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Editorial

Compositing Semiconductor Photocatalysts and Their Microstructure Modulation

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Photocatalytic materials have attracted increasing interests owing to the potential applications on solving global energy and environmental problems. However, the rapid recombination of photogenerated charge carriers and the limited spectral response range greatly restricted their further development and practical applications. Compositing semiconductor photocatalysts, by combining semiconductors with other materials, can not only effectively expand the visible-light absorption, but also improve the photogenerated charge carriers' separation, which would effectively solve the above problems and improve the photocatalytic activities. Moreover, it also provides a way to develop an efficient photocatalyst by tailoring the band gaps and band positions to meet the requirements for specific applications. The microstructures of photocatalysts also greatly affect their photocatalytic performances. Therefore, it has become a hot topic in photocatalysis on the synthesis, photocatalytic characterization, and microstructure modulation of compositing semiconductor photocatalysts.

The selected topics and papers in this special issue presented the recent progresses on the synthesis of compositing semiconductor photocatalysts, as well as the practical applications on solving energy and environmental problems. Limited by the numbers of the papers,they cannot cover the whole areas in photocatalysis, but they also provide rich information and knowledge that we would like to share with the readers. Moreover, we would like to thank the authors for their excellent contributions and patience in assisting us. Finally, the fundamental work of all reviewers on the special issue is also warmly acknowledged.

The special issue contains twenty-nine papers, which mainly focused on the synthesis, microstructure modulation, and practical applications of compositing semiconductor photocatalysts. Among them eight papers are dealing with hetero-structured composite photocatalysts. Five papers are related to modified photocatalysts with noble metal or other sensitizing materials. Eleven papers are regarding the doping or co-doping of wide band gap semiconductor photocatalysts. Finally, five papers addresses the applications of photocatalysts on solving environmental and energy problems.

In the paper entitled "*One-pot template-free hydrothermal synthesis of monoclinic $BiVO_4$ hollow microspheres and their enhanced visible-light photocatalytic activity,*" B. Cheng et al. present a one-pot template-free hydrothermal synthesis of $BiVO_4$ hollow microspheres via a localized Ostwald ripening mechanism. The reaction duration and urea concentration played important roles in the formation of $BiVO_4$ hollow microspheres. And photocatalytic properties of $BiVO_4$ under visible-light irradiation were also discussed.

In the paper entitled "*Preparation, characterization, and activity evaluation of CuO/F-TiO_2 photocatalyst,*" W. Liu et al. present the synthesis of CuO/F-TiO_2 photocatalysts by ball milling process. The light absorption range of CuO/F-TiO_2 was effectively expanded comparing to pure TiO_2. And the photocatalytic reduction activity was greatly improved by increasing the amount of doped p-CuO in CuO/F-TiO_2 composites. The effects of ball milling time and the photocatalytic mechanism were also discussed.

In the paper entitled "*Simultaneous elimination of formaldehyde and ozone byproduct using noble metal modified TiO_2*

films in the gaseous VUV photocatalysis," P. Y. Zhang et al. present asystematical investigations on the removal of low concentration formaldehyde and ozone byproduct in a gaseous VUV (vacuum ultraviolet) photocatalytic system by using noble metal modified TiO_2 films. Metallic Pt or Au could reduce the recombination of h^+/e^- pairs, thus, simultaneously increase the elimination of HCHO and ozone, but PdO oxide seemed to inhibit the HCHO oxidation in the UV_{254nm} photocatalysis. And the effects of O_3 on the decomposition of HCHO and ozone under VUV were also investigated.

In the paper entitled "*Synthesis of core-shell Fe_3O_4@ SiO_2@TiO_2 microspheres and their application as recyclable photocatalysts,*" Z. H. Wang et al. report the fabrication of Fe_3O_4@SiO_2@TiO_2 core-shell microspheres through a wet-chemical approach. The TiO_2 nanoparticles on the surfaces of microspheres can degrade organic dyes under the illumination of UV light, and the samples can be easily separated from the solution after the photocatalytic process due to the ferromagnetic Fe_3O_4 core, which provided a way to recycle the photocatalysts for practical applications.

