marked surface oxygen evolution ability.

In the paper entitled “*Mesoporous  $\text{TiO}_2$  micro-nanometer composite structure: synthesis, optoelectric properties, and photocatalytic selectivity*,” mesoporous anatase  $\text{TiO}_2$  micro-nanometer composite structure was prepared using solvothermal method at  $180^\circ\text{C}$ , followed by calcination at  $400^\circ\text{C}$  for 2 h. The photocatalytic activity was characterized by photodegradation of sole rhodamine B (RhB) and sole phenol aqueous solutions under simulated sunlight irradiation and compared with that of Degussa P-25 under the same conditions. The photodegradation preference of this mesoporous  $\text{TiO}_2$  was also investigated for an RhB-phenol mixed solution. The results showed that the  $\text{TiO}_2$  composite structure consisted of microspheres with a size of  $\sim 0.5\text{--}2\ \mu\text{m}$  and irregular aggregates with rough surfaces. The photodegradation activities of this mesoporous  $\text{TiO}_2$  on both RhB and phenol solutions were higher than those of P25. Moreover, the prepared  $\text{TiO}_2$  exhibited photodegradation preference on RhB in the RhB-phenol mixture solution.

The article entitled “*Rapid decolorization of cobalamin*” examined the photocatalytic decolorization of cobalamin in aqueous solution with different types of catalysts including ZnO,  $\text{TiO}_2$  (Degussa P25),  $\text{TiO}_2$  (Hombikat UV100),  $\text{TiO}_2$  (Millennium PC105), and  $\text{TiO}_2$  (Koronose 2073) under UVA irradiation. The effects of experimental parameters on photocatalytic oxidation were investigated. The results indicated that the photocatalytic decolorization of cobalamin was well described by pseudo-first-order kinetics according

to the Langmuir-Hinshelwood model. The activation energy was calculated according to Arrhenius plot and was found to be  $28 \pm 1\ \text{kJ}\cdot\text{mol}^{-1}$  for ZnO and  $22 \pm 1\ \text{kJ}\cdot\text{mol}^{-1}$  for  $\text{TiO}_2$  (Degussa P25). The total organic carbon (TOC) analysis indicated that the decolorization rate of dye was faster than the total mineralization. The activity of different types of catalysts used in this study was of the following sequence:  $\text{ZnO} > \text{TiO}_2$  (Degussa P25)  $> \text{TiO}_2$  (Hombikat UV100)  $> \text{TiO}_2$  (Millennium PC105)  $> \text{TiO}_2$  (Koronose 2073).

The article entitled “*Feasibility of carbonaceous nano-material-assisted photocatalysts calcined at different temperatures for indoor air applications*” examined the characteristics and photocatalytic activity of multiwall carbon nanotube-assisted  $\text{TiO}_2$  (MWNT- $\text{TiO}_2$ ) nanocomposites and their potential indoor air applications. The results indicated that the MWNT- $\text{TiO}_2$  composites calcined at low temperatures showed higher photocatalytic activity for decomposition of aromatic hydrocarbons at indoor concentrations than those calcined at high temperatures. The mean rates for the decomposing benzene, toluene, ethyl benzene, and o-xylene (BTEX) by the composite calcined at  $300^\circ\text{C}$  were 32%, 70%, 79%, and 79%, respectively, whereas they were 33%, 71%, 78%, and 78% for the composite calcined at  $400^\circ\text{C}$ , respectively. In contrast, the rates decreased to close to zero when the calcination temperature increased to  $600^\circ\text{C}$ . Moreover, the MWNT- $\text{TiO}_2$  exhibited superior photocatalytic performance for the decomposition of indoor air pollutants compared to pure  $\text{TiO}_2$  under conventional UV-lamp irradiations.

The article entitled “*Heterogeneous photo-Fenton reaction catalyzed by nanosized iron oxides for water treatment*” reviewed the recent developments in the heterogeneous photo-Fenton reaction which utilized nanosized iron oxides as catalysts for maximizing the activity due to the enhanced physical and chemical properties caused by the unique structures. This paper also summarized the fundamentals of the Fenton reaction, which determined the inherent drawbacks and associated advances, to address the advantages of iron oxides and nanosized iron oxides.

