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ORIGINAL RESEARCH

Does noble metal modification improve the photocatalytic activity of BiOCl?

Liang Kong[a], Zheng Jiang[a,b,*], Henry H.-C. Lai[a], Tiancun Xiao[a], Peter P. Edwards[a,]**

[a]*Department of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, UK*
[b]*Environment and Sustainability Institute, University of Exeter, Cornwall Campus, Penryn, Cornwall TR10 9EZ, UK*

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Abstract Noble metal-surface-deposited BiOCl photocatalysts were prepared through photo-deposition and used for photodecomposition of Rhodamine B (RhB). The received materials were characterised using X-ray photoemission spectroscopy (XPS), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), and X-ray diffraction (XRD) to understand the influence of surface deposited noble metals. The results showed that the noble metal species on the surface of BiOCl are in metallic state, which also brought about enhanced light absorption in broad UV–vis region due to plasmonic effects induced by the surface-deposited noble metal species. All the samples showed good activity in photodecomposition of RhB under UV-light irradiation, but only Ag/BiOCl was more active than bulk BiOCl. The mechanism of the different reactivity of these noble-metal modified BiOCl was tentatively proposed based on the band structure and the interactions between noble metals and the BiOCl.

1. Introduction

The increasing applications of solar energy have been stimulating the increasing demand of semiconductor photocatalysts, which play vital roles in solar cells, artificial photosynthesis (photocatalytic water splitting, CO_2 photo-reduction) and environmental cleanup [1–3]. Besides the extensively investigated TiO_2 photocatalyst, great efforts have been made to explore more efficient semiconductor photocatalysts as alternatives to TiO_2 [4].

As a typical p-type main group V–VI–VII ternary semiconductor, BiOCl is a stable but more active photocatalyst than TiO_2 due to the unique optical, electrical and catalytic properties of the

*Corresponding author at: University of Exeter, Environment and Sustainability Institute, Cornwall Campus, Penryn, Cornwall TR10 9EZ, UK.
**Corresponding author at: University of Oxford, Inorganic Chemistry Laboratory, OX1 3QR, UK.
E-mail addresses: zheng.jiang@jesus.ox.ac.uk (Z. Jiang), peter.edwards@chem.ox.ac.uk (P.P. Edwards).

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layered structure of BiOCl [4]. However, BiOCl is still facing the same challenges encountered by most photocatalysts, such as limited light absorption, and great energy loss associated with the fast recombination of photo-generated charge carriers (electron–hole) [5]. A variety of strategies, such as formation of heterojunctions [6], impurity doping [7], and surface metallisation [8], have been employed to improve the light absorption and reduce the recombination of charge carriers. Semiconductor heterojunctions require specific band positions of the dual semiconductors and impurity doping highly depends on the doping level; in contrast, surface metallisation takes great advantage of enhanced trapping ability of photo-generated electrons because of the high conductivity and additional plasmonic effect of the surface noble metals [9]. So far, Ag/TiO_2 [10] and Ag/AgCl [11] have been proved as efficient photocatalysts under visible-light irradiation, which has arisen from the fact that surface noble-metal nano-particles (i.e., Au and Ag) can strongly absorb visible-light due to their localised surface plasmonic resonance (SPR) [12,13]. To date, research regarding semiconductor surface metallisation mainly concentrated on the n-type semiconductors (i.e., TiO_2, AgX, etc.) rather than p-type semiconductor photocatalysts [14]. Though Ag/BiOBr and Pt/BiOI showed enhanced photocatalytic performance in previous reports [15,16], the effects of various noble metals deposited on the photocatalyst of BiOCl have not been well explored.

In this work, we deposited a small amount of various noble metals (Ag, Pt, Pd, and Rh) on BiOCl via a simple photo-deposition method and found that those noble metals have different influences on the structure, property and photocatalytic performance of BiOCl. The interaction between noble metal and BiOCl has also been discussed to interpret the effects of surface-deposited noble metal.

2. Experimental

2.1. Preparation of the photocatalysts

All the reagents were of analytic grade and were used without further purification. The BiOCl employed was prepared as follows: stoichiometric amount of bismuth nitrate pentahydrate (Riedel-de Haën, 98.5%) was dissolved in 50 mL aqueous solution containing 5 mL acetic acid (HAc) with magnetic stirring. The acidic $Bi(NO_3)_3 \cdot 5H_2O$ solution was vigorously stirred for 30 min prior to adding to 30 mL distilled water containing stoichiometric amounts of KCl (BDH AnalaR, 99.5%). White precipitates were immediately observed upon mixing the solutions. After stirring for another 30 min at room temperature, the suspension was aged for 3 h. The resulting precipitate was filtered, washed thoroughly with distilled water, and then dried at 65 °C overnight.

