Improved photocatalytic and disinfection efficiency of 2D BiOCl modified by Ag nanoparticles

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Abstract
2D BiOCl nanodiscs were synthesized by one step hydrothermal method as photocatalyst. To enhance its photocatalytic activity, Ag nanoparticles were deposited on the surface of BiOCl generating BiOCl-Ag heterogeneous composites. A samples were characterized by X-ray diffraction (XRD), Raman spectra, Scanning electron microscope (SEM), Transmission electron microscopy (TEM), X-ray photoelectron spectra (XPS) and UV-vis absorption spectra. To evaluate their photocatalytic performance, photodegradation of sulfanilamide (SAM) was studied. Results show that after introducing Ag NPs, the degradation efficiency was increased by 71.7%, indicating that Ag nanoparticles have an essential effect on the photocatalytic process. Specifically, Ag nanoparticles can work as electron trappers to increase the photo-induced electron-hole pair separation efficiency during the photocatalytic process. As excellent antibacterial agent, Ag may benefit BiOCl on its antibacterial ability. By using *E. coli* and *B. subtilis* as target bacteria, the antibacterial activity of BiOCl and BiOCl-Ag was investigated. Though BiOCl existed antibacterial efficiency to some extent under visible light irradiation, they performed much better after being modified by Ag NPs. Nearly 100% *E. Coli* and *B. subtilis* were killed in 2 h under solar light illumination, suggesting that the doping of Ag NPs has successfully improve the antibacterial ability of BiOCl under solar light irradiation. The degradation of SAM and the antibacterial effect against suggest that Ag modified BiOCl nanodiscs have promising application in dealing with water polluted by sulfonamide kind antibiotics or by pathogens which the energy power mainly comes from solar energy.

Keywords
semiconductor; photocatalysis; solar energy

INTRODUCTION

Semiconductor photocatalysis is regarded as an efficient technology to degrade pollutant and to split water. To improve the photocatalitic efficiency, one promising solution is to synthesis multifunctional co-catalyst/semiconductor photocatalysts (heterogeneous photocatalysts). Especially, decoration the semiconductor with metal nanoparticles is a quite popular strategy to decrease charge carrier recombination rate. Among various metals, noble metals (e.g. Pt, Au, and Ag) are widely used because of their noble and/or catalytica character (Marschall, 2014). In this paper, we synthesized two dimensional BiOCl nanodiscs, and modified them with Ag nanoparticles to study the possible effect on photocatalytic property caused by the deposition of Ag. Addtionally, the disinfection effect of BiOCl as well as BiOCl-Ag composites against *E. Coli* and *B.subtilis* were also investigated.

MATERIALS AND METHODS

Materials

$Bi(NO_3)_3{\cdot}5H_2O$, WCl_6, NaCl, KCl, Ethylene glycol ($(CH_2OH)_2$,EG), Urea (CO(NH2)2), ethanol and sulfanilamide (SNM)

Synthesis of BiOCl and BiOCl-Ag composites

The synthesis of 2D BiOCl was carried out by hydrothermal method while the BiOCl-Ag plasmonic composites was synthesized through a simple photoreduction method.

Mateirals Characterization

The products were characterized XRD, SEM, TEM, XPS, UV-Vis Spectra.

Photocatalytic activity test

Photodegadation of SAM and antibacterial activity under solar light

Photocatalytic activity of BiOCl and BiOCl-Ag was evaluated by photocatalytic degradation SAM (20 ppm) using a 1.5 AM solar simulator with a 200 W Xe arc lamp where UV part is removed. Similar conditions were applied in testing antibacterial activity against against *E. coli* and *B.subtilis*.

RESULT AND CONCLUSIONS

Morphology and crystal structure characterization

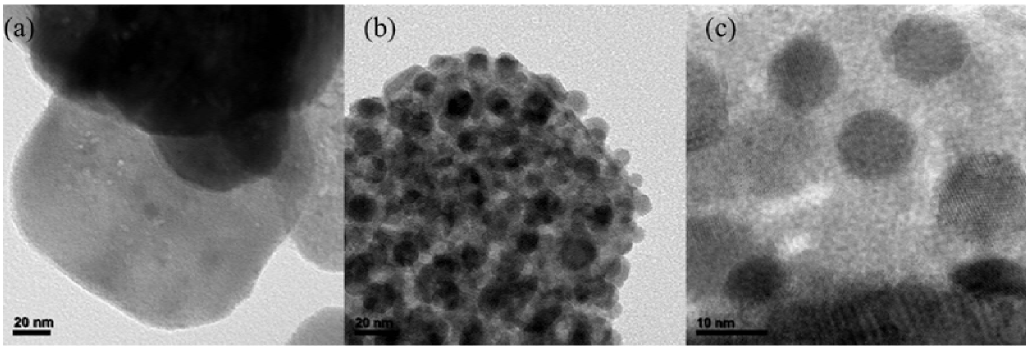

Figure 1. TEM images of BiOCl (a), BiOCl-Ag (b) and (c).

