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Hydrothermal synthesis of BiOBr/semi-coke composite as an emerging photo-catalyst for nitrogen monoxide oxidation under visible light

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ABSTRACT

BiOBr/semi-coke (SC) composite photo-catalyst was synthesized by a facile hydro-thermal method. The obtained samples were characterized by N_2 adsorption–desorption, X-ray diffraction (XRD) and UV–visible diffuse reflectance spectroscopy (UV–vis DRS). The photo-catalytic activity of as-prepared samples was evaluated by the oxidation of nitrogen monoxide (NO) under visible light irradiation. The results revealed that BiOBr/SC composite exhibited higher photo-catalytic activity than pure BiOBr.

1. Introduction

Nitrogen oxides (NO*x*) have been considered as the most toxic gases that contribute to the acid rain and photochemical smog. Hence, how to control the NO*x* emissions becomes challenging. Selective catalytic reduction (SCR) of NO and NO_2 with ammonia is a common strategy for abating NO*x* emissions. Although these SCR processes appear effective and well-established, there still remain several problems, such as the requirement of high reaction temperatures, reheating of the flue gas, and the presence of H_2O and SO_2, which detrimentally impact on the activity of catalysts [1].

The heterogeneous photo-catalytic technique is reported as an environmental-friendly technique for the elimination of organic contaminants [2], especially for the purification of air pollutants at low concentrations, TiO_2 is the most widely used photo-catalyst that only work under ultraviolet (less than 4% of solar light), which limits its practical applications. Thus, more efforts have been done focusing on exploring new photo-catalysts to utilize solar light more effectively [3–5].

Recently, BiOBr has attracted many attentions owing to its special physical and chemical properties, such as typical nanostructures/micro-morphologies, suitable band gap and optical properties, high stability and low cost [6,7]. In addition, the valence band (VB) edge potential of BiOBr semiconductor (3.19 eV) is more positive than the oxidation potential of H_2O_2 (1.77 eV) and O_3 (2.07 eV), which indicate that BiOBr may have stronger oxidation activity [8]. Various carbon materials, including activated carbon, active coke, as well as the carbon nano-tubes (CNTs), have been found to play important roles in heterogeneous catalysis as either catalysts or catalyst supports [9]. Semi-coke is a product of coal pyrolysis at a relatively low temperature (600–700 °C). As a material rich in micro-pores, it is used as a kind of adsorbents or catalysts [10–12].

In this article, we report a novel BiOBr/SC composite synthesized by a facile hydro-thermal method. The photo-catalytic activity was evaluated by photo-catalytic removal of gaseous NO under visible light irradiation. In addition, the mechanisms of NO catalytic oxidation over BiOBr/SC are also proposed.

2. Experimental

2.1. Reagents and synthesis method

Semi-coke was obtained from Ordos Inner Mongolia, PR China, and other chemicals were of analytical grade and were used as received without further purification. BiOBr/SC composite was

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Table 1
Pore structure properties of Sc and different catalyst samples.

Sample	BET surface area (m^2/g)	Pore volume (cm^2/g)	Pore size (nm)
SC	318.7	0.168	2.19
BiOBr	23.6	–	–
BiOBr/SC	304.5	0.161	2.17

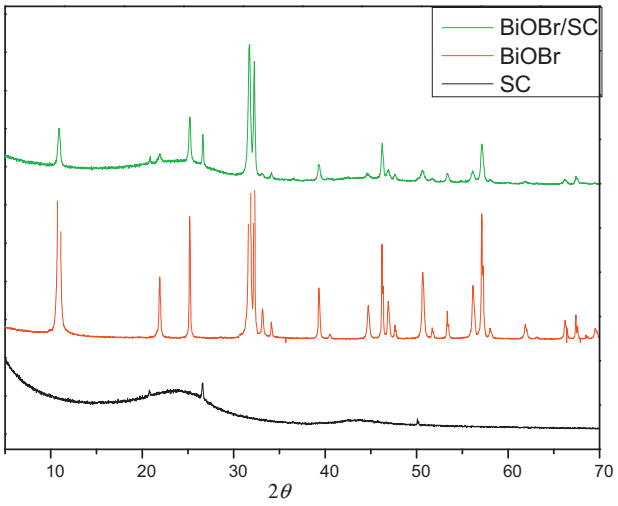

Fig. 1. XRD patterns of BiOBr/SC, BiOBr and SC.

