

Enhanced Photocatalytic Decomposition Of Organic Dye Over A Novel Biochar/Rose-Like Biocl Composite Photocatalysts

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Abstract: *Biochar, as a new carbon source, has attracted more and more people's attention. In addition, the new catalyst bismuth oxychloride has been widely used for photocatalytic degradation, not only due to the special structure, high stability, but also has excellent electrical and optical properties. However, BiOCl can not be excited under visible light irradiation on account of its broad band gap. In this work, BiOCl is loaded on pine needle biochar to further improve the photocatalytic degradation efficiency. When the mass ratio of BiOCl and biochar at 3:4, it has exhibited the highest degradation efficiency.*

Keywords : Carbon materials; BiOCl; RhB; Photocatalytic degradation; Semiconductors

1. Introduction

The growing demand for the environmental remediation by photocatalysis needs to develop stable and effective photocatalytic materials, especially with high photoresponse ability, since the contaminated water and polluted air has become a widespread threat to public health^[1].

In recent years, as the novel photocatalyst, bismuth oxychloride (BiOCl) has come into people's notice, it has been widely used for photocatalytic degradation, not only due to the special structure, high stability, but also has excellent electrical and optical properties. In addition, rose-like BiOCl could not only enhance the absorbability to increase the photoabsorption efficiency but also reduce the recombination opportunities of the photo-generated electron-hole pairs, thus they could transfer to the surface rapidly to degrade the organic molecules^[2]. It is noteworthy that the layered structure is conducive to the separation of photogenerated electric-hole pairs and the transferring of charges. One thing to note is that BiOCl belongs to the wide-band-gap semiconductor and can only be activated under ultraviolet light irradiation. Meanwhile, its low absorbability and electronic transmission efficiency has seriously restricted photocatalytic activity. Therefore, it is imperative to develop efficient strategies to modify BiOCl photocatalyst. In fact, over the past decades,

several strategies have been developed to extend the photocatalytic activity of wide-band-gap photocatalysts, including the band-gap energy tailoring by surface deposition of noble metal nanoparticles with plasmon absorption, doping the exotic ions, coupling with a narrow band-gap semiconductor or colored dye, coupling with other electron acceptor materials^[3].

Of all the methods above, the most widely used is coupling with other electron acceptor materials. Because of its high absorbability and electronic transmission efficiency, carbon has been an idea electron acceptor material. As conventional carbon source, considering of the dwindling of fossil fuels and the environmental pollution, investigators are trying hard to seek for the green succedaneum. Recently, as a novel carbon source, because of its wide distribution, renewable, cheap and easy to get, biochar has attracted more and more researchers' attention. On the one hand, with abundant pore structure and huge specific surface area^[4], biochar can be used as an ideal adsorption material in the application of removing the organic contaminant from water^[5]. On the other hand, carbon is conductor, for this property it can be widely used as carrier to increase the transferring of charges. In China, pine needles regeneration speed fast, about 2~3 million tons of pine needles can be harvested throughout the year, that means pine needle biochar can be achieved easily from raw material.

In this work, in order to reduce the broad band gap of BiOCl, and increase the photoresponse ability, rose-like BiOCl is synthesized by hydrothermal and then loaded on modified biochar by means of tube furnace calcine. The photocatalyst has exhibited better photodegradation efficiency on degradation Rhodamine B (RhB) solution under UV-light irradiation. Therefore, by coupling with modified biochar, band gap is reduced effectively.

2. Experimental

Preparation of modified pine needle biochar

Pine needle biochar was obtained by high temperature calcination in the protection of N₂. The pretreated pine

needles were grinded to powder and reserved. Post pre-treatments, 1g pine needle powder were dissolved in 50ml 1mol/L $ZnCl_2$ solution with stirring for 6h. The product was collected through centrifugation and dried at $60^\circ C$. Next, the product was calcinated in tube furnace with the heating rate of $3^\circ C/min$ from $30^\circ C$ to $750^\circ C$, and lasted for 6h. After calcination, the black powders were dissolved in HCl solution and stirring for 30min, washing to neutral with deionized water and dried. Then the dried powders were dissolved in toluene with 3-aminopropyltriethoxysilane, stirred and refluxed in a nitrogen atmosphere for 12h. Finally, modified pine needle biochar was achieved.