In the paper entitled "*Synthesis and photocatalytic activity of TiO_x powder with different oxygen defects,*" F. M. Meng et al. reported the synthesis of TiO_x powders by mechanochemical technique and heating process. Carbon and chromium were used to control the degree of oxygen vacancies in TiO_x by doping into the TiO_x crystal matrix. The photocatalytic measurements indicate that the TiO_x sample with 66.93% mass fraction of Ti_7O_{13} is the most efficient on the degradation of MO dye. Moreover, the origin for the visible-light absorption and the effect of band gap on photocatalytic activities were also discussed in this paper.

In the paper entitled "*Nitrogen incorporation in TiO_2—does it make a visible-light photoactive material?,*" B. Viswanathan et al. examined the state and location of nitrogen doped in TiO_2 lattice and the optical absorption induced by nitrogen doping. They found that the surface of N-doped TiO_2 adopted a non-native configuration, while the bulk material was still in the native configuration of pure TiO_2. Though N-doped TiO_2 showed visible-light response, the improvement on photocatalytic activity is only marginal in most of the cases.

In the paper entitled "*The synthesis of anatase nanoparticles and the preparation of photocatalytically active coating based on wet chemical methods for self-cleaning applications,*" D. Verhovšek et al. reported an improved sol-gel method for producing highly photocatalytic anatase TiO_2 nanoparticles and tested the coating for self-cleaning glass and ceramic surfaces. Both the sol-gel synthesis and the coating preparation are based on a wet chemical process, which provided an economic, facile, and non-toxic process for numerous applications.

In the paper entitled "*Synthesis, characterization, and photocatalytic activity of TiO_2 microspheres functionalized with phorphyin*", J.-H.Cai et al. reported a way to expand the visible-light absorption of TiO_2 by loading 5-(4-allyloxy)phenyl-10,15,20-tri(4-methylphenyl)porphyrin (APTMPP) on TiO_2 surfaces. The photocatalytic experiment by the oxidation of α-terpinene under visible-light irradiation indicated the photocatalytic activities were significantly enhanced in presence of APEMPP-MPS-TiO_2 compared with the nonmodified TiO_2.

In the paper entitled "*Synthesis, characterization, and photocatalysis of Fe-doped TiO_2: a combined experimental and theoretical study,*" B. S. Liu et al. prepared Fe-doped TiO_2 nanoparticles using hydrothermal method. The photocatalytic activity of as-prepared Fe-doped TiO_2 first increases and then decreases as the Fe concentration increases. And the different effects of bulk dopant and surface dopant on photocatalytic activity were investigated systematically.

In the paper entitled "*Enhanced photoactivity of Fe + N Co-doped anatase-rutile TiO_2 nanowire film under visible-light irradiation,*" R. Xiong et al. synthesized Fe + N codoped rutile-anatase mix-phase TiO_2 nanowires by a two-step anodic oxidation method. The co doping with nitrogen and iron could enhance the visible-light absorption and improved the photocatalytic activity of TiO_2 nanowires. The reasons for the increase of photocatalytic activity in the Fe + N codoped sample were also discussed.

In the paper entitled "*Effects of calcination temperature on preparation of boron-doped TiO_2 by sol-gel method,*" W. J. Zhang et al. present the synthesis of boron-doped TiO_2 by a modified sol-gel method. The effects of calcination temperature on the properties of the boron-doped TiO_2 were investigated. The photocatalytic activity of the samples were examined by degradation of methyl orange and the sample with the optimal activity was obtained after being calcinated at 400°C.

In the paper entitled "*Preparation and characterization of $(I_2)_n$ sensitized nanoporous TiO_2 with enhanced photocatalytic activity under visible-light irradiation,*" S. M. Gao et al. present an unique template-free synthetic strategy to prepare$(I_2)_n$ sensitized nanoporous TiO_2. I_2 hydrosol is used as nucleation center and sensitizer, while $TiCl_4$ was used as the precursor for TiO_2 and the calcination temperature has acrucial role in the amount of $(I_2)_n$ sensitized nanoporous TiO_2. The as-prepared samples shows enhanced photocatalytic activity in visible region and the possible mechanism for the enhanced photocatalytic activity was also proposed.

