Development of Ti-Bi-based nanomaterials to purify mercury in the simulated flue gas

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Abstract. The photocatalytic oxidation technology is a new technology for the oxidation treatment of Hg^0 developed in the existing Wet Flue Gas Desulfurization (WFGD) equipment, in which the removal efficiency of Hg^{2+} is high and the removal efficiency of Hg^0 is very low. When ultraviolet light (UV) is used to irradiate a substance containing TiO₂ to pass the flue gas, photocatalytic catalytic oxidation reaction occurs, and Hg^0 is oxidized to Hg^{2+} , which is easily absorbed later in the WFGD apparatus, thereby improving the removal efficiency of mercury. The technology is still in the experimental development stage and needs further research. It has brought widespread interests to introduce surface defect or form interface heterostructure to improve the photocatalytic activity of the nanomaterials. The Ti-Bi-based nanomaterial photocatalyst with defect TiO₂/BiOIO₃ heterostructure has been fabricated via calcination method. The results showed that to introduce surface defect and form interface heterostructure on photocatalysts together can increase the response of the visible light, promoting the transfer velocity of the photocarriers and in turn suppressing the recombination of photo-generated electrons and holes, and this may become a developing trend in the near future.

1 Introduction

China is a large coal country that the main source of energy is coal, and many pollutants emitted during the coal combustion process, because mercury is a highly toxic trace element in coal and is discharged into the atmosphere with the combustion process of coal. It has the physicochemical properties of low melting point, low boiling point, high volatility and so on.

There exist three forms of mercury in the coal-fired power plant: elemental mercury(Hg⁰), oxidized mercury(Hg²⁺), and particulate-bound mercury(Hg^p)^[1]. The removal of mercury in the flue gas is largely dependent on the form of mercury. The oxidized mercury (Hg²⁺) is easily soluble in water, so the oxidized mercury can be removed by the wet electrostatic precipitator, and the efficiency can reach 90%. Particulate-bound mercury can easily pass through the dedusting devices in the power plant. But the elemental mercury is volatility, insoluble in water and chemical stability, it's not easily removed by the existing power plant air pollutant removal equipment. Thus, the elemental mercury removal in coal-fired power plants is a huge challenge, the key difficulty being converting Hg⁰ into Hg²⁺.

It has great harm to the environment and human body. Removing mercury from flue gas, photocatalytic oxidation technology has the advantages of strong oxidation capacity, no twice pollution and stable chemical properties. Thus, it has broad application prospects in the treatment of flue gas mercury removal.

In this paper, we conducted the physicochemical property of Ti-Bi-based nanomaterials by XRD, SEM and XPS. The performance of the catalyst was evaluated by visible light photocatalytic removal of gas mercury. In addition, the mechanism of the removal of zero valent mercury by photocatalytic oxidation is also clarified. After modification, the visible light absorption is enhanced, the photoelectron hole separation efficiency is increased, and its recombination is inhibited. The surface performance parameters are improved. All these factors are favorable for the photocatalytic removal of mercury efficiency.

2 Experimental

2.1. Chemicals and materials

Bismuth nitrate pentahydrate, commercial P25 (TiO₂) and potassium iodate were all obtained from Shanghai Aladdin Reagent Co., Ltd. All solutions were prepared with deionized water and all chemicals used were analytical grade and were used without further purification.

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2.2 Preparation of defect TiO₂

The synthesis of defect TiO_2 was described, which was similar to that used in our previous study ^[2]. In a typical process, TiO_2 powder was dissolve in 50 ml Ethyl stirring for 1 h, and then, the powder was dried at 80°C for 12h. Finally, the defect TiO_2 was obtained.

2.3 Preparation of defect BiOIO₃

In a typical process, 1 mmol bismuth nitrate pentahydrate was added to 70 ml deionized water and stirring 30 min, then 1mmol potassium iodate was dissolved in the above suspension. After stirring for 1h in dark, the product was acquired by filtering and obtained after being washed with deionized water and ethanol for three times respectively, and then dried at 80°C for 12 h. The obtained product was ground into powders, then calcined in the muffle furnace for 1h under 200 °C.

