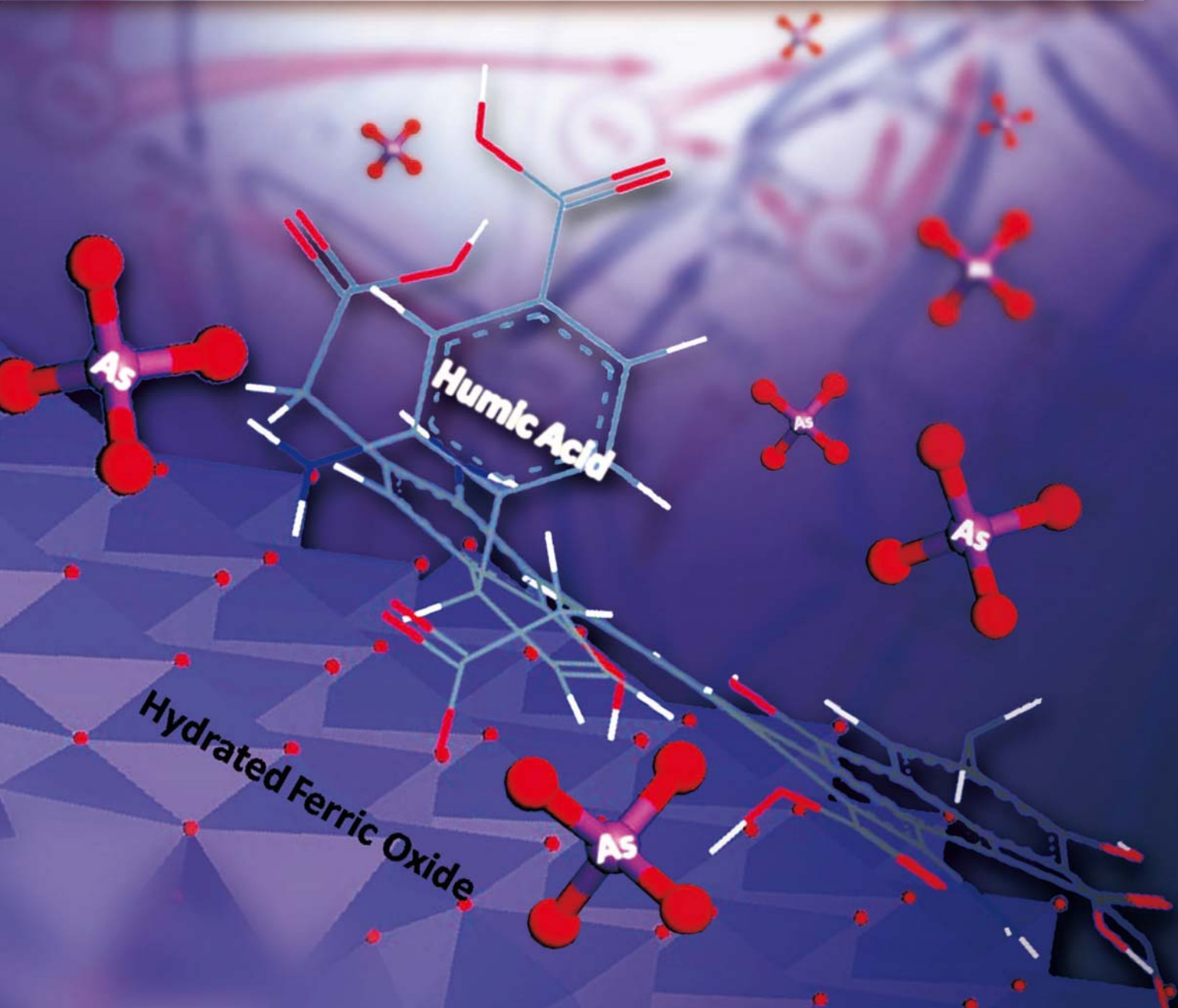


JES

JOURNAL OF
ENVIRONMENTAL
SCIENCES

ISSN 1001-0742
CN 11-2629/X

February 1, 2014 Volume 26 Number 2
www.jesc.ac.cn



Sponsored by
Research Center for Eco-Environmental Sciences
Chinese Academy of Sciences

CONTENTS

Aquatic environment

Removal of total cyanide in coking wastewater during a coagulation process: Significance of organic polymers Jian Shen, He Zhao, Hongbin Cao, Yi Zhang, Yongsheng Chen	231
Removal of arsenate with hydrous ferric oxide coprecipitation: Effect of humic acid Jingjing Du, Chuanyong Jing, Jinming Duan, Yongli Zhang, Shan Hu	240
Arsenic removal from groundwater by acclimated sludge under autohydrogenotrophic conditions Siqing Xia, Shuang Shen, Xiaoyin Xu, Jun Liang, Lijie Zhou	248
Characteristics of greenhouse gas emission in three full-scale wastewater treatment processes Xu Yan, Lin Li, Junxin Liu	256
Effect of temperature on anoxic metabolism of nitrites to nitrous oxide by polyphosphate accumulating organisms Zhijia Miao, Wei Zeng, Shuying Wang, Yongzhen Peng, Guihua Cao, Dongchen Weng, Guisong Xue, Qing Yang	264
Efficacy of two chemical coagulants and three different filtration media on removal of <i>Aspergillus flavus</i> from surface water Hamid Mohammad Al-Gabr, Tianling Zheng, Xin Yu	274
Beyond hypoxia: Occurrence and characteristics of black blooms due to the decomposition of the submerged plant <i>Potamogeton crispus</i> in a shallow lake Qiushi Shen, Qilin Zhou, Jingge Shang, Shiguang Shao, Lei Zhang, Chengxin Fan	281
Spatial and temporal variations of two cyanobacteria in the mesotrophic Miyun reservoir, China Ming Su, Jianwei Yu, Shenling Pan, Wei An, Min Yang	289
Quantification of viable bacteria in wastewater treatment plants by using propidium monoazide combined with quantitative PCR (PMA-qPCR) Dan Li, Tiezheng Tong, Siyu Zeng, Yiwen Lin, Shuxu Wu, Miao He	299
Antimony(V) removal from water by hydrated ferric oxides supported by calcite sand and polymeric anion exchanger Yangyang Miao, Feichao Han, Bingcai Pan, Yingjie Niu, Guangze Nie, Lu Lv	307
A comparison on the phytoremediation ability of triazophos by different macrophytes Zhu Li, Huiping Xiao, Shuiping Cheng, Liping Zhang, Xiaolong Xie, Zhenbin Wu	315
Biostability in distribution systems in one city in southern China: Characteristics, modeling and control strategy Pinpin Lu, Xiaojian Zhang, Chiqian Zhang, Zhangbin Niu, Shuguang Xie, Chao Chen	323

Atmospheric environment

Characteristics of ozone and ozone precursors (VOCs and NO _x) around a petroleum refinery in Beijing, China Wei Wei, Shuiyuan Cheng, Guohao Li, Gang Wang, Haiyang Wang	332
Identification of sources of lead in the atmosphere by chemical speciation using X-ray absorption near-edge structure (XANES) spectroscopy Kohei Sakata, Aya Sakaguchi, Masaharu Tanimizu, Yuichi Takaku, Yuka Yokoyama, Yoshio Takahashi	343
Online monitoring of water-soluble ionic composition of PM ₁₀ during early summer over Lanzhou City Jin Fan, Xiaoying Yue, Yi Jing, Qiang Chen, Shigong Wang	353
Effect of traffic restriction on atmospheric particle concentrations and their size distributions in urban Lanzhou, Northwestern China Suping Zhao, Ye Yu, Na Liu, Jianjun He, Jinbei Chen	362

