Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Ternary Ag/AgCl-$(BiO)_2CO_3$ composites as high-performance visible-light plasmonic photocatalysts

Wen Cui [a], Xinwei Li [a], Chunfeng Gao [a], Fan Dong [a,*], Xiongbo Chen [b,*]

[a] Chongqing Key Laboratory of Catalysis and Functional Organic Molecules, College of Environment and Resources, Chongqing Technology and Business University, Chongqing 400067, China
[b] South China Institute of Environmental Sciences, The Ministry of Environment Protection of PRC, Guangzhou 510655, China

ARTICLE INFO

Article history:
Received 16 June 2016
Received in revised form
23 September 2016
Accepted 23 October 2016
Available online xxx

Keywords:
Ag/AgCl-$(BiO)_2CO_3$ composites
Visible-light plasmonic photocatalysis
Charge separation and transfer
NO removal
in situ DRIFTS

ABSTRACT

A ternary plasmonic Ag/AgCl-$(BiO)_2CO_3$ photocatalyst was successfully synthesized via a facile method. The as-prepared samples were characterized by X-ray diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy, UV–vis diffuse reflection spectra, N_2 adsorption-desorption isotherms, photoluminescence spectra, photocurrent generation measurement, time-resolved fluorescence and in situ FT-IR spectra. The Ag/AgCl-$(BiO)_2CO_3$ composites exhibited outstanding visible-light photocatalytic performance for removal of NO in air, which can be ascribed to the cooperation of surface plasmon resonance effect (SPR effect), surface scattering and reflecting effect (SSR effect) and efficient separation of electron-hole pairs. Moreover, the in situ DRIFTS were applied to elucidate the photocatalytic oxidation process for NO removal and also can further explain the enhanced photocatalytic activity of ternary Ag/AgCl-$(BiO)_2CO_3$ composites. And a conceivable visible-light photocatalysis mechanism was proposed in detail. The present work could provide a new perspective for the fabrication and understanding of plasmon-enhanced visible-light photocatalysts.

1. Introduction

Nitric oxide (NO), a typical indoor and outdoor air pollutant, has aroused wide public concern since it is one of the major contributors to haze, photochemical smog, acid rain and so on. And it also could trigger serious respiratory diseases, cardiopulmonary diseases and even premature death [1–3]. Therefore, a number of techniques have been developed for NO purification. However, traditional methods including physical adsorption, biofiltration and thermal catalysis are not economically feasible for the removal of NO at part-per-billion (ppb) levels [4,5]. So the visible-light-driven photocatalysts as a green technology haa received considerable attention due to its potential applications in environmental pollution control and solar energy conversion by utilizing natural sunlight or artificial indoor light [6–8].

Recently, a series of efficient visible-light-driven photocatalysts have been developed, including metal-containing, metal-free and plasmonic properties-containing photocatalysts [9–12]. Among them, Bi-based semiconductor photocatalysts have received considerable attentions due to the high visible-light photocatalytic activity [13–16]. Many Bi^{3+}-containing compounds possess a suitable band gap and exhibit high visible-light photocatalytic activity, which can be ascribed to the pronounced overlap of hybridized O 2*p* and Bi 6*s* valence bands to facilitate the transfer of photogenerated charge carriers [17,18].

$(BiO)_2CO_3$ (BOC), one of the Bi-based semiconductors, has been demonstrated to be a highly promising photocatalyst. Also, BOC is an outstanding candidate for coupling with various functional materials to enhance photocatalytic performance. Many efforts have been made on fabricating BOC-based nanocomposites and six primary systems of BOC-based nanocomposites can be classified [19]: metal/BOC heterojunction [20,21], single metal oxides/BOC heterostructure [22,23], bismuth-based metallic acid salts/BOC [24,25], bismuth oxyhalides/BOC [26,27], metal-free semiconductor/BOC [28,29] and the BOC-based complex heterojunction [30,31]. Recently, Ag/AgX (X = Cl, Br and I) has been widely used to modify the semiconductor photocatalysts. It can improve the separation efficiency of charge carriers and enhance the photocatalytic activity of the substrates because of the surface plasmon resonance effect (SPR effect) of Ag particles which is reduced from the surface of AgX under visible-light irradiation [32–35]. To our knowledge, using Ag/AgCl as cocatalyst to couple with BOC for enhancing photocatalytic performance has not been reported yet