The morphology of BiOCl and BiOCl-Ag composites were characterized by TEM in **Figure 1**. BiOCl has disc-like shape with a size around 100 nm while after photoreduction of AgNO3 for 2 h, clearly Ag NPs were observed on BiOCl-Ag composites.

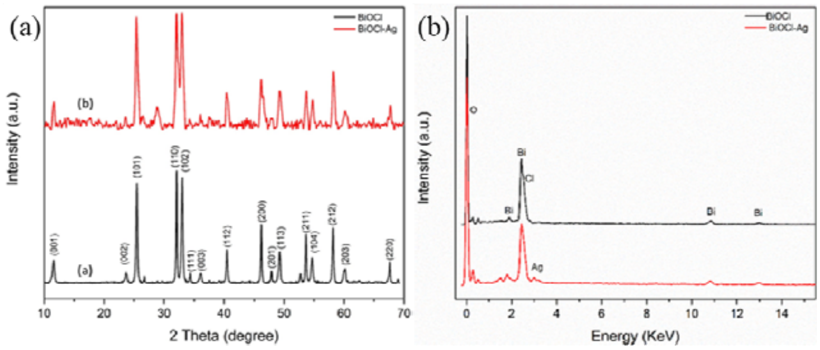

Figure 2. XRD patterns (a) and EDX (b) of BiOCl and BiOCl-Ag composites.

XRD spectra was used to study the loading effect of Ag NPs on the crystallinity of BiOCl where no significant detriment was found in the pattern of BiOCl-Ag composites **Figure 2**(a). Ag peaks were also not obvious due to the low amount of Ag deposited. However, when used EDX to study these two catalysts **Figure 2**(b), new peaks belonging to Ag could be observed in the EDX spectra of BiOCl-Ag composites proving that Ag had been successfully introduced.

Ag NPs could affect the optical properties of BiOCl as indicated in **Figure 3**. Especially, BiOCl-Ag had higher absorption in the range of solar light (**Figure 3**(a)) implying that such improvement in the light absorption may bring higher photocatalytic efficiency. Similarly, loading of Ag NPs changed the Raman spectra of BiOCl (**Figure 3**(a)). Though share the similar pattern, BiOCl-Ag composites had peaks with much higher intensities compared to those of BiOCl. This is caused by the SRP effect of Ag NPs.

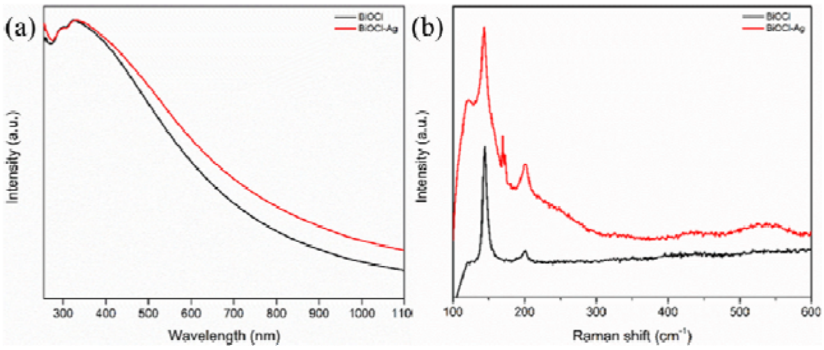

Figure 3. Comparison of UV-vis spectra of BiOCl and BiOCl-Ag (a); Comparison of Raman spectra of BiOCl and BiOCl-Ag (b).

To further study the elemental compositions of BiOCl and BiOCl-Ag, XPS was applied as displayed in **Figure 4**. Compared to pure BiOCl, Ag peaks were found in the XPS pattern of BiOCl-Ag (**Figure 4**(a)). High resolution scan spectra Ag 3d (**Figure 4**(b)) were also conducted. Mainly two peaks associated with the 3d doublet at 365.1 and 371.0 eV were detected, which assigned to the binding energy of Ag 3d5/2 and 3d 3/2 of metal Ag, respectively (Zhu, Chen, & Liu, 2011)[31-33]. Based on the results of XPS, the Ag content was calculated to be 1.835 at. %.