In the paper entitled "*Enhanced visible-light photocatalytic activity of V_2O_5 cluster modified N-doped TiO_2 for degradation of toluene in air,*" F. Dong et al. reported the fabrication of V_2O_5 cluster modified N-doped TiO_2 nanocomposites photocatalyst. The conduction band (CB) potential of V_2O_5 is lower than the CB level of N-doped TiO_2, which favors the photogenerated electron transfer from CB of N-doped TiO_2 to V_2O_5 clusters. This helps promote the transfer and separation of photogenerated; thus, the visible-light activity of N-doped TiO_2 was significantly enhanced by loading V_2O_5 clusters.

In the paper entitled "*Statistical optimization of operational parameters for enhanced naphthalene degradation by TiO_2/Fe_3O_4-SiO_2 Photocatalyst,*" A. J. Wang et al. optimize the operational parameters for enhanced naphthalene degradation by TiO_2/Fe_3O_4-SiO_2 (TFS) photocatalyst using statistical experimental design and analysis. The central composite design method was adopted and the experimental results showed that irradiation time, pH, and TFS

photocatalyst loading had significant influence on naphthalene degradation.

In the paper entitled "*Synthesis and characterization of iron oxide nanoparticles and applications in the removal of heavy metals from industrial wastewater,*" Z. L. Cheng et al. synthesized maghemite (γ-Fe_2O_3) nanoparticles of 60 nm using a co-precipitation method and investigated the applicability of maghemite nanoparticles for the removal of Pb^{2+} from electroplating wastewater. This study showed that the prepared γ-Fe_2O_3 nanoparticles could be used as an alternate to the conventional adsorbents for the removal of metal ions from wastewater with high removal efficiency within a very short time.

In the paper entitled "*Enhanced photocatalytic activity of hierarchical marcro-meso porous anatase by ZrO_2 incorporation,*" M. E. Contreras-García et al. fabricated TiO_2/ZrO_2 macro-mesoporous nanostructure by sol-gel hydrothermal method. The mesoporous sizes of the binary oxides could be tailored by the variation of the molar ratios of the metal precursors. With high surface areas, the meso-macroporous binary oxides exhibit high photocatalytic activities and are potential for photocatalytic applications.

In the paper entitled "*Synthesis of neutral SiO_2/TiO_2 hydrosol and its application as antireflective self-cleaning thin film,*" H. L. Bai et al. present a synthesis of neutral SiO_2/TiO_2 composite hydrosol by a coprecipitation-peptization method. The addition of SiO_2 not only decreases the refractive index, but also suppresses the aggregation of TiO_2, by forming Ti–O–Si bond with TiO_2. And the as-prepared SiO_2/TiO_2 thin film also demonstrates antireflection and photocatalytic self-cleaning effect.

In the paper entitled "*Preparation and characterization of visible-light activated Fe-N co-doped TiO_2 and Its photocatalytic inactivation effect on leukemia tumors*", J. W. Xiong et al. presented a study of inactivation effect on leukmia tumors by using Fe-N co-doped TiO_2 as photocatalysts under visible-light irradiation. Fe-N co-doped TiO_2 exhibit a significant inhibition on the growth of HL60 cells and high inactivation efficiency in photo-deconstruction of HL60 cancer cells.

In the paper entitled "*Facile low-temperature synthesis of carbon nanotube/TiO_2 nanohybrids with enhanced visible-light-driven photocatalytic activity,*" Y. L. Xie et al. report a facile and novel low-temperature chemical precipitation route to synthesize CNT/TiO_2 nanohybrids which exhibit high photocatalytic activity in decomposition of RhB under visible-light irradiation.

In the paper entitled "Light-driven preparation, microstructure, and visible-light photocatalytic property of porous carbon-doped TiO_2," G.-D. Li et al. report an unusual light-driven strategy for the preparation of highly porous C-doped TiO_2. With thermal treatment at 200°C, Ti–O–C bonds and the coke species were formed, which were regarded to play a critical role on enhancing the visible-light photocatalytic activity for the as-prepared C-doped TiO_2.

In the paper entitled "*Doped titanium dioxide films prepared by pulsed laser deposition method,*" X. D. Lin et al. presented the fabrication of N-doped TiO_2 film by pulsed laser deposition method using novel ceramic target of mixture of TiN and TiO_2 and developed a continuous optical transmission auto-recorder method to evaluate the photocatalytic properties. The results indicated the as-prepared N-doped TiO_2 film exhibits high photocatalytic activity on decomposing MO dye under visible-light irradiation.