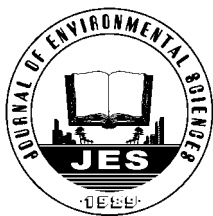
Environmental health and toxicology

A review on completing arsenic biogeochemical cycle: Microbial volatilization of arsines in environment Peipei Wang, Guoxin Sun, Yan Jia, Andrew A Meharg, Yongguan Zhu	371
Alginate modifies the physiological impact of CeO ₂ nanoparticles in corn seedlings cultivated in soil Lijuan Zhao, Jose R. Peralta-Videa, Bo Peng, Susmita Bandyopadhyay, Baltazar Corral-Diaz, Pedro Osuna-Avila, Milka O. Montes, Arturo A. Keller, Jorge L. Gardea-Torresdey	382
Humification characterization of biochar and its potential as a composting amendment Jining Zhang, Fan Lü, Chenghao Luo, Liming Shao, Pinjing He	390
Immigrant <i>Pantoea agglomerans</i> embedded within indigenous microbial aggregates: A novel spatial distribution of epiphytic bacteria Qing Yu, Anzhou Ma, Mengmeng Cui, Xuliang Zhuang, Guoqiang Zhuang	398
Remediation of nutrient-rich waters using the terrestrial plant, <i>Pandanus amaryllifolius</i> Roxb. Han Ping, Prakash Kumar, Bee-Lian Ong	404

Construction of a dual fluorescence whole-cell biosensor to detect <i>N</i> -acyl homoserine lactones	
Xuemei Deng, Guoqiang Zhuang, Anzhou Ma, Qing Yu, Xuliang Zhuang	415
Digestion performance and microbial community in full-scale methane fermentation of stillage from sweet potato-shochu production	
Tsutomu Kobayashi, Yueqin Tang, Toyoshi Urakami, Shigeru Morimura, Kenji Kida	423
Health risk assessment of dietary exposure to polycyclic aromatic hydrocarbons in Taiyuan, China	
Jing Nie, Jing Shi, Xiaoli Duan, Beibei Wang, Nan Huang, Xiuge Zhao	432
Acute toxicity formation potential of benzophenone-type UV filters in chlorination disinfection process	
Qi Liu, Zhenbin Chen, Dongbin Wei, Yuguo Du	440
Exposure measurement, risk assessment and source identification for exposure of traffic assistants to particle-bound PAHs in Tianjin, China	
Xiaodan Xue, Yan You, Jianhui Wu, Bin Han, Zhipeng Bai, Naijun Tang, Liwen Zhang	448

Environmental catalysis and materials

Fabrication of Bi ₂ O ₃ /TiO ₂ nanocomposites and their applications to the degradation of pollutants in air and water under visible-light	
Ashok Kumar Chakraborty, Md Emran Hossain, Md Masudur Rhaman, K M A Sobahan	458
Comparison of quartz sand, anthracite, shale and biological ceramsite for adsorptive removal of phosphorus from aqueous solution	
Cheng Jiang, Liyue Jia, Bo Zhang, Yiliang He, George Kirumba	466
Catalytic bubble-free hydrogenation reduction of azo dye by porous membranes loaded with palladium nanoparticles	
Zhiqian Jia, Huijie Sun, Zhenxia Du, Zhigang Lei	478
Debromination of decabromodiphenyl ether by organo-montmorillonite-supported nanoscale zero-valent iron:	
Preparation, characterization and influence factors	
Zhihua Pang, Mengyue Yan, Xiaoshan Jia, Zhenxing Wang, Jianyu Chen	483
Serial parameter: CN 11-2629/X*1989*m*261*en*P*30*2014-2	

Available online at www.sciencedirect.com

Journal of Environmental Sciences

www.jesc.ac.cn

Fabrication of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ nanocomposites and their applications to the degradation of pollutants in air and water under visible-light

Ashok Kumar Chakraborty^{1,*}, Md Emran Hossain¹, Md Masudur Rhaman¹, K M A Sobahan²

¹. Department of Applied Chemistry and Chemical Technology, Islamic University, Kushtia-7003, Bangladesh

². Department of Applied Physics, Electronics and Communication Engineering, Islamic University, Kushtia-7003 Bangladesh

ARTICLE INFO

Article history:

Received 31 March 2013

revised 19 July 2013

accepted 29 July 2013

Keywords:

nanoheterojunction

$\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite

photocatalyst

pollutants

visible-light

DOI: 10.1016/S1001-0742(13)60428-3

ABSTRACT

A nanoheterojunction composite photocatalyst $\text{Bi}_2\text{O}_3/\text{TiO}_2$ working under visible-light ($\lambda \geq 420$ nm) was prepared by combining two semiconductors Bi_2O_3 and TiO_2 varying the $\text{Bi}_2\text{O}_3/\text{TiO}_2$ molar ratio. Maleic acid was employed as an organic binder to unite Bi_2O_3 and TiO_2 nanoparticles. The SEM, TEM, XRD and diffuse reflectance spectra were utilized to characterize the prepared $\text{Bi}_2\text{O}_3/\text{TiO}_2$ nanoheterojunction. The nanocomposite exhibited unusual high photocatalytic activity in decomposing 2-propanol in gas phase and phenol in aqueous phase and, evolution of CO_2 under visible light irradiation while the end members exhibited low photocatalytic activity. The composite was optimized to 5 mol% $\text{Bi}_2\text{O}_3/\text{TiO}_2$. The remarkable high photocatalytic efficiency originates from the unique relative energy band position of Bi_2O_3 and TiO_2 as well as the absorption of visible light by Bi_2O_3 .

Introduction

Photocatalytic degradation of organic pollutants on semiconductor surfaces has attracted much attention as a ‘green’ technique. TiO_2 , commonly regarded as one of the most active and stable photocatalysts, has long been investigated for environmental applications (Chen and Mao, 2007; Fujishima et al., 2000; Kubacka et al., 2012). However, the band gap of TiO_2 is 3.2 eV which requires the excitation wavelength longer than 387.5 nm. It is a major disadvantage of TiO_2 using as a photocatalyst working under visible-light ($\lambda \geq 420$ nm). The high rate of electron-hole recombination often results in a low quantum yield and poor efficiency of photocatalytic reactions. Therefore, the development of photocatalysts with a high activity under visible-light irradiation is required. However, an efficient photocatalytic process over a semiconductor de-

mands the high mobility for photoinduced electron-hole separation and for their transportation in crystal lattice, which would lower the probability for electron-hole recombination. Considerable efforts have been made to dope TiO_2 with various metals (In et al., 2007; Wang et al., 2000; Song et al., 2012) as well as non-metals so as to make it photoactive under visible light (Anpo and Takeuchi, 2003; Ho et al., 2012; Sato, 1986). Combination of semiconductors is considered as an effective way to improve the photostimulated electron-hole separation and effectively inhibits their recombination. The major characteristic of this technique is to assemble a heterojunction interface between wide and narrow band gap semiconductors with matching energy band potentials. In this way, electric field assisted transportation of charges from one particle to the other through interfaces is favorable for the electron-hole separations in the composite materials, and thus the electron and hole could move to the surface of the semiconductors. The extensive research published on this composite system were mostly focused on TiO_2 based pho-

* Corresponding author. E-mail: akc.iu@yahoo.co.uk

photocatalysts, such as WO_3/TiO_2 , $\text{In}_2\text{O}_3/\text{TiO}_2$, $\text{SiO}_2/\text{TiO}_2$, MgO/TiO_2 , $\text{Fe}_2\text{O}_3/\text{TiO}_2$, $\text{Bi}_2\text{O}_3/\text{TiO}_2$, $\text{FeTiO}_3/\text{TiO}_2$ and so on (Bian et al., 2008; Chakraborty and Kebede, 2012; Ding et al., 2000; Gondal et al., 2004; Gao et al., 2008; Kim et al., 2009; Naeem and Ouyang, 2013; Song et al., 2001).