2.4 Preparation of defect TiO₂/BiOIO₃ nanomaterials.

Defect TiO₂ and defect BiOIO₃ was transferred into 80 ml deionized water and stirred for 10 min, then transferred into 100 ml Teflon under 150°C for 8h. The product washing thoroughly with deionized water and ethanol three times respectively, the obtained sample was dried in an oven at 80°C for 12h. The mole ratios of TiO₂:BiOIO₃ at 1:0.1 and 1:0.2 were labeled as TiO₂-0.1 and TiO₂-0.2.

2.5 Materials Characterization

Powder X-ray diffraction (XRD) with Cu K α radiation (BRUKER D8 ADVANCE Diffractometer, Germany) was applied to exam the crystalline phase of as-prepared samples. Scanning electron microscope (SEM, Phillips XL-30 FEG/NEW) was used to investigate the morphology of the samples. X-ray photoelectron spectroscopy (XPS, PHI5300) was utilized to investigate the surface chemical composition and chemical states of the samples.

2.6 Measurement of photoactivity

The photocatalytic experimental system is developed by ourselves ^[3]. The experimental system consists of a simulated flue gas mercury system, a mercury generating device, a photocatalytic reaction system, a flue gas mercury testing system, and an exhaust gas system. They are all connected by Teflon tube. A certain concentration of elemental mercury (Hg⁰) is produced at a certain temperature and carried into the photocatalytic system by simulated flue gas or pure nitrogen. The high-purity nitrogen gas is divided into two paths, which are controlled by the mass flow controller. One gas is used as a carrier gas through the U-shaped glass tube, and the zero-valent mercury volatilized from the mercury permeation tube is carried out, and the other gas is evenly distributed in the gas mixing tank. mixing. Nitrogen carrying mercury vapor was tested online for mercury removal by a mercury analyzer (RA-915M, Lumex, Russia). Finally, the gas was introduced into the potassium permanganate solution to absorb residual mercury and then emptied.

3. Results and discussions

3.1. Structure, Composition, and Morphology

XRD of defect TiO₂, defect BiOIO₃, and defect TiO₂/BiOIO₃ heterostructures are shown in Fig. 1. For defect TiO₂, the seven diffraction peaks at $2\theta = 25.16^{\circ}$, 27.25°, 37.65°, 47.89°, 53.82°, 55.02°, 62.62° agree well with commercial P25. For defect BiOIO₃, the characteristic diffraction peaks at 27.28°, 32.79°, 44.87°, 45.53°, and 53.65° are observed and these peaks could be perfectly indexed to (121), (002), (040), (212), and (123) planes of orthorhombic BiOIO₃(ICSD # 262019). For defect TiO₂/BiOIO₃ heterostructures, TiO₂-0.1 and TiO₂-0.2, all the peaks can be match with TiO₂ or BiOIO₃. Thus, it was successfully fabricated.



Fig. 1. Typical XRD patterns of defect TiO₂, defect TiO₂/BiOIO₃ heterostructures, and defect BiOIO₃^[11].

As shown in Figure 2, FESEM characterization is used to observe the morphology of the as-prepared samples. The defect TiO_2 possesses a diameter of ca. 25 nm, which is the mix phase of anatase and rutile, as confirmed by the above XRD analysis. The defect BiOIO₃ (Fig. 2d) exhibits irregular shapes because of fabrication by calcination method. For TiO_2 -0.1 and TiO_2 -0.2(Fig. 2b and c), the defect BiOIO₃ is distributed in the defect TiO_2 with an intimate interfacial contact. The tight heterostructure formed by TiO_2 attaching to BiOIO₃ forming the tight heterostructure can enhance the photocarriers' transferring velocity between the TiO_2 and BiOIO₃. For defect BiOIO₃ shown in figure 2d, all the BiOIO₃ exhibits irregular shapes.