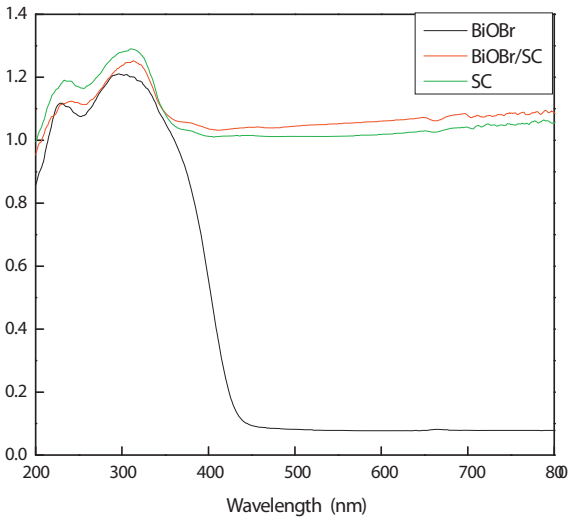

Fig. 2. UV–vis DRS spectra of obtained samples.

synthesized by a facie hydrothermal method. 1 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in 30 ml of aqueous solution with 5 ml of acetic-acid under stirring for 0.5 h. 1.2 mmol of KBr and an appropriate amount of semi-coke were subsequently added and stirred for 30 min. The resulting precursor solution was poured into a 100 ml Teflon-lined autoclave. Finally, the autoclave was kept at 160 °C for 12 h and cooled down to room temperature. The precipitate was washed by distilled water for three times, followed by drying at 120 °C for 12 h. Pure BiOBr was prepared through same procedure just without the addition of semi-coke.

2.2. Characterization

The Brunauer Emmett Teller (BET) surface area was measured using Sorptmatic 1990. The phase composition of the as-prepared samples was characterized by means of X-ray diffractometer (XRD, Bruker D8 Advance with CuKa1 radiation at 40 kV and 30 mA). The UV–vis diffusion reflectance spectra of the samples were obtained on a UV–Vis spectrophotometer (UV-3600, Shimadzu, Japan).

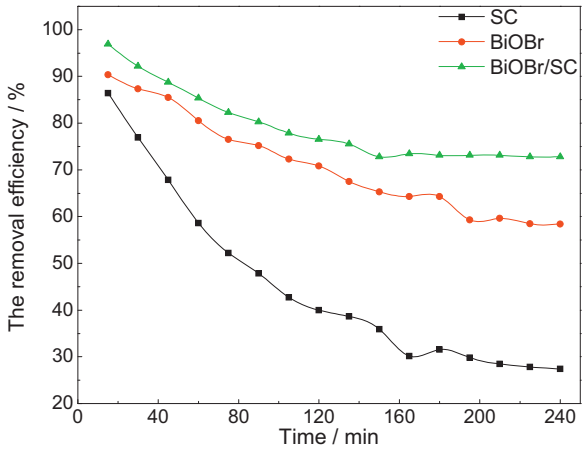

Fig. 3. The removal efficiency on irradiation time in the presence of BiOBr, semi-coke and BiOBr/SC under visible light.

2.3. Photo-catalytic test

The photo-catalytic experiments on the removal of NO were carried out in a designed reactor, A 50 W xenon lamp was used as the light source and a glass filter was placed to remove light below 420 nm. 100 ml catalysts were loaded in the photo-catalyst reactor, and then a gas mixture of 5% of H_2O, 5% of O_2, NO and N_2 was introduced into the reactor at 110 °C. The space velocity of the gases was kept at 800 h^{-1}. The concentration of NO was continuously measured by combustion analyzer, and the removal efficiency (η) of NO was calculated by Eq. (1):

$$\eta = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

where C_0 and C are the concentrations of NO in the feeding stream and in the outlet stream, respectively.

3. Results and discussion

3.1. BET

The specific surface area and porosity of the as-prepared samples were investigated by N_2 adsorption–desorption. The obtained data for all the samples are shown in Table 1. The specific surface areas of SC, BiOBr, and BiOBr/SC are 318.7, 23.6 and 304.5 m^2/g, respectively. Obviously, BiOBr/SC has a much higher BET specific surface area compared to the other two, we know that the nitrogen adsorption–desorption isotherm of SC is identified as type IV with hysteresis loop [10], this information indicates that BiOBr/SC is meso-porous materials, such a mesoporous structure is very favorable for the diffusive transport of photo-generated carriers to oxidated species [13].

3.2. XRD

XRD patterns for SC, BiOBr and BiOBr/SC composites are shown in Fig. 1. It can be seen that the inflection peaks were indexed into the tetragonal phase BiOBr of (JCPDS no. 09-0393) for pure BiOBr power and BiOBr/SC. The results indicated that pure BiOBr power was coated on the surface of SC. In addition, it is found from Fig. 2, the existence of SC affects the crystallization of BiOBr in the