Bi_2O_3 , with a band gap of 2.8 eV is known as p-type semiconductor (Hameed et al., 2008; Lin et al., 2007; Xu and Schoonen, 2000), and it has widely been used in gas sensors, optical coatings and solid oxide fuel cells. Moreover, Bi_2O_3 has proved to be a good photocatalyst for water splitting and pollutant decomposing under visible-light irradiation (Adamian et al., 1996; Fan et al., 2005; Fruth et al., 2005; Leontie et al., 2002; Yang et al., 2004; Zhou et al., 2009). Bi_2O_3 semiconductor possesses good electron (e^-) conduction ability. On the other hand, TiO_2 has a loosely packed structure as well as higher degree of openness (Lin et al., 2006), which favors the hole (h^+) transport in the crystal lattice by the available displacement of the oxygen atoms through the strong vibration model (associated with O^-). Thus, in such a heterojunction system, one component, Bi_2O_3 of the composite with fair electron (e^-) conductivity cooperates with a semiconducting material, TiO_2 with an open structure and the fair mobility for the hole (h^+) conduction. Hence, when $\text{Bi}_2\text{O}_3/\text{TiO}_2$ heterojunction is formed, the inner electric field will be established in the interface (Lin et al., 2007). The photogenerated electron-hole pairs will be separated effectively by the inner electric field, and the photocatalytic activity is enhanced. Such a phenomenon gives us an implication for a design scheme for the efficient heterojunction photocatalysts between Bi_2O_3 and TiO_2 .

In the present study, we have developed a heterojunction $\text{Bi}_2\text{O}_3/\text{TiO}_2$ system utilizing maleic acid as an organic binder. The role of maleic acid is to bind Bi_2O_3 and TiO_2 using two end carboxylic functional groups. The prepared $\text{Bi}_2\text{O}_3/\text{TiO}_2$ nanoheterojunction was applied to the photocatalytic degradation of 2-propanol in gas phase and phenol in aqueous phase under visible-light irradiation. The composite $\text{Bi}_2\text{O}_3/\text{TiO}_2$ demonstrated enhanced photocatalytic efficiency compare to that of Bi_2O_3 and Degussa P25 under-visible light irradiation.

1 Materials and methods

1.1 Preparation of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite

$\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite photocatalyst was prepared by utilizing maleic acid. Degussa P25 was chosen as the standard TiO_2 nanoparticle. In a typical preparation for 5/95 $\text{Bi}_2\text{O}_3/\text{TiO}_2$ (the composite consisting 5 mol% Bi_2O_3 and 95 mol% TiO_2) heterojunction photocatalyst, 0.3070 g of Bi_2O_3 (99.9% Aldrich) was suspended in 40 mL of absolute ethanol. A 0.1987 g of maleic acid (99.99% Aldrich) dissolved in absolute ethanol was added to this

suspension. Afterward, 1 g of TiO_2 nanoparticle was added to the above suspension and stirred vigorously for 6 hr at ambient condition. Subsequently, the suspension was centrifuged and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite was washed several times with ethanol to remove unreacted maleic acid. The composite was dried at 60°C in an oven overnight. After that, the $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite was annealed at 300°C for 3 hr and used as catalyst for photocatalytic degradation reactions without further treatment.

1.2 Characterization

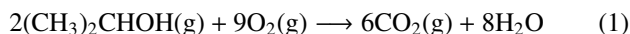
The crystallographic phase of prepared samples was characterized by a Rigaku Multiflex diffractometer with monochromated high-intensity Cu $K\alpha$ radiation. XRD scanning was performed under ambient conditions over the 2θ region of 20°–60° at a rate of 2°/min (40 kV, 20 mA). The morphologies of the prepared powders were examined by a scanning electron microscope (Hitachi S-4500). The surface morphology of the $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite was analyzed by a transmission electron microscope (TEM, Philips CM30) operating at 250 kV. For this measurement, 1 mg of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite was dispersed in 50 mL of ethanol, and a drop of the suspension was then spread on a holey amorphous carbon film deposited on a Ni grid (JEOL Ltd.). Diffuse reflectance spectra were also obtained for the dry-pressed disk sample using a UV-Visible spectrometer (Perkin-Elmer Lambda 40).

1.3 Measurement of photocatalytic efficiency

The composite $\text{Bi}_2\text{O}_3/\text{TiO}_2$ films were tested as photocatalysts for the decomposition of 2-propanol in gas phase. An aqueous suspension containing 4×10^{-4} mol of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite were spread on a 2.5×2.5 Pyrex glass in the film form, which was subsequently dried at 50°C for 2 hr. The gas reactor system used for this photocatalytic reaction is described elsewhere (Kwon et al., 2000). The reaction cell was placed closed to GC and it was connected to GC of which one window is open and the cutoff filter was set in front of this window face of the reaction cell to ensure the desired irradiation condition. The volume of the reaction cell was 200 mL. The film was located at the center of this gastight reactor. After evacuation of the reactor, 0.08 μL of 2-propanol mixed in 1.6 μL of water was injected into the reactor. The total pressure of the reactor was then controlled to 750 Torr by addition of oxygen gas. Under these conditions, 2-propanol and H_2O remained in the vapor phase. The reactor was irradiated from a 300 W Xenon lamp equipped with a water filter and UV filter (< 420 nm, Oriel) to cut off infrared and UV component, respectively. On the surface of the photocatalytic film, the overall light intensity was 0.1 W/cm^2 . After irradiation for a certain period of time, 0.5 mL of the gas in the reactor was automatically picked up and sent to a gas chromatograph (Agilent Technologies, Model 6890N). The whole photocatalytic reaction was batch process. The

evolved CO₂ and remnant 2-propanol were detected by a methanizer installed between the GC column outlet and the FID detector.

The initial concentration of gaseous 2-propanol in the reactor was kept to 117 ppm in volume (ppmV). Thus the ultimate concentration of evolved CO₂ will be 351 ppmV when the whole 2-propanol is completely decomposed, as shown in the following Reaction:



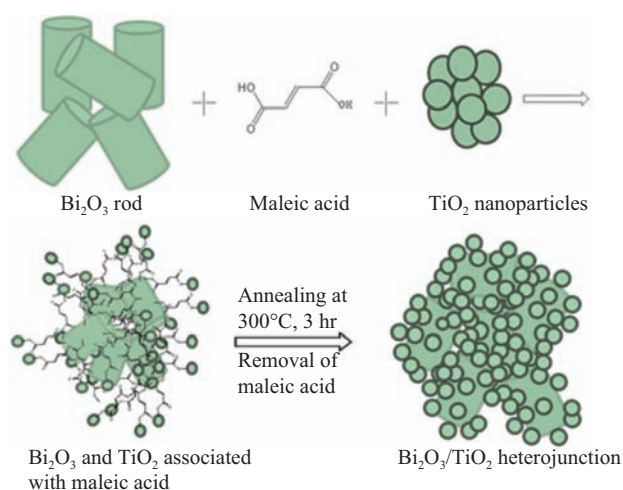
The photocatalytic activity of the prepared nanocomposite sample was evaluated by the decomposition of phenol in aqueous solution. Each photocatalyst was dispersed in water and then mixed with phenol aqueous solution in darkness. Total volume of the aqueous solution for the photocatalytic reaction was 50 mL, and the concentration of phenol was 1.00×10^{-4} mol/L, and 1.00×10^{-4} mol of photocatalytic sample was suspended in this solution. The prepared solution was then irradiated by a 300-W Xe lamp with an UV cutoff filter (< 420 nm, Oriol) and a water filter to remove IR. The concentration of residual phenol after irradiation was evaluated from the intensity of the characteristic absorption peak.