2.2. Modification of BiOCl with noble metals

Metal modification of BiOCl samples was performed by photo-deposition of Pt, Pd, Ag and Rh from the stocked solution using noble metal chloride (all purchased from Sigma-Aldrich, 98+%) as precursors. 1.2 g BiOCl sample was added into 100 mL distilled water with magnetic stirring and ultrasonication treatment for 20 min to ensure good dispersion of BiOCl particles. Stocked solutions of the noble metal chloride (corresponding to a 0.5 wt% metal loading) in 0.02 mol/L HCl were prepared and mixed with suspensions of BiOCl in distilled water ($RhCl_3$ was dissolved in 0.02 mol/L NaOH solution, and then acetic acid was added to maintain the pH of the solution). 20 mL of ethanol was added into the mixture as a sacrificial donor. Photo-deposition was performed by illuminating the suspensions for 2 h with an overhead 300 W Xenon lamp (PLS-SXE300, Beijing TrustTech). The product was filtered, washed with distilled water and ethanol, and dried at 80 °C overnight.

2.3. Characterisation of the catalysts

The bulk and surface characteristics of all the samples were investigated by XRD, XPS and UV–vis DRS. Powder X-ray diffraction (PXRD) measurements were carried on a PANalytical X'Pert PRO diffractometer using Cu Kα1 ($\lambda = 0.15418$ nm) radiation under 45 kV, 40 mA with scanning in the range of 10–60° 2-θ. Crystallite sizes of the samples were estimated from the corresponding X-ray diffraction peaks on (110) diffraction of BiOCl by using the Scherrer Equation: $\tau = K\lambda/\beta\cos\theta$, where τ is the mean crystallite size of the ordered domains, K is the shape factor, which has a typical value of about 0.9, λ is the incident X-ray wavelength, β is the line width at half the maximum intensity (FWHM), and θ is the Bragg angle.

Surface elemental analysis by X-ray photoelectron spectroscopy (XPS) was conducted on a VG ESCALAB2 XPS spectrometer with an Al Kα monochromatic source and a charge neutraliser. All the binding energies are referenced to C 1*s* peak at 284.5 eV. Core levels of Bi 4*f*, O 1*s*, Cl 2*p*, Ag 3*d*, Pd 3*d*, Pt 4*f* and Rh 3*d* are identified individually.

Optical properties of the samples were studied by UV–vis spectroscopy. The diffuse reflectance spectra (DRS) were recorded on a Varian Cary 5000 UV–vis spectrometer with scan rate of 600 nm min^{-1}. Both absorbance and diffuse reflectance spectra were recorded for all samples. The band gap was derived from the formula $E_g = 1239.8/\lambda_g$, in which λ_g represents the absorption edge. The optical absorption near the band gap edge follows the equation $\alpha h\nu = A(h\nu - E_g)^{n/2}$ which has been reported in the previous literature [17]. For a specific semiconductor, the square of absorption coefficient ($n = 4$) is linear with energy for direct optical transitions in the absorption edge region, whereas the square root of absorption coefficient ($n = 1$) is linear with energy for indirect transitions.

2.4. Photocatalytic activity measurement

The photocatalytic activity of the samples was determined by degradation of Rhodamine B (RhB) in an aqueous solution under UV light irradiation with an overhead 300 W Xenon lamp (PLS-SXE300, Beijing Trust Tech) as the light source. The intensity of the incident UVA light on the solution was detected to be 4.98 mW cm^{-2} by using a radiometer (Beijing). In each experiment, 0.1 g photocatalyst was dispersed into 100 mL RhB aqueous solution (20 mg/L) in a 500 mL beaker. Prior to irradiation, the suspension was magnetically stirred in dark for 60 min to establish the adsorption–desorption equilibrium between catalyst and RhB. During the photocatalytic reaction, approximately 3 mL suspension was collected at given time intervals and centrifuged (14,000 rpm, 3 min) to remove photocatalyst particles. The collected solution was tested by a Perkin-Elmer Lamda 750S UV–visible spectrophotometer. The characteristic adsorption peak of RhB at 553 nm is used to determine its degradation.

2.5. Band structure estimation

The activity of a photocatalyst closely relates to its electron band structures in terms of the excitation, transportation and fate of the