In the paper entitled “*UV-irradiated photocatalytic degradation of nitrobenzene by titania binding on quartz tube*,” a new method for UV-irradiated degradation of nitrobenzene by titania photocatalysts was presented. Titania nanoparticles were coated on a quartz tube by the addition of tetraethyl orthosilicate into the matrix. The dependence of nitrobenzene photodegradation on pH, temperature, concentration, and air feeding was discussed, and the physical properties such as the activation energy, entropy, enthalpy, adsorption constant, and rate constant were acquired by conducting the reactions in a variety of experimental conditions. The optimum efficiency of the photodegradation with the nitrobenzene residue as low as 8.8% was obtained and the photodegradation mechanism was also investigated by HPLC, GC/MS, ion chromatography (IC), and chemical oxygen demand (COD) analyses.

In the paper entitled “*Hydrothermal synthesis of iodine-doped  $\text{Bi}_2\text{WO}_6$  nanoplates with enhanced visible and ultraviolet-induced photocatalytic activities*,” the iodine-doped

$\text{Bi}_2\text{WO}_6$  (I-BWO) photocatalyst was prepared by a hydrothermal method using KI as the source of iodine. The photocatalytic activity of I-BWO for the degradation of rhodamine B (RhB) was higher than that of pure BWO and  $\text{I}_2$ -loaded  $\text{Bi}_2\text{WO}_6$  ( $\text{I}_2$ -BWO) sample regardless of visible light ( $>420$  nm) or ultraviolet light ( $<400$  nm) irradiation. The results of DRS analysis showed that the I-BWO and  $\text{I}_2$ -BWO catalysts had narrower band gaps. XPS analysis proved that the multivalent iodine species including  $\text{I}^0$  and  $\text{I}^-$  were coadsorbed on the defect surface of  $\text{Bi}_2\text{WO}_6$  in I-BWO. The enhanced photocatalytic activity of I-BWO for degradation of RhB was due to the synergetic effect of a small crystalline size, a narrow band gap, and plenty of oxygen vacancies.

The article entitled “*Synthesis and photocatalytic properties of one-dimensional composite  $\text{Bi}_2\text{O}_3$ - $\text{Bi}_2\text{CrO}_6$  nanowires*” reported preparation of one-dimensional composite  $\text{Bi}_2\text{O}_3$ - $\text{Bi}_2\text{CrO}_6$  nanowires by a simple microwave-assisted hydrothermal method. The diameter of the nanowires varied from 30 to 100 nm and the length was a few micrometers. Methylene blue (MB) solutions were used to evaluate the visible light photocatalytic activities of the prepared samples. Compared with  $\text{Bi}_2\text{O}_3$ , the  $\text{Bi}_2\text{O}_3$ - $\text{Bi}_2\text{CrO}_6$  composite nanowires showed enhanced performance in oxidization of MB under visible light.

In the paper entitled “*Pretreatment of color filter wastewater towards biodegradable by Fresnel-lens-assisted solar  $\text{TiO}_2$  photocatalysis*,” the experimental design of response surface methodology (RSM) was employed to assess the effect of critical process parameters (including initial pH,  $\text{TiO}_2$  dosage, and reaction time) on pretreatment performance in terms of BOD5/COD, COD, and TOC removal efficiency. Appropriate reaction conditions were established as an initial pH of 7.5, a  $\text{TiO}_2$  dosage of 1.5 g/L with a reaction time of 3 h for increasing the BOD5/COD ratio to 0.15, which implied that the treated wastewater would be possibly biodegradable. Meanwhile, the rates of COD and TOC removals reached 32.9% and 24.4%, respectively. With the enhancement of Fresnel lens, the required reaction time for improving the biodegradability of wastewater to 0.15 was 1 h only. Moreover, the rates of COD and TOC removals were promoted to 37.4% and 25.8%, respectively. This was mainly due to the concentrated effect of Fresnel lens for solar energy, including an increase of 2 times of solar irradiation and an increase of 15–20°C of wastewater temperature. Consequently, solar  $\text{TiO}_2$  photocatalytic process with the use of a PMMA Fresnel lens could offer an economical and practical alternative for the pretreatment of industry wastewater containing diversified biorefractory pollutants with a high concentration of COD such as color filter wastewater.

In the paper entitled “*Photocatalytic degradation of rhodamine B with  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$  sensitized by  $\text{H}_2\text{O}_2$* ,” the Keggin-type  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  was loaded on the surface of  $\text{SiO}_2$  by the sol-gel method and sensitized by  $\text{H}_2\text{O}_2$  solution. The photocatalytic degradation of rhodamine B (RhB) by  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$  (x) under simulated natural light irradiation was investigated. The results indicated that at optimal condition (initial concentration of methyl orange is 10 mg/L, catalyst dosage is 0.8 g, and the pH is 2.5) the degradation rate of RhB was as high as 97.7% after 2 h

under simulated natural light irradiation. The photocatalytic reaction of RhB could be expressed as a first-order kinetic model.