Prior to photocatalytic reactions, the reaction medium were magnetically stirred for 30 min in the dark, and the concentration of the pollutants were monitored. The concentration of pollutants did not change after stirring for 30 min which indicates that 30 min is enough to reach the adsorption equilibrium of organics. Blank experiments were also performed at the same experimental condition except photocatalyst.

2 Results and discussion

In preparing Bi₂O₃/TiO₂ heterojunction, maleic acid has been considered. The function of maleic acid is to chemically combine Bi₂O₃ and TiO₂ nanoparticles utilizing the two carboxylic functional groups as shown in **Scheme 1**.

Thus, the Bi₂O₃ and TiO₂ nanoparticles move towards each other and, Bi₂O₃ and TiO₂ could make an intimate contact which is vital for interfacial charge transfer between the two semiconductors. However, the composite was annealed for 300°C to eliminate maleic acid. Hence, the maleic could not influence the photocatalytic activity. The SEM images of pure Bi₂O₃ rod and 5/95 Bi₂O₃/TiO₂ composite structure are shown in **Fig. 1**. Images in **Fig. 1a**, **b** reveal the Bi₂O₃ exhibits a rod like morphology, where



Scheme 1 Schematic illustration of the formation mechanism of Bi₂O₃/TiO₂ heterojunction.

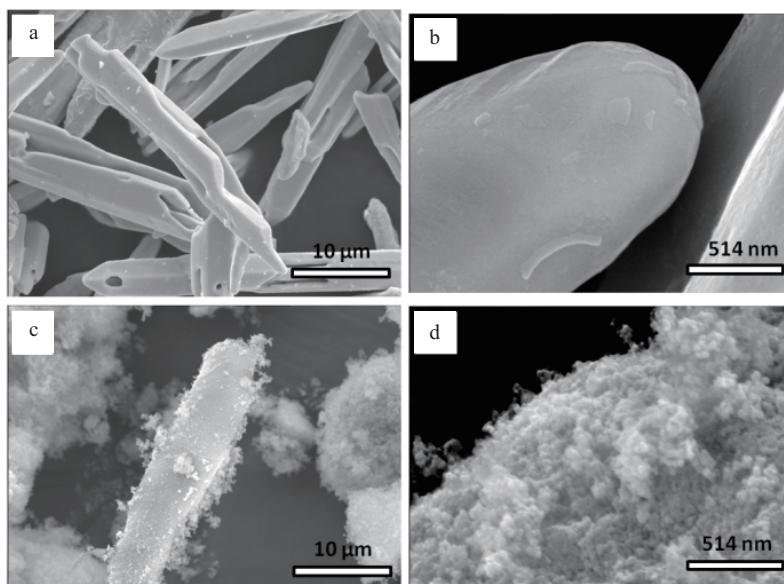


Fig. 1 SEM images of Bi₂O₃ (a, b) and Bi₂O₃/TiO₂ (c, d) nanocomposite calcined at 300°C for 3 hr.

the length and diameter of the rods varied over the ranges of 4–33 and 0.4–3.0 μm , respectively. Maleic acid plays a crucial role in combining Bi_2O_3 and TiO_2 nanoparticles. The surface of Bi_2O_3 is fine and smooth as shown in **Fig. 1a, b**. The surface morphology of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite is shown in **Fig. 1c, d**. The surface of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite is completely different from pure Bi_2O_3 and uneven which is shown in **Fig. 1c**. To reveal the detail structure of the composite, **Fig. 1c** was further magnified and shown in **Fig. 1d**. **Figure 1d** clearly demonstrates the surface structure of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite that the surface of heterojunction is rough and uniformly covered with TiO_2 nanoparticles.

In order to investigate the surface structure and the interface of the composite very closely, the sample of 5/95 $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite calcined at 300°C was chosen to take TEM and HRTEM characterization. **Figure 2** gives an overview of the typical TEM image of the 5/95 $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite. Nanoparticles of Degussa P25 with mean size of about 20–30 nm can be observed over the entire surface of Bi_2O_3 . The high resolution TEM image of the magnified view of the composite is shown in **Fig. 2c, d**. A clear and sharp interface can be found in these

images. It is indicated that the two components of the composite are contacted well after the preparation and subsequent heat treatment. The high crystalline quality and the sharp interface between Bi_2O_3 and TiO_2 nanoparticles are advantageous for the separation of the photogenerated charge carriers.

Figure 3 shows the XRD patterns of TiO_2 nanoparticles, Bi_2O_3 and several compositions of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite samples. The diffraction peaks at 21.82° , 27.48° , 28.12° , 32.61° , 46.49° , 52.56° and 54.99° were indexed to the (020), (120), (012), (211), (223), (321) and (241) planes, respectively to the pure Bi_2O_3 (JCPDS #72-0398). As shown in **Fig. 3** that the diffraction planes of (101), (004), (200) and (211) clearly indicate the presence of anatase and that of (110) and (101) planes demonstrate the existence of rutile phase of TiO_2 nanoparticles. Hence, Degussa P25 contains anatase and rutile phase. It is worth mentioning that the XRD patterns of the composites $\text{Bi}_2\text{O}_3/\text{TiO}_2$ showed the diffraction peaks of phases of Bi_2O_3 and TiO_2 without any other impurity phases suggesting that there was no sufficient chemical reaction took place among the component Bi_2O_3 and TiO_2 of the composite during the preparation of heterojunction and subsequent heat-