The surface composition and chemical status of the asprepared defect TiO₂, TiO₂-0.1, TiO₂-0.2 and defect BiOIO₃^[4] are investigated by XPS characterization. The high resolution XPS spectra of TiO₂-0.1 and TiO₂-0.2 are demonstrated in the Fig. 3, the peaks at 458.23 and 464.26eV can be attributed Ti 2p3/2 and Ti 2p1/2, consistent with other researchers reports^[5, 6]. The O 1s spectra of TiO₂-0.1 shown in Fig. 3b. The peaks at 528.98, 530.17, 531.28, and 532.26eV can be defined as Bi-O^[7, 8], Ti-O^[9], I-O^[10], and surface absorbed oxygen (-OH group and chemisorbed oxygen-containing species) respectively.



Fig. 2. FESEM images of defect TiO₂(a), TiO₂-0.1(b); TiO₂-0.2(c), and defect BiOIO₃(d)^[11].





Fig. 3. XPS spectra of TiO2-0.1: (a) Ti 2p, (b) O 1s (All the peak maxima were calibrated to C 1s at 284.6 eV, which was mainly ascribed to remnant organic precursors not completely removed from the employed defect TiO₂/BiOIO₃ heterostructure ^[11].

3.2 Photocatalytic activity properties

3.2.1 Hg⁰ removal under LED irradiation

At present, there are two main sources of light sources for existing photocatalytic reactors: natural light sources and artificial light sources. Among them, the natural light source is sunlight; the artificial light source is generally divided into a visible light source and an ultraviolet light source. All the light sources in this experiment are artificial light sources. The ultraviolet light source uses an ultraviolet lamp with a power of 400W. The ultraviolet light has a peak wavelength of 365nm and the overall length of the lamp is 150mm. It is equipped with UV lamps around it. Reflective device. The visible light source uses a white LED light source with a power of 9W. The simulated solar light source uses an LED light source with a 410 nm filter, which filters the light source with a wavelength of less than 410 nm.

The defect TiO₂, defect BiOIO₃, and defect TiO₂/BiOIO₃ heterostructure photocatalysts were adopted to remove the gas-phase Hg⁰ for investigating the photocatalytic performance of the as-prepared photocatalysts. As shown in Table 1, the photocatalytic efficiency of defect TiO₂ was 28.56% and the photocatalytic efficiency of defect BiOIO₃ was 58.23% under LED irradiation.

Table 1. Photocatalytic removal gas-phase Hg⁰ under 9W LED lamp irradiation for 1h by defect TiO₂, defect TiO₂/BiOIO₃ heterostructures, and defect BiOIO₃.

Samples	Defect	Defect	TiO ₂ -	TiO ₂ -
	TiO ₂	BiOIO ₃	0.1	0.2
Efficiency	28.56%	58.23%	89.15%	72.35%

3.2.2 The stability of the photocatalysts

The stability of photocatalysts is vitally important for its application. In this paper, we used TiO_2 -0.1 as a representative sample to investigate the stability of asprepared photocatalysts. The stability of TiO_2 -0.1 is not changed after seven cycles tests, which confirms that TiO_2 -0.1 possesses high stability.

3.3 Photocatalytic reaction mechanisms

3.3.1 Introducing surface defect

For pure TiO₂ and BiOIO₃, the band gap is 3.15 and 3.13eV, respectively. According to the equation: $\lambda_{absorbance\ edge}$ =1240/E_{bg}, thus the absorbance edge of pure TiO₂ and BiOIO₃ is 393.65 and 396.16 nm respectively. The broad band gap and low absorbency severely restrict the pure TiO₂ and BiOIO₃ visible light photocatalytic activity. Furthermore, the charge separation efficiency between conduction band and valence band is weak, which is another reason for low photocatalytic activity. Introducing surface defect may distort the crystal lattice on the surface of TiO₂ and BiOIO₃, which would

produce a lot of mid-gap states. Because the lowerenergy mid-gap lies below the Fermi level, they can account for a large blue shift of the valence band edge result in a reduced band gap. For defect TiO₂ and BiOIO₃, the band gap is 2.66 and 2.96eV, respectively and the absorbance edge of defect TiO₂ and BiOIO₃ is 466 and 418nm, respectively. Despite all this, the photocatalytic activity of defect TiO₂ and defect BiOIO₃ is low due to the rapid combination of photo generated electron-hole pairs ^[11].