In the paper entitled “*Synthesis and characterization of Mn-C-codoped  $\text{TiO}_2$  nanoparticles and photocatalytic degradation of methyl orange dye under sunlight irradiation*,” novel visible-light-driven Mn-C- $\text{TiO}_2$  nanoparticles were synthesized by sol-gel method using polyoxyethylenes orbital monooleate (Tween 80) as template and carbon precursor and manganese acetate as manganese precursor. The photocatalytic activity of synthesized catalyst was evaluated by photocatalytic oxidation of methyl orange (MO) solution under the sunlight irradiation. The results showed that Mn-C- $\text{TiO}_2$  nanoparticles had higher activity than other samples under sunlight, which was due to their high specific surface area, smaller particle size, and lower band gap energy.

The article entitled “*Photocatalytic performance of ZnO:Al films under different light sources*” reported preparation of ZnO and Al doped ZnO films by spray pyrolysis. Their photocatalytic activity was evaluated by the decomposition of the methyl orange dye using different light sources: ultraviolet light, artificial white light, and direct sunlight. The Al doped ZnO films presented a very high degradation rate not only under UV and sunlight (100% degradation), but also under white light (90% degradation after the same irradiation time). An unexpected high degradation was also obtained in the dark, which indicated that a nonphotonic process took place parallel to the photocatalytic process. This was due to the extra electrons—provided by the aluminum atoms—that migrated to the surface and produced  $\text{O}_2^{\bullet-}$  radicals favoring the decomposition process even in the dark. The high activity achieved by the ZnO:Al films under natural conditions could be potentially applied to water treatment processes.

The article entitled “*Supported nanosized  $\alpha$ -FeOOH improves efficiency of photoelectro-Fenton process with reaction-controlled pH adjustment for sustainable water treatment*” demonstrated that the overall efficiency of photoelectro-Fenton process was improved by rapidly recycling the iron substance. Nanosized iron oxide was prepared and employed to ensure such rapid recycling. SEM and XRD results showed that the as-prepared iron oxide was  $\alpha$ -FeOOH with 20 nm in size. The experimental results of dimethyl phthalate (DMP) degradation indicated that diatomite-supported  $\alpha$ -FeOOH (N- $\alpha$ -FeOOH/diatomite) could reduce the DMP concentration and total organic carbon. Furthermore, compared with  $\text{Fe}^{3+}$ , the N- $\alpha$ -FeOOH/diatomite saved 160 min for iron settlement at 20 mg L<sup>-1</sup> DMP concentration. Also, with increasing the initial DMP concentration, extra energy consumed by the individual step of PE-Fenton reaction using the N- $\alpha$ -FeOOH/diatomite became negligible compared with that using free iron ions with increasing the initial DMP concentration.

The article entitled “*Photocatalytic degradation of organic dyes under visible light on N-doped  $\text{TiO}_2$  photocatalysts*” focused on the application of white and blue light emitting diodes (LEDs) as light sources for the photocatalytic degradation of organic dyes in liquid phase with visible light. The photocatalytic activity of N-doped  $\text{TiO}_2$ , synthesized

by direct hydrolysis of titanium tetraisopropoxide with ammonia, was evaluated by means of a batch photoreactor. The bandgap energy of  $\text{TiO}_2$  was moved into the visible range from 3.3 eV to 2.5 eV. The results demonstrated that the right selection of operating conditions was allowed to effectively degrade different dyes with the N-doped  $\text{TiO}_2$  photocatalysts irradiated with visible light emitted by LEDs.

In the paper entitled “*Photocatalytic treatment of rhodamine 6G in wastewater using photoactive  $\text{ZnO}$* ,” the photocatalytic activity of zinc oxide, prepared by precipitation followed by calcinations, was tested using rhodamine 6G as an organic pollutant. The results were compared with those obtained on P-25 titania and one of the samples had similar performances in terms of dye degradation degree, but needed higher pH values to prevent the photocatalyst degradation.

The above synopsis of the articles collected in this special issue on environmental photocatalysis indicates that this area of research is continuously expanding. Our hope is this special issue will stimulate further developments in the field of environmental photocatalysis.

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