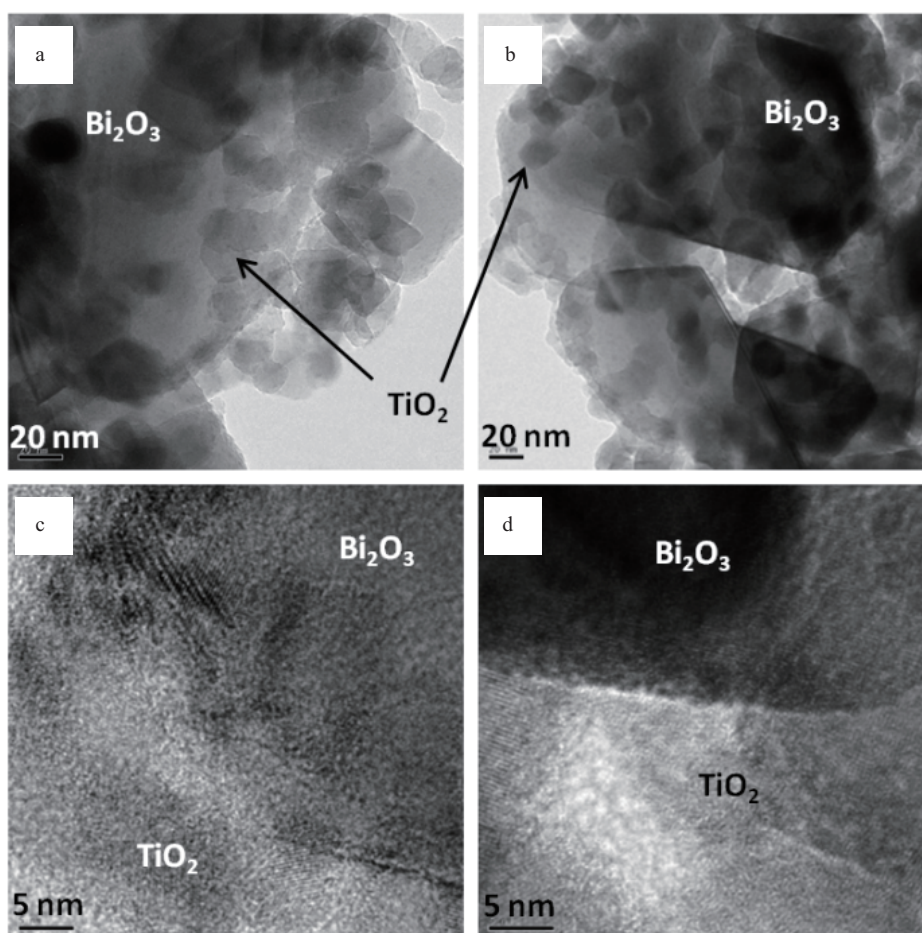


Fig. 2 TEM (a, b) and HRTEM (b, c) images of 5/95 $\text{Bi}_2\text{O}_3/\text{TiO}_2$ heterojunction calcined at 300°C for 3 hr.

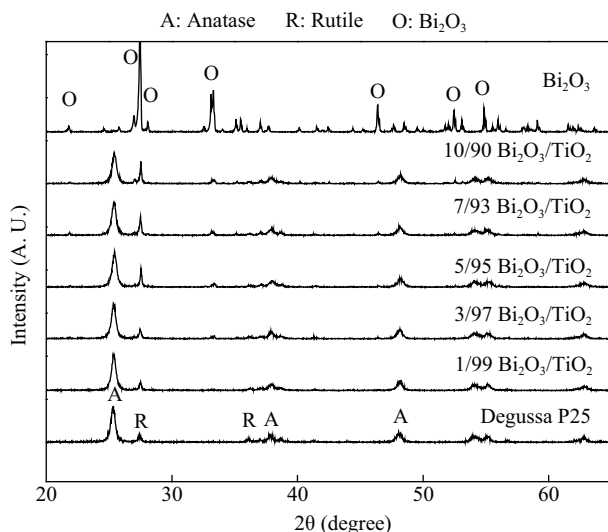


Fig. 3 X-ray diffraction pattern of TiO_2 , Bi_2O_3 and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite synthesized at 300°C for 3 hr with several composition of Bi_2O_3 and TiO_2 .

treatment at 300°C . As shown in **Fig. 3** that the intensity of the major peak of Bi_2O_3 of (120) plane at 27.48° gradually increases with increasing amount of Bi_2O_3 from 0% to 100% in the composite $\text{Bi}_2\text{O}_3/\text{TiO}_2$. However, the annealing temperature 300°C is sufficiently enough to make a tight contact between Bi_2O_3 and TiO_2 nanoparticles as shown in **Fig. 2c** and **d**. The well contact will facilitate interparticle electron transfer between Bi_2O_3 and TiO_2 .

The UV-Vis diffuse reflectance spectra of the as-prepared composite powders are shown in **Fig. 4**. The band gaps of Bi_2O_3 and TiO_2 were reported to be 2.8 and 3.2 eV, respectively (Hameed et al., 2008; Xu and Schoonen, 2000). The optical absorptions of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite powders start at about 450 nm, corresponding to the absorption edge of Bi_2O_3 . The second absorption edge at about 387 nm can be attributed to the TiO_2 nanoparticles. It is mentionable from **Fig. 4** that with increasing the

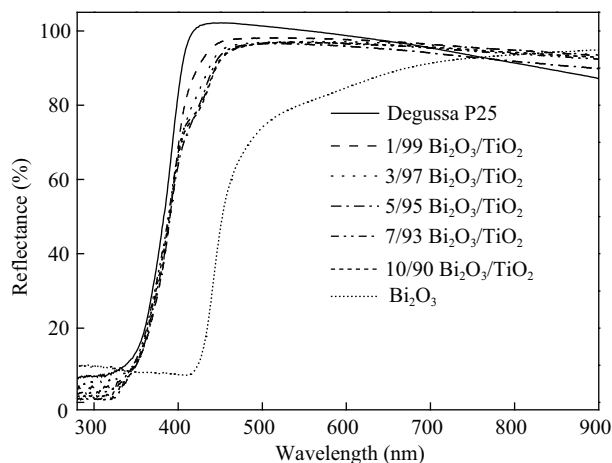


Fig. 4 UV-Visible diffuse reflectance spectra of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite, Bi_2O_3 and TiO_2 nanoparticle.

component of the Bi_2O_3 in the composite $\text{Bi}_2\text{O}_3/\text{TiO}_2$ system, the absorption in visible-light of the composite powders also increased. These results revealed that the composite powders could absorb the photon in the visible region of the solar spectrum.

The dependence of photocatalytic activity on the composition of the composite $\text{Bi}_2\text{O}_3/\text{TiO}_2$ system under visible light ($\lambda \geq 420$ nm) irradiation is represented in **Fig. 5**. The catalyst samples were evaluated for the degradation of 2-propanol and the production of CO_2 in gas phase and phenol in aqueous phase under visible light irradiation at room temperature. It is generally accepted that IP is first decomposed to acetone and finally to CO_2 . Thus, we measured the photocatalytic decomposition behavior of IP first. **Figure 5a** shows the visible light ($\lambda \geq 420$ nm) activity of the

Bi_2O_3 , TiO_2 and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite photocatalyst for the decomposition of 2-propanol. Bi_2O_3 , TiO_2 exhibited negligible activity, while $\text{Bi}_2\text{O}_3/\text{TiO}_2$ in several compositions showed higher visible light induced photocatalytic activity. When photocatalytic reaction proceeded for 2 hr, the decomposition degrees of gaseous 2-propanol was 75% with 5/95 $\text{Bi}_2\text{O}_3/\text{TiO}_2$ heterojunction as shown in **Fig. 5a**.

The photocatalytic efficiency of the composite sample was investigated for the evolution of CO_2 . **Figure 5b** displays the photocatalytic behavior of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite samples including the component of the composite Bi_2O_3 and Degussa P25 to compare the efficiency. The composite $\text{Bi}_2\text{O}_3/\text{TiO}_2$ samples with a wide range of composition demonstrated significant production of CO_2 . As that of the decomposition of gaseous 2-propanol, 5/95 $\text{Bi}_2\text{O}_3/\text{TiO}_2$ demonstrated the highest activity among the composition for the production CO_2 . After 2 hr of visible light ($\lambda \geq 420$ nm) irradiation, the detected CO_2 yield was reached to a stable value of 21 ppmV, whereas both the bare Bi_2O_3 and Degussa P25 showed only 2.1 and 2.9 ppmV, respectively.

We evaluated the photocatalytic activities of these catalysts in aqueous phase for the decomposition of phenol under visible light ($\lambda \geq 420$ nm). The remnant phenol after the irradiation of visible light was analyzed from its characteristic absorption peak detected by UV-vis spectroscopy. **Figure 5c** shows decomposition rates of phenol with several $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composition, Bi_2O_3 , and P25 samples as a function of irradiation time. It was found that the photocatalytic activity of the composite was increased with increasing Bi_2O_3 . Similar results were obtained as that of decomposition of gaseous 2-propanol, 5/95 $\text{Bi}_2\text{O}_3/\text{TiO}_2$ showed the highest photocatalytic efficiency in decomposing phenol in aqueous phase. The decomposition of phenol was 69% with this composition in 2 hr of visible light irradiation. Blank experiments as shown in **Fig. 5** that the photodecomposition of the organics in gas and aqueous phases was not took place.

Coupling of TiO_2 with other narrow band gap semi-

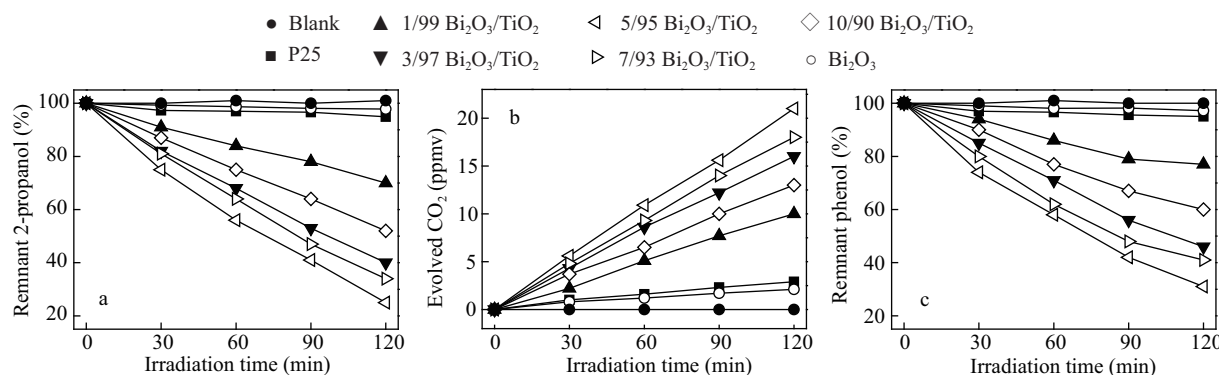
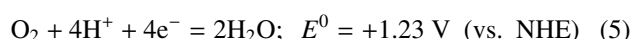
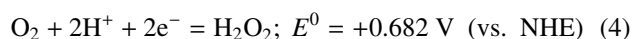
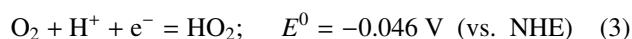
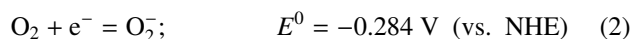


Fig. 5 Photocatalytic activity of TiO_2 , Bi_2O_3 and $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite for (a) degradation of 2-propanol, (b) evolution of CO_2 and (c) decomposition of phenol under visible light ($\lambda \geq 420$ nm) irradiation.

conductors has been extensively studied to promote the separation of photogenerated charge-carriers and/or to extend the absorption of photon up to visible-region as well as to enhance the photocatalytic behavior in decomposing organic pollutants. The present investigated heterojunction $\text{Bi}_2\text{O}_3/\text{TiO}_2$ exhibited extraordinary high photocatalytic efficiency but both the components Bi_2O_3 and TiO_2 demonstrated very low photocatalytic activity under visible-light irradiation. Presumably, the unusual high photocatalytic activity of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ originates from the unique relative energy band positions of these two semiconductors (Chai et al., 2009; Chakraborty and Kebede, 2012; Chakraborty et al., 2012; Gao et al., 2008, 2010; Kim et al., 2009) and the absorption of visible light by Bi_2O_3 . As shown in **Fig. 6**, the VB of Bi_2O_3 is located below than that of TiO_2 by 0.22V, while CB of Bi_2O_3 is positioned below than that of the TiO_2 by 0.62V (Hameed et al., 2008; Xu and Schoonen, 2000). During visible-light irradiation, Bi_2O_3 absorbs visible-light as the band gap of Bi_2O_3 is 2.8 eV and the electrons (e^-) in the VB of Bi_2O_3 would be excited to its CB and the VB of Bi_2O_3 become partially vacant, and the generated holes (h^+) in the VB of Bi_2O_3 can be transferred to VB of TiO_2 , since the VB of TiO_2 is located higher than the VB of Bi_2O_3 . Thus, the holes (h^+) in the VB of TiO_2 can be utilized for various oxidation reactions.

The CB potential of Bi_2O_3 is +0.33V. Hence, the reduc-

tion of oxygen utilizing single electron is quite difficult (Reactions (2) and (3)). Thus, the CB electrons of Bi_2O_3 would be consumed through multi-electron process (Abe et al., 2008; Liu et al., 2009; Rawal et al., 2012) according to following reactions (Reactions (4) and (5)).



By the inter-semiconductor hole-transfer mechanism, the photogenerated charge-carriers can be effectively separated so that this heterojunction can utilize the visible-light in mineralizing organic pollutants. In this photocatalytic system, TiO_2 works as principal photocatalyst, while the role of Bi_2O_3 is a sensitizer absorbing visible-light to sensitize TiO_2 . We expect that this synthesis process can also be extended to the development of other heterojunction type composite photocatalysts working under sunlight to remove organic pollutants.

3 Conclusions

A series of $\text{Bi}_2\text{O}_3/\text{TiO}_2$ heterocomposite photocatalyst have been prepared by utilizing maleic acid. It was observed that the composite could absorb energy up to visible-region. The new composite demonstrated notably higher photocatalytic activity for the degradation of 2-propanol in gas phase and phenol in aqueous phase and, evolution of CO_2 than Bi_2O_3 and TiO_2 nanoparticles under visible light ($\lambda \geq 420$ nm) irradiation. After 2 hr of visible light ($\lambda \geq 420$ nm) irradiation, the decomposition of 2-propanol and phenol is 75% and 69%, respectively and, the evolution of CO_2 is about 7.5 times that of Degussa P25. TiO_2 works as a principal photocatalyst while Bi_2O_3 acts as the photosensitizer absorbing visible light in the $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite.

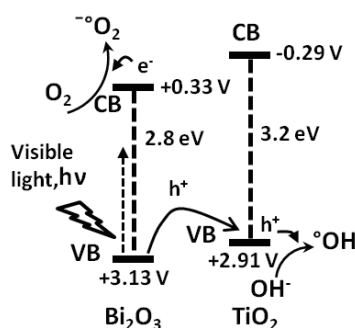


Fig. 6 Proposed mechanism for the photocatalytic degradation of organic pollutants over $\text{Bi}_2\text{O}_3/\text{TiO}_2$ heterojunction photocatalyst.

The extraordinary high photocatalytic efficiency of the $\text{Bi}_2\text{O}_3/\text{TiO}_2$ composite originates from the unique relative energy band position of the component semiconductors. The VB level of Bi_2O_3 (+3.13V vs. NHE) is located lower than that of TiO_2 (+2.91V vs. NHE). The visible light generated hole (h^+) in the VB of Bi_2O_3 can be transferred to the VB of TiO_2 . Therefore, with the irradiation of visible light the holes (h^+) in the VB of TiO_2 can induce the complete decomposition of organic pollutants.

Acknowledgments

The authors gratefully acknowledge the Evonik Degussa GmbH for Degussa P25.