In the paper entitled "*Nitrogen-doped TiO_2 nanotube arrays with enhanced photoelectrochemical property,*" S. W. Lin et al. report a fabrication of N-doped TiO_2 nanotube (NTN) arrays by electrochemical anodization in glycerol electrolyte. Systemic studies are done in electrochemical anodization process. And the prepared N-doped NTN arrays exhibit high visible-light-driven photocatalytic activity.

In the paper entitled "*Facile preparation and photoinduced superhydrophilicity of highly ordered sodium-free titanate nanotube films by electrophoretic deposition*," H. G. Yu et al. prepared highly ordered sodium-free titanate nanotube films by one-step preparation on F-doped SnO_2-coated (FTO) glass via an electrophoretic deposition method by using sodium titanate nanotubes as precursor. The self-assembled formation of highly ordered sodium titanate nanotube films was accompanied with the effective removal of sodium ions in the nanotubes during the EPD process, resulting in the final formation of protonated titanate nanotube film. The effects of calcination temperatures on the surface morphology, microstructures as well as the properties of superhydrophilicity were studied.

In the paper entitled "*High -efficiently photoelectrochemical hydrogen production over Zn-incorporated TiO_2 nanotubes (Zn-TNT)*," M. Kang et al. designed Zn-incorporated TiO_2 nanotube (Zn-TNT) photocatalyst to investigate the Zn dopant and nanotube morphology effects of TiO_2 in electrochemical hydrogen production from the photosplitting of methanol/water solution. The hydrogen production over the Zn-TNT photocatalysts was higher than that over the TNT, which was attributed to the shift toward the visible region and increased number of excited electrons and holes.

In the paper entitled "*Enhanced hydrogen production over C-doped CdO photocatalyst in Na_2S/Na_2SO_3 solution under visible-light irradiation,*" J. L. Long et al. report the fabrication of the C-doped CdO photocatalysts by high-temperature solid-state process. The doping of C results in the red-shift of the optical absorption of CdO. The C-doped CdO photocatalysts have higher photocatalytic activity over parent CdO under visible-light irradiation. The results indicate that the H_2 production is due to the existence of CdS and the enhancement of visible-light photocatalytic activity of H_2 production is originated from the doping of carbon into the CdO lattice. The probably reaction mechanism was also discussed and proposed.

In the paper entitled "*Photo-etching of Immobilized TiO_2-ENR_{50}-PVC Composite for Improved Photocatalytic Activity*", M. A. Nawi et al. present the preparation of a highly reusable immobilized TiO_2-ENR_{50}-PVC composite via simple dip-coating method. It exhibited better photocatalytic efficiency than the TiO_2 powder in a slurry. The photo-etched catalyst and the photo-mineralization capability of the product are also investigated. Such efficient immobilized photocatalyst system offers excellent advantage of use and reuse without the need to filter the treated water after the treatment and can be easily adapted for continuous flow reactor.

In the paper entitled "*Photocatalytic activity of titanate nanotube powders in a hybrid pollution control system,*" S.-C. Jung et al. present a novel microwave/UV/photocatalyst hybrid system to evaluate the photocatalytic activity of the titanate nanotubes. The effects of each element technique as well as the synergy effects on decomposition of organic material were investigated.

In the paper entitled "*Synthesis of hollow CdS-TiO_2 microspheres with enhanced visible-light photocatalytic activity,*" Y. N. Huo et al. synthesized CdS-TiO_2 hollow microsphere via the hard-template preparation with polystyrene microspheres followed by ion-exchange approach. The introduction of CdS can effectively extend the photo-response of TiO_2 to visible-light region and improve the separation of photoinduced charges, thus enhances photocatalytic activity of decomposition of rhodamine B (RhB) in aqueous solution.

In the paper entitled "*Solar photocatalytic removal of chemical and bacterial pollutants from water using Pt/TiO_2-coated ceramic tiles,*" E. P. Yesodharan et al. immobilized Pt/TiO_2 on a ceramic tile in order to enhance the commercial viability of the catalyst by recycling. Optimum loading of Pt on TiO_2 was found to be 0.5%. This catalyst was found effective for the solar photocatalytic removal of chemical and bacterial pollutants from water. Once the parameters are optimized, the Pt/TiO_2/tile can find application in swimming pools, hospitals, water theme parks, and even industries for the decontamination of water.

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