* Corresponding authors.
E-mail addresses: dfctbu@126.com (F. Dong), chenxiongbo@scies.org (X. Chen).

http://dx.doi.org/10.1016/j.cattod.2016.10.020
0920-5861/

and the photocatalytic NO oxidation process also has not been demonstrated with in situ DRIFTS.

Herein, we developed a two-step method to synthesize ternary Ag/AgCl-$(BiO)_2CO_3$ (Ag/AgCl-BOC) composites and elaborated the in situ DRIFTS results to understand the related oxidation processes. BOC was synthesized by the hydrothermal method and Ag/AgCl was deposited on the surface of BOC via a precipitation-photoreduction reaction. And considering the effect of ratios between AgCl and BOC, the different mass ratio have been carried out to ensure the optimized ratio between BOC and Ag/AgCl and the subsequent research work are centered on the optimal sample [36–38]. The Ag/AgCl-BOC composites showed higher visible-light photocatalytic performance than pure Ag/AgCl and BOC for NO removal. The enhanced photocatalytic activity can be ascribed to the cooperation of SPR effect, SSR effect and efficient separation of electron-hole pairs. The possible photocatalysis mechanism was also proposed in detail. So the Ag/AgCl-BOC composites as high-performance plasmonic visible-light photocatalysts can be potentially applied in air purification.

2. Experimental

2.1. Materials and synthesis

All the reagents employed in this study were analytical grade and used without further purification. BOC was obtained by a simple hydrothermal method [39]. In a typical synthesis, 0.46 g Na_2CO_3 was added to 70 mL distilled water and stirred vigorously for 10 min. Then, 1.6 g $C_6H_5BiO_7$ was added to the above aqueous solution and stirred continuously for 30 min. And the suspension was hydrothermally treated at 160 °C for 24 h. Subsequently, the obtained samples were filtered, washed with ethanol and dried at 60 °C for 12 h.

The Ag/AgCl-BOC composites were synthesized by a chemical precipitation method at room temperature. First, 1.0 g BOC was added to 60 mL distilled water to get suspension A and the suspension were sonicated for 30 min. Then, $AgNO_3$ was added to solution A and stirred vigorously for 30 min to form suspension B. NaCl were added to 10 mL distilled water and then added dropwise to suspension B and stirred for 2 h. The resulted products were collected by filtration, washed with water and ethanol four times and dried at 60 °C to obtain the final products. Ag/AgCl was synthesized by a chemical precipitation method at room temperature without adding BOC. The mass ratio of AgCl/BOC was controlled at 10, 30 and 50%. The samples were labeled as Ag/AgCl-BOC-10, Ag/AgCl-BOC and Ag/AgCl-BOC-50, respectively. The Ag metal was produced by photoreduction with the irradiation of surrounding light.