REFERENCES

- Abe, R., Takami, H., Murakami, N., Ohtani, B., 2008. Pristine simple oxides as visible light driven photocatalysts: Highly efficient decomposition of organic compounds over platinum-loaded tungsten oxide. *J. Amer. Chem. Soc.* 130, 7780–7781.
- Bian, Z. F., Zhu, J., Wang, S. H., Cao, Y., Qian, X. F., Li, H. X., 2008. Self-assembly of active $\text{Bi}_2\text{O}_3/\text{TiO}_2$ visible photocatalyst with ordered mesoporous structure and highly crystallized anatase. *J. Phys. Chem.* 112, 6258–6262.
- Chai, S. Y., Kim, Y. J., Jung, M. H., Chakraborty, A. K., Jung, D. W., Lee, W. I., 2009. Heterojunctioned $\text{BiOCl}/\text{Bi}_2\text{O}_3$, A new visible light photocatalyst. *J. Catal.* 262, 144–149.
- Chakraborty, A. K., Kebede, M. A., 2012a. Preparation and characterization of $\text{WO}_3/\text{Bi}_3\text{O}_4\text{Cl}$ nanocomposite and its photocatalytic behavior under visible light irradiation. *Reaction Kinetics, Mechanism, Catal.* 106, 83–98.
- Chakraborty, A. K., Ganguli, S., Kebede, M. A., 2012. Photocatalytic degradation of 2-propanol and phenol using Au loaded MnWO_4 nanorod under visible light irradiation. *J. Cluster Sci.* 23, 437–448.
- Chakraborty, A. K., Kebede, M. A., 2012b. Efficient decomposition of organic pollutants over $\text{In}_2\text{O}_3/\text{TiO}_2$ nanocomposite photocatalyst under visible light irradiation. *J. Cluster Sci.* 23, 247–257.
- Ding, Z., Hu, X., Lu, G. Q., Yue, P. L., Greenfield, P. F., 2000. Novel silica gel supported TiO_2 photocatalyst synthesized by CVD method. *Langmuir* 16, 6216–6222.
- Fan, H. T., Teng, X. M., Pan, S. S., Ye, C., Li, G. H., Zhang, L. D., 2005. Optical properties of $\delta\text{-Bi}_2\text{O}_3$ thin films grown by reactive sputtering. *Appl. Phys. Lett.* 87, 231916–231918.
- Fruth, V., Popa, M., Berger, D., Ramer, R., Gartner, M., Ciulei, A. et al., 2005. Deposition and characterisation of bismuth oxide thin films. *J. Eur. Ceram. Soc.* 25, 2171–2174.
- Fujishima, A., Rao, T. N., Tryk, D. A., 2000. Titanium dioxide photocatalysis. *J. Photochem. Photobiol. C* 1, 1–21.
- Gao, B. F., Kim, Y. J., Chakraborty, A. K., Lee, W. I., 2008. Efficient decomposition of organic compounds with $\text{FeTiO}_3/\text{TiO}_2$ heterojunction under visible light irradiation. *Appl. Catal. B: Environ.* 83, 202–207.
- Gao, B. F., Chakraborty, A. K., Yang, J. M., Lee, W. I., 2010. Visible-light photocatalytic activity of $\text{BiOCl}/\text{Bi}_3\text{O}_4\text{Cl}$ nanocomposites. *Bull. Korean Chem. Soc.* 31, 1941–1944.
- Gondal, M. A., Hameed, A., Yamani, Z. H., Suwaiyan, A., 2004. Laser induced photo-catalytic oxidation/splitting of water over $\alpha\text{-Fe}_2\text{O}_3$, WO_3 , TiO_2 and NiO catalysts: Activity comparison. *Chem. Phys. Lett.* 385, 111–115.
- Hameed, A., Montini, T., Gombac, V., Fornasiero, P., 2008. Surface phases and photocatalytic activity correlation of $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_4\text{-x}$ nanocomposite. *J. Amer. Chem. Soc.* 130, 9658–9659.
- In, S., Orlov, A., Berg, R., Garcia, F., Jimenez, S. P., Tikhov, M. S. et al., 2007. Effective visible light-activated B-doped and B, N-codoped TiO_2 photocatalysts. *J. Amer. Chem. Soc.* 129, 13790–13791.
- Kim, Y. J., Gao, B., Han, S. Y., Jung, M. H., Chakraborty, A. K., Ko, T. et al., 2009. Heterojunction of FeTiO_3 nanodisc and TiO_2 nanoparticle for a novel visible light photocatalyst. *J. Phys. Chem. C* 113, 19179–19184.
- Kubacka, A., Fernández-García, M., Colón, G., 2012. Advanced nanoarchitectures for solar photocatalytic applications. *Chem. Rev.* 112, 1555–1614.
- Kwon, Y. T., Song, K. Y., Lee, W. I., Choi, G. J., Do, Y. R., 2000. Photocatalytic behavior of WO_3 -loaded TiO_2 in an oxidation reaction. *J. Catal.* 191, 192–199.
- Leontie, L., Caraman, M., Alexe, M., Harnagea, C., 2002. Structural and optical characteristics of bismuth oxide thin films. *Surf. Sci.* 507–510, 480–485.
- Lin, X. P., Xing, J. C., Wang, W. D., Shan, Z. C., Xu, F. F., Huang, F. Q., 2007. Photocatalytic activities of heterojunction semiconductors $\text{Bi}_2\text{O}_3/\text{BaTiO}_3$: A strategy for the design of efficient combined photocatalysts. *J. Phys. Chem. C* 111, 18288–18293.
- Lin, X. P., Huang, F. Q., Wang, W. D., Wang, Y. M., Xia, Y. J., Shi, L. L., 2006. Photocatalytic activities of $\text{M}_2\text{Sb}_2\text{O}_7$ ($\text{M} = \text{Ca}, \text{Sr}$) for degrading methyl orange. *Appl. Catal.* 313, 218–223.
- Liu, G., Wang, L. Z., Sun, C. H., Yan, X. X., Wang, X. W., Chen, Z. G. et al., 2009. Band-to-band visible-light photon excitation and photoactivity induced by homogeneous nitrogen doping in layered titanates. *Chem. Mater.* 21, 1266–1274.
- Naeem, K., Ouyang, F., 2013. Influence of supports on photocatalytic degradation of phenol and 4-chlorophenol in aqueous suspensions of titanium dioxide. *J. Environ. Sci.* 25, 399–404.
- Rawal, S. B., Chakraborty, A. K., Kim, Y. J., Kim, H. J., Lee, W. I., 2012. Double-heterojunction structure of $\text{Sb}_3\text{Sn}_2\text{-xO}_2/\text{TiO}_2/\text{CdSe}$ for efficient decomposition of gaseous 2-propanol under visible-light irradiation. *RSC Advances* 2, 622–630.
- Song, K. Y., Park, M. K., Kwon, Y. T., Lee, H. W., Chung, W. J., Lee, W. I., 2001. Preparation of transparent particulate $\text{MoO}_3/\text{TiO}_2$ and WO_3/TiO_2 films and their photocatalytic properties. *Chem. Mater.* 13, 2349–2355.
- Wang, C., Bahnemann, D. W., Dohrmann, J. K., 2000. A novel preparation of iron-doped TiO_2 nanoparticles with enhanced photocatalytic activity. *Chem. Commun.* 16, 1539–1540.
- Xu, Y., Schoonen, M. A. A., 2000. The absolute energy positions of conduction and valence bands of selected semiconducting minerals. *Amer. Miner.* 85, 543–556.
- Yang, B. J., Mo, M. S., Hu, H. M., Li, C., Yang, X. G., Li, Q. et al., 2004. A Rational self-sacrificing template route to $\beta\text{-Bi}_2\text{O}_3$ nanotube arrays. *Eur. J. Inorg. Chem.* 2004, 1785–1787.
- Song, S. Z., Sheng, Z. Y., Liu, Y., Wang, H. Q., Wu, Z. B., 2012. Influences of pH value in deposition-precipitation synthesis process on Pt-doped TiO_2 catalysts for photocatalytic oxidation of NO. *J. Environ. Sci.* 24, 1519–1524.
- Sato, S., 1986. Photocatalytic activity of NO_x -doped TiO_2 in the visible light region. *Chem. Phys. Lett.* 123, 126–128.

