The effect of pH on Synthesis of BiOCl and its photocatalytic oxidization performance

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Abstract: To explore the effect of pH on the photocatalytic oxidation activities of BiOCl catalysts, the BiOCl catalysts under different pH values were prepared via a facile hydrothermal method. The as-prepared catalysts were characterized by BET, XRD, HRSEM, SEM and UV-vis to find out the impact of pH values. Photocatalytic ability of BiOCl catalysts were evaluated by oxidation of gaseous elemental mercury under UV light irradiation. It was found that BiOCl catalysts prepared under alkaline condition exhibited the best photocatalytic oxidation activities. The difference of photocatalytic activity among the as-prepared catalysts can be attribute to the growth orientation of the crystal BiOCl catalyst and the adsorption capacity of elemental mercury.

Keywords: BiOCl catalyst; photocatalysis; elemental mercury; pH value

1. Introduction

Mercury has the characteristics of toxicity and persistent bioaccumulation in the environment, which is threat to human health. One of the major anthropogenic source is coal -fired flue gas from the power plant emission. There are three forms of mercury in the coal-fired flue gas: elemental mercury(Hg^0), oxidized $\text{Hg}(\text{Hg}^{2+})$ and particulate $\text{Hg}(\text{Hg}_p)$.^{1,2} Hg^{2+} can be removed by wet scrubbers, whereas electrostatic precipitator (ESP) or fabric filter (FF) can easily remove Hg_p . The removal efficiency of Hg_p and Hg^{2+} can reach up to 90%. However, due to the volatility, insolubility and chemical stability, Hg^0 is difficult to remove.³

Bismuth oxychloride is of lower valence band energy, so it has strong oxidation ability. Furthermore, bismuth oxychloride has been taken more and more attention because of its layered structure. Its layered structure feature may promote its photocatalytic performance due to self-built internal static electric fields, which can enhance effective separation of the photoinduced electron-hole pairs.⁴⁻⁵ Electron-hole pairs are the important factors for photocatalytic oxidation on elemental mercury, which has been reported in our previous research⁶. The Cl 2p, O2p and Bi6s orbitals constituted valence band of BiOCl, and the Bi6p and Bi 6s orbitals constituted the conduction band(0.308V Bi³⁺/Bi vs.SHE)⁷. The bandgap energy was estimated at approximately 3.46 eV⁸⁻¹³, which can be excited by UV light. However, bandgap energy is not the single factor for photocatalytic oxidation on elemental mercury. As we known, pH could influence the size, stability and morphology of the prepared catalysts¹⁸. In order to further explore the effect of pH values on photocatalytic oxidation elemental mercury activity, we prepared BiOCl samples by using hydrothermal method under different pH values.

2. Experimental methods

2.1 Materials and reagents

Bi(NO₃)₃·5H₂O and NaCl were purchased from Guoyao Chemical Reagent Co. Ltd. All chemicals were analytical grade and used without further purification.

2.2 Preparation

The preparation of detailed process was as follows: 4mmol Bi(NO₃)₃·5H₂O was dissolved in 48ml ultra-water. The suspension was stirred for 20 min until Bi(NO₃)₃·5H₂O was completely dissolved. Then, 4mmol NaCl was dissolved in the mixture. When the solution turned into transparent, 10M NaOH was added by drop to adjust the pH value of the mixture. After a further 1h continuous stirring, the samples were put in 100ml Teflon-lined stainless steel autoclave and kept in an 160°C electric oven for 24 h. When the temperature was cooled to ambient temperature, the white products were collected and washed with ultrapure water and ethanol several times and dried at 80°C for 12h. The BiOCl photocatalysts with different pH value (2, 7 and 10) were labeled BiOCl-2, BiOCl-7 and BiOCl-10 respectively.