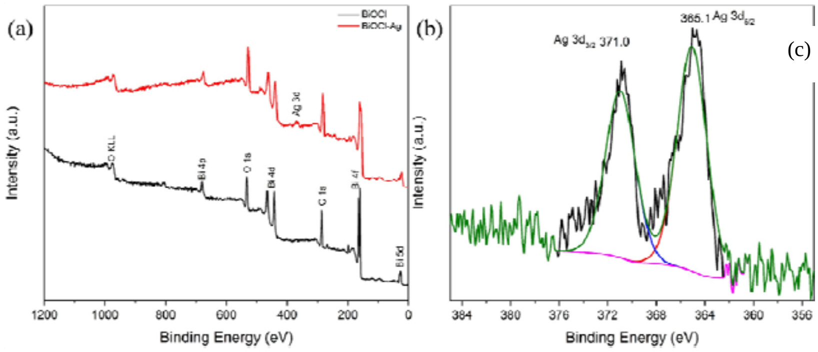

Figure 4. Survey spectrum of BiOCl and BiOCl-Ag (a); high resolution Ag 3d band (b).

Photocatalytic properties under solar light irradiation

The degradation of SAM (20 ppm) under solar light is presented in **Figure 5**(a). Significant improvement in degradation can be observed by using BiOCl-Ag where the efficiency increase from 23.3% to 40%. This was achieved by the enhanced electron-hole pair separation efficiency assigned to Ag NPs which act as electron sink. This would enhance the ROS generation efficiency during the photocatalytic process. (1)

Figure 6 presents the photos of colonies formed after treatment. When being irradiated, results show that BiOCl-Ag could strongly suppress the growth and reproduction of both bacteria. As a result, no colony was found. Such excellent antibacterial efficiency may be due to both the photocatalytic effect and antibacterial effect of Ag NPs.

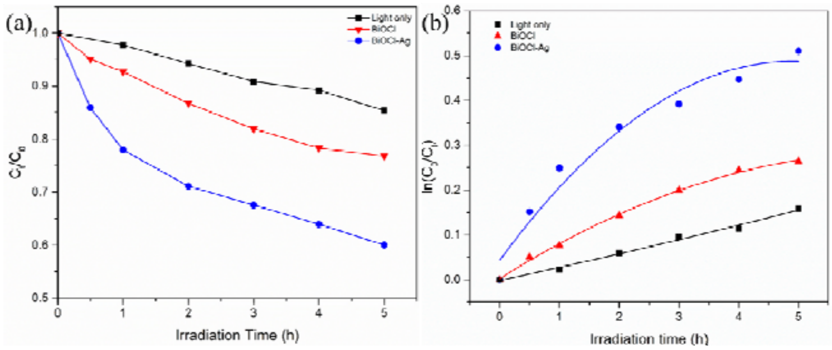

Figure 5 Degradation rate of SNM by light, BiOCl and BiOCl-Ag (a); Kinetic plot of degradation of SAM (b); (concentration of catalysts: 1g L^{-1})

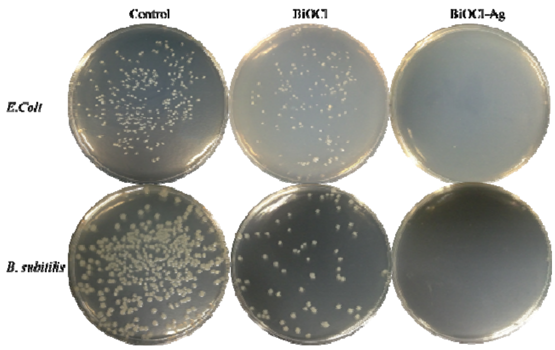

Figure 6. Photos of bacterial colonies formed by *E. coli* and *B. subtilis* cells treated by BiOCl and BiOCl-Ag after 2 h irradiation (concentration of catalysts: 1g L^{-1}).

In summary, after Ag NPs were loaded on the surface of BiOCl, significant improved photocatalytic and disinfection efficiency could be observed. These results strongly indicate that modifying BiOCl with Ag NPs is an effective way to enhance its photocatalytic performance. This would benefit the treatment of water with antibiotics like SAs group and pathogens.

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