- Adamian, Z. N., Abovian, H. V., Aroutiounian, V. M., 1996. Smoke sensor on the base of Bi_2O_3 sesquioxide. *Sens. Actuat. B: Chem.* 35, 241–243.
- Anpo, M., Takeuchi, M., 2003. The design and development of highly reactive titanium oxide photocatalysts operating under visible light irradiation. *J. Catal.* 216, 505–516.
- Chen, X. B., Mao, S. S., 2007. Titanium dioxide nanomaterials: Synthesis, properties, modifications, and applications. *Chem. Rev.* 107, 2891–2959.
- Zhou, L., Wang, W. Z., Xu, H. L., Sun, S. M., Shang, M., 2009. Bi_2O_3 Hierarchical nanostructures: Controllable synthesis, growth mechanism, and their application in photocatalysis. *Chem. A Eur. J.* 15, 1776–1782.
- Ho, L. N., Ong, S. A., Osman, H., Chong, F. M., 2012. Enhanced photocatalytic activity of fish scale loaded TiO_2 composites under solar light irradiation. *J. Environ. Sci.* 24, 1142–1148.



Editorial Board of Journal of Environmental Sciences

Editor-in-Chief

Hongxiao Tang Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

Associate Editors-in-Chief

Jiuhui Qu Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China
Shu Tao Peking University, China
Nigel Bell Imperial College London, United Kingdom
Po-Keung Wong The Chinese University of Hong Kong, Hong Kong, China

Editorial Board

Aquatic environment

Baoyu Gao
Shandong University, China
Maohong Fan
University of Wyoming, USA
Chihpin Huang
National Chiao Tung University
Taiwan, China
Ng Wun Jern
Nanyang Environment &
Water Research Institute, Singapore
Clark C. K. Liu
University of Hawaii at Manoa, USA
Hokyoung Shon
University of Technology, Sydney, Australia
Zijian Wang
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China
Zhiwu Wang
The Ohio State University, USA
Yuxiang Wang
Queen's University, Canada
Min Yang
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China
Zhifeng Yang
Beijing Normal University, China
Han-Qing Yu
University of Science & Technology of China

Terrestrial environment

Christopher Anderson
Massey University, New Zealand
Zucong Cai
Nanjing Normal University, China
Xinbin Feng
Institute of Geochemistry,
Chinese Academy of Sciences, China
Hongqing Hu
Huazhong Agricultural University, China
Kin-Che Lam
The Chinese University of Hong Kong
Hong Kong, China
Erwin Klumpp
Research Centre Juelich, Agrosphere Institute
Germany
Peijun Li
Institute of Applied Ecology,
Chinese Academy of Sciences, China

Michael Schloter

German Research Center for Environmental Health
Germany

Xuejun Wang

Peking University, China

Lizhong Zhu

Zhejiang University, China

Atmospheric environment

Jianmin Chen

Fudan University, China

Abdelwahid Mellouki

Centre National de la Recherche Scientifique
France

Yujing Mu

Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China

Min Shao

Peking University, China

James Jay Schauer

University of Wisconsin-Madison, USA

Yuesi Wang

Institute of Atmospheric Physics,
Chinese Academy of Sciences, China

Xin Yang

University of Cambridge, UK

Environmental biology

Yong Cai

Florida International University, USA

Henner Hollert

RWTH Aachen University, Germany

Jae-Seong Lee

Hanyang University, South Korea

Christopher Rensing

University of Copenhagen, Denmark

Bojan Sedmak

National Institute of Biology, Ljubljana

Lirong Song

Institute of Hydrobiology,
the Chinese Academy of Sciences, China

Chunxia Wang

National Natural Science Foundation of China

Gehong Wei

Northwest A & F University, China

Daqiang Yin

Tongji University, China

Zhongtang Yu

The Ohio State University, USA

Environmental toxicology and health

Jingwen Chen

Dalian University of Technology, China

Jianying Hu

Peking University, China

Guibin Jiang

Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China

Sijin Liu

Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China

Tsuyoshi Nakanishi

Gifu Pharmaceutical University, Japan

Willie Peijnenburg

University of Leiden, The Netherlands

Bingsheng Zhou

Institute of Hydrobiology,
Chinese Academy of Sciences, China

Environmental catalysis and materials

Hong He

Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China

Junhua Li

Tsinghua University, China

Wenfeng Shangguan

Shanghai Jiao Tong University, China

Yasutake Teraoka

Kyushu University, Japan

Ralph T. Yang

University of Michigan, USA

Environmental analysis and method

Zongwei Cai

Hong Kong Baptist University,
Hong Kong, China

Jiping Chen

Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, China

Minghui Zheng

Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China

Municipal solid waste and green chemistry

Pinjing He

Tongji University, China

Environmental ecology

Rusong Wang

Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China

Editorial office staff

Managing editor Qingcai Feng
Editors Zixuan Wang Suqin Liu Zhengang Mao
English editor Catherine Rice (USA)

JOURNAL OF ENVIRONMENTAL SCIENCES

环境科学学报(英文版)
(<http://www.jesc.ac.cn>)

Aims and scope

Journal of Environmental Sciences is an international academic journal supervised by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The journal publishes original, peer-reviewed innovative research and valuable findings in environmental sciences. The types of articles published are research article, critical review, rapid communications, and special issues.

The scope of the journal embraces the treatment processes for natural groundwater, municipal, agricultural and industrial water and wastewaters; physical and chemical methods for limitation of pollutants emission into the atmospheric environment; chemical and biological and phytoremediation of contaminated soil; fate and transport of pollutants in environments; toxicological effects of terrorist chemical release on the natural environment and human health; development of environmental catalysts and materials.

For subscription to electronic edition

Elsevier is responsible for subscription of the journal. Please subscribe to the journal via <http://www.elsevier.com/locate/jes>.

For subscription to print edition

China: Please contact the customer service, Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China. Tel: +86-10-64017032; E-mail: journal@mail.sciencep.com, or the local post office throughout China (domestic postcode: 2-580).

Outside China: Please order the journal from the Elsevier Customer Service Department at the Regional Sales Office nearest you.

Submission declaration

Submission of an article implies that the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The submission should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Submission declaration

Submission of the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The publication should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Editorial

Authors should submit manuscript online at <http://www.jesc.ac.cn>. In case of queries, please contact editorial office, Tel: +86-10-62920553, E-mail: jesc@263.net, jesc@rcees.ac.cn. Instruction to authors is available at <http://www.jesc.ac.cn>.

Journal of Environmental Sciences (Established in 1989)

Vol. 26 No. 2 2014

Supervised by	Chinese Academy of Sciences	Published by	Science Press, Beijing, China
Sponsored by	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences	Distributed by	Elsevier Limited, The Netherlands
Edited by	Editorial Office of Journal of Environmental Sciences P. O. Box 2871, Beijing 100085, China Tel: 86-10-62920553; http://www.jesc.ac.cn E-mail: jesc@263.net , jesc@rcees.ac.cn	Domestic	Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China Local Post Offices through China
Editor-in-chief	Hongxiao Tang	Foreign	Elsevier Limited http://www.elsevier.com/locate/jes
CN 11-2629/X	Domestic postcode: 2-580	Printed by	Beijing Beilin Printing House, 100083, China
		Domestic price per issue	RMB ¥ 110.00

ISSN 1001-0742