2.3 Characterization of Materials

The obtained samples were characterized by X-ray diffraction (Bruker D8 Advance, Germany), FE-SEM (Phillips XL-30 FEG/NEW), HRTEM (Phillips Model CM200), UV-vis absorbance spectra (SHIMADZU UV-3600, Japan), and BET (Micromeritics ASAP 2020).

2.4 Photocatalytic Tests

A bench-scale experimental system was shown in the **Fig.1(a)** to evaluate the catalytic activities, which was similar to that used in our previous study⁶. Briefly, N₂ stream with a flow rate of 0.2 Lmin⁻¹ passed through mercury generating device (PSA 10.525 SIR GALAHAD II, UK) to introduce Hg⁰ vapor into photocatalytic reaction system. The reactor was flat-plate shape, which was consisted of hollow stainless steel square cell and a quartz glass used as a lid. Catalysts were loaded on a rectangular glass plate, and put into the cavity of the photocatalytic reactor, shown as **Fig.1(b)**. The Hg⁰ inlet concentration was controlled around 55 μgm⁻³. UV lamp (254nm) was fixed right on the top of reactor at the 5 cm height. An on-line mercury analyzer (VM-3000 Mercury Vapor Monitor, Mercury Instruments, Germany) was applied to detect the gas

phase concentration of Hg^0 based on atomic absorption spectrometry.

Hg^0 removal efficiency (η) over can be defined using eq. 1.

$$\eta = \frac{Hg_{in}^0 - Hg_{out}^0}{Hg_{in}^0} \times 100\% \quad (1)$$

where Hg_{in}^0 and Hg_{out}^0 represented the concentration of Hg^0 at the inlet and outlet of the photocatalytic reactor, respectively.

3. Results and discussions

Fig.1(c) showed the XRD patterns of BiOCl photocatalysts in the 2θ range 10° - 70° . The diffraction peaks of XRD patterns were in accordance with tetragonal BiOCl (PDF #06-0249) perfectly. The main X-ray diffraction peaks of BiOCl located at $2\theta=11.97^\circ$, 24.03° , 25.90° , 32.46° and 33.48° corresponded to the planes of (001), (002), (101), (110) and (102) respectively. The sharp diffraction peaks indicated the as-prepared samples were the perfect crystalline phase. However, the intensities of dominated diffraction peaks of different BiOCl photocatalysts were various. The intensity ratios of (002/101) diffraction peak for BiOCl-2, BiOCl-7 and BiOCl-10 were 0.46, 1.24 and 0.19 respectively. The standard value was 0.16. When the pH value equaled to 10, the intensity ratios of (002/101) diffraction peak were close to standard value. At the pH value equaled to 2 and 7, the intensity ratios of (002/101) diffraction peak were much higher than standard value, which indicated that the dominated diffraction peaks of BiOCl-7 was (002). Under different pH value, the growth direction of BiOCl was different. Under alkaline condition, the growth direction of BiOCl was similar to that of standard BiOCl.

SEM and HRTEM analysis were conducted to observe the morphology of photocatalysts under different pH value conditions and the results were shown in the **Fig.2**. The morphologies of photocatalysts all were regular and nanosheets, and the surfaces of the three photocatalysts were extremely smooth. Basically, pores were barely observed on the surface of the BiOCl photocatalysts. As we can see(**Fig.2a**), the shape of BiOCl-2 photocatalysts were round. There were no obvious morphology difference between the BiOCl-7 and BiOCl-10 photocatalysts (**Fig.2b and c**). Both shapes were rectangle nanosheets. Their average thickness were very small at around 70nm, which was a third of the BiOCl-2 thickness. The different morphologies under acidic condition indicated that excessive H^+ effected the mechanism of crystal growth, such as growing orientation, which agreed with the different intensity ratios of XRD patterns. For the further demonstration of BiOCl, high-resolution HRTEM image was conducted and the results were shown in **Fig. 2(d)**. The lattice fringes were clearly observed in HRTEM image. The interplane space of 0.275nm was corresponding to (110) plane of BiOCl and the interplane space of 0.375nm was corresponding to (110) plane¹⁴.