Preparation of rose-like BiOCl

0.005mol $Bi(NO_3)_3 \cdot 5H_2O$, 0.005mol KCl and 0.005mol CA were dissolved in 30mL methanol and stirred for 30min, then transferred to autoclave at $150^\circ C$ for 6h. After washing and drying, rose-like BiOCl was obtained.

0.2g modified pine needle biochar (A procedure for preparation of modified pine needle biochar was described in detail in the Supplementary Materials) was dissolved in 10mL methanol, and ultrasound for 30min. At the same time, a certain amount of BiOCl (A procedure for preparation of rose-like BiOCl was described in detail in the Supplementary Materials) was dissolved in another 10mL methanol, after stirring for 30min, mixed with the solution above. Then heating in water bath until methanol was evaporation. Next, the samples were calcinated at $250^\circ C$ for 3h. Finally, the sample was combined.

Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis was analyzed by scanning electron microscope (SEM: JSM-7001F, Japan). The transmission electron microscopy (TEM), were examined by transmission electron microscopy (TEM: JEM-2010, Japan). The crystal phase was analyzed by powder X-ray diffraction. The optical properties of the samples were analyzed by UV-vis diffuse reflectance spectroscopy. Surface electronic states were analyzed on X-ray photoelectron spectroscopy.

The photocatalytic activity of the as-prepared photocatalysts was tested by photocatalytic degradation RhB. 0.05g as-prepared catalyst was added in 100ml RhB solution at the initial concentration of 15mg/L, stirring for 30min in the dark to reach adsorption-desorption balance. After then, photocatalytic degradation started under the irradiating with ultraviolet light, for each 10min taking 5ml solution, centrifugation. The concentration is calculated by absorbance

which is measured by a UV-vis spectrophotometer at a wavelength of 552nm.

3. Results

XRD is used to reveal the phase structure and crystal form. Figure. 1 shows XRD patterns of the as-prepared samples, there is no obvious difference between these diffraction peaks beside the intensity. The main peaks of pure BiOCl at 25.9° , 32.5° , 33.4° , 46.6° , 54.1° , 58.6° corresponds to (101), (110), (102), (200), (211) and (212) which can be indexed to the tetragonal phase with lattice constants of $a=b=3.891\text{\AA}$, $c=7.369\text{\AA}$ (JCPDS 06-0249). And no other peaks like Bi_2O_3 or $BiCl_3$ were found. The diffraction peak rate of (110) possesses larger value, which suggests that the synthesis of BiOCl ultrathin nanosheets with high percentage of exposed {110} facet, indicative of that rose-like BiOCl is preferential to grow among {110} facet. The diffraction peak at about 77.7° belongs to biochar, with the increase content of BiOCl, the intensity of this peak is a little weaker^[6,7]. As biochar is amorphous structure, it can not be identical with any standard card which is known. However, compared with the similar standard cards it can be sure that peak at 77.7° belongs to biochar^[8,9].

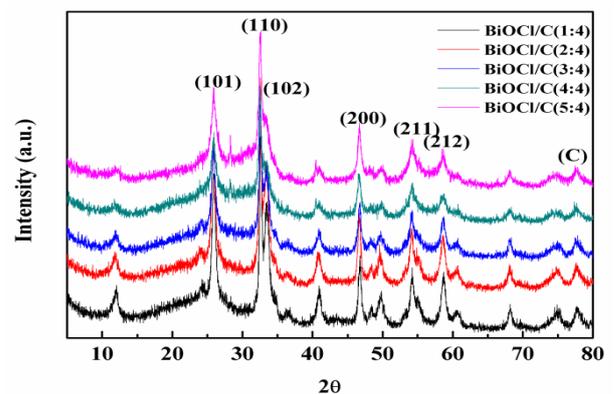


Figure 1. XRD patterns of BiOCl/C with different mass ratio

SEM, EDS and