2.2. Characterization

The crystal phases of the samples were analyzed by X-ray diffraction (XRD) with Cu Kα radiation (model D/max RA, Rigaku Co., Japan). Scanning electron microscopy (SEM, model JSM-6490, JEOL, Japan) was used to characterize the morphology of the obtained products. The morphology and structure of the samples were examined by transmission electron microscopy (TEM, JEM-2010, JEOL, Japan). X-ray photoelectron spectroscopy (XPS) with Al Kα X-rays ($h\nu$ = 1486.6 eV) radiation operated at 150 W (Thermo ESCALAB 250, USA) was used to investigate the surface properties. The UV–vis diffuse-reflectance spectrometry (UV-vis DRS) spectra were obtained for the dry-pressed disk samples using a scanning UV–vis spectrophotometer (TU-1901, China) equipped with an integrating sphere assembly, using 100% $BaSO_4$ as the reflectance sample. N_2 adsorption-desorption isotherms were obtained on N_2 adsorption apparatus (ASAP 2020, Micromeritics, USA). Photoluminescence (PL) studies (F-7000, HITACHI, Japan) were conducted to investigate the optical properties of the samples. The photocurrent was measured using an electrochemical system (CHI-660B, Chinehwa, Shanghai, China), using the FTO glass with the as-prepared samples coated on the working electrode, saturated calomel electrode as the reference electrode, and Pt wire as the counter electrode. For the photocurrent measurement, the working electrode was irradiated by a 300 W Xe lamp with a 420 nm cut-off filter. The photocurrent-time dependence at open circuit potential was measured in 0.5 M Na_2SO_4 under chopped illumination. Steady and time-resolved fluorescence emission spectra were recorded at room temperature with a fluorescence spectrophotometer (Edinburgh Instruments, FLSP-920). In situ DRIFTS measurements (Tensor II, FTIR spectrometer, Bruker) equipped with an in situ diffuse-reflectance cell (Harrick) were conducted to understand the related photocatalytic oxidation processes over the as-prepared photocatalysts.

2.3. Evaluation of photocatalytic activity

The photocatalytic activity was evaluated by the removal efficiency of NO at ppb levels in a continuous flow reactor at ambient temperature. The rectangular reactor (30 cm × 15 cm × 10 cm) is made of polymeric glass and covered with Saint-Glass. A 150 W commercial tungsten halogen lamp was vertically placed under the reactor and the UV cut-off filter (420 nm) was also applied to remove UV light during the tests of visible-light photocatalytic activity. The as-prepared sample (0.20 g) was dispersed in distilled water (30 mL) via ultrasonic treatment. The resulting suspension was coated onto two glass dishes (12.00 cm in diameter) and then pretreated at 70 °C to remove water. The NO gas acquired from a compressed gas cylinder at a concentration of 100 ppm of NO (N_2 balance). The initial concentration of NO was diluted to about 550 ppb by a zero air generator. And the relative humidity (RH) level of the NO flow was controlled at 50% by passing the zero air stream through a humidification chamber. The flow rates of the air stream and NO were controlled at 2.4 L/min and 15 mL/min, respectively. The lamp was turned on when the adsorption-desorption equilibrium was achieved. The concentration of NO was continuously measured by a NO_x analyzer (Thermo Environmental Instruments Inc., model 42c-TL), which can monitor the concentration of NO, NO_2 and NO_X (NO_X represents NO + NO_2). The removal ratio (η) of NO was calculated as $\eta = (1 - C/C_0) \times 100\%$, where C and C_0 are the concentrations of NO in outlet steam and feeding stream, respectively.

3. Results and discussion

3.1. Phase structure

The X-ray diffraction (XRD) patterns of Ag/AgCl, BOC and Ag/AgCl-BOC composites are shown in Fig. 1. The diffraction peaks of BOC and Ag/AgCl can be indexed to the tetragonal BOC structure (JCPDS-ICDD Card no. 41-1488) and cubic phase of AgCl (JCPDS 31-1238), respectively. And in the Ag/AgCl-BOC ternary composites, the diffraction peaks of BOC and AgCl can be detected simultaneously, which indicated that AgCl has coupled with BOC. However, owing to the low content and high dispersity of Ag particles, the diffraction peaks belong to cubic Ag phase have not been observed in Ag/AgCl-BOC composites.

3.2. Chemical state

XPS were carried out to further determine the chemical state of elements present in the ternary composites, as shown in Fig. 2. The

Please cite this article in press as: W. Cui, et al., Ternary Ag/AgCl-$(BiO)_2CO_3$ composites as high-performance visible-light plasmonic photocatalysts, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.10.020