The optical properties of all photocatalysts were characterized by UV-vis diffuse reflectance spectroscopy. **The Fig. 3(a)** showed the absorption spectra of different BiOCl at the wavelength ranging from 200 nm to 800nm. As we can see, all absorption spectra showed similar adsorption intensity at the wavelength range under 350nm. The absorption spectrum of BiOCl-2 existed a

small red shift compared to the absorption spectra of BiOCl-7, BiOCl-10.

To explore the physical properties, nitrogen adsorption-desorption measurement was conducted and the data were displayed in **Table 1**. As we can see, the BET surface area and pore volume of BiOCl were very small under acidic condition. The BET surface area and pore volume of BiOCl were similar under neutral and alkaline condition.

The efficiency of photocatalytic oxidation on gaseous Hg^0 under UV light irradiation was shown in **Fig. 3(b)**. As we can see, the most effective catalyst was BiOCl under alkaline condition. Its efficiency of photocatalytic oxidation on gaseous Hg^0 reached up to 60%. Since we have already explore the effect of pH on the band gap of BiOCl and observed a neglect difference, we can confirm that the bandgap was not the reason of the enhancement on the efficiency of photocatalytic oxidation mercury. The main difference of BiOCl under different condition was BET surface area and pore volume.

A larger BET surface area and pore volume led to more exposed active sites and residence time of gaseous Hg^0 on catalyst surface, which was helpful to photocatalytic oxidation reaction. This can explain the low efficiency of BiOCl under acidic condition. However, both BET surface area and pore volume were similar under neutral and alkaline condition. So the different efficiency of photocatalytic oxidation on gaseous Hg^0 under neutral and alkaline condition may be contribute to the different growth direction. Since, the dominant diffraction peak of BiOCl-7 was (002) and the dominated diffraction peak of BiOCl-7 was (101), we can make the conclusion that exposed (002) facet limited the photocatalytic oxidation reactions, which was clarified in our previous research⁶.

4 Conclusions

In this paper, we synthesis BiOCl by hydrothermal method under different pH value and explore the effect of pH on its photocatalytic oxidization performance. The efficiency of photocatalytic mercury was increased as the pH increased. Firstly, BET surface area and pore volume were very small under acidic condition which limited the exposed active sites and residence time of gaseous Hg^0 on catalyst surface. Secondly, dominant diffraction peak of BiOCl under neutral condition. The dominated diffraction peak of BiOCl under neutral alkaline was (101), we can make the conclusion that exposed (002) facet limited the photocatalytic oxidation reactions.

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Fig.1 (a) Schematic diagram of the experimental system; (b) Schematic diagram of the the photocatalytic reactor; (c) XRD patterns for BiOCl photocatalysts

Fig.2 SEM images of (a)BiOCl-2; (b)BiOCl-7; (c)BiOCl-10; and (d)HRTEM image of BiOCl-10

Fig. 3 (a) UV-vis absorbance spectra of BiOCl photocatalysts;
(b) efficiency of photocatalytic oxidation gaseous Hg^0 under UV light irradiation

Tabel 1. Physicochemical properties of BiOCl-2, BiOCl-7, BiOCl-10

Samples	$E_g(\text{eV})$	$S_{\text{BET}}^{\text{a}}$ ($\text{cm}^2 \cdot \text{g}^{-1}$)	V_t^{b} ($\text{cm}^3 \cdot \text{g}^{-1}$)	$D_{\text{BJH}}^{\text{c}}$ (nm)
BiOCl-2	3.46	0.31	0.002	21.3
BiOCl-7	3.52	3.40	0.014	16.1
BiOCl-10	3.54	3.02	0.013	17.17

a S_{BET} , BET surface area calculated by the adsorption branch of N_2 isotherm.

b V_t , pore volume.

c D_{BJH} , pore diameter determined by BJH model.