3.3.2 Effect of interface heterostructure

The crystal lattice defects on the surface of TiO₂ and BiOIO₃ produce mid-gap states. The mid-gap between the conduction band and valence band can narrow the band gap and absorb more visible light. When the light irradiates on the surface of defect TiO₂ or defect BiOIO₃, the photo-generated electrons transfer from the valence band to conduction band, forming photo separation electron-hole pairs. Due to the rapid recombination of electron-hole pairs and the low transfer velocity between the conduction band and valence band, the photocatalytic removal Hg⁰ efficiency of defect TiO₂ or defect BiOIO₃ is poor. Under the LED irradiation, the photocatalysts can absorb the low light response range, slow transfer velocity of photocarriers and rapid recombination of the electron-hole pairs. However, under the UV irradiation, the photocatalysts can extend the light absorbance to the visible even infrared light region. Therefore, under the UV irradiation, the photocatalysts have higher catalytic efficiency than LED irradiation. However, when attaching the defect BiOIO₃ to the surface of defect TiO₂ to form the interface heterostructures, the photogenerated electrons can transfer from conduction of TiO₂ to the conduction of BiOIO₃. Meanwhile, the photogenerated holes can transfer from the valence of BiOIO₃ to the valence of TiO2. Thus, the transformation of photo-generated electron-hole pairs between defect TiO₂ and BiOIO3 can effectively inhibit the recombination of photo-generated electron-hole pairs and efficiently enhance the transfer velocity of photo carriers. The generated 'O2' and 'OH by defect TiO2/BiOIO3 heterostructure deserve strong oxidizing property, which can oxide the absorbent Hg^0 into $Hg^{2+[11]}$.

4 CONCLUSION

In summary, the defect TiO₂/BiOIO₃ heterostructure was synthesized and may become a new research and defect TiO₂/BiOIO₃ trend. The application heterostructure exhibited excellent photocatalytic removal gas-phase mercury properties under visible light. The surface defect and interface heterostructure can greatly enhance the absorbance of the visible light, improve the transfer velocity of the photocarriers and reduce the recombination of the photo electron-hole pairs. However, these materials are not up to practical needs, from the entire field of photocatalysis technology research development. At present, there is an urgent need for photocatalytic physics starting from the quality,

revealing the influence light with advanced experimental techniques the key factors in the catalytic reaction process. It is vital important that the understanding of the catalytic reaction mechanism, by macroscopic and qualitative description microscopic, quantitative research, on light absorption, electrons hole excitation, transport process and interface dynamics process.

References

- 1. E.G. Pacyna, J.M. Pacyna, N. Pirrone, Atmos. Environ. **35**, 2987 (2001)
- 2. J. Li, Y. Yu, L. Zhang, Nanoscale 6, 8473 (2014)
- R. X Zhou, J Wu, J Zhang, H Tian, P. K Liang, Appl. Catal. B: Envir. 204, 465 (2017)
- R.L.V. Wal, V.M. Bryg, M.D. Hays, Anal. Chem. 83, 1924 (2011)
- J. Cai, Y. Zhu, D. Liu, M. Meng, Z. Hu, Z. Jiang, Acs Catal. 5, 150 (2016)
- A. Naldoni, M. Allieta, S. Santangelo, M. Marelli, F. Fabbri, S. Cappelli, C.L. Bianchi, R. Psaro, S.V. Dal, J. Am. Chem. Soc. 134, 7600 (2012)
- R.X Zhou, J. Wu, J. Zhang, H. Tian, P.K Liang, T. Zeng, P. Lu, J.X Ren, T.F Huang, X. Zhou, Appl. Catal. B Envir. 45, 465 (2017)
- Y. Sun, T. Xiong, F. Dong, H. Huang, W. Cen, Chem. Commun. 52, 8243 (2016)
- 9. X. Pan, Y.J. Xu, J. Phys. Chem. C 117, 17996 (2013)
- Y. Huang, H. Li, M.S. Balogun, W. Liu, Y. Tong, X. Lu, H. Ji, Acs Appl. Mater. Inter. 6, 22920 (2014)
- 11. X.M Sun, J Wu, F.G Tian, W.B Zhang, Q.F Li, Mater. Res. Bull. **103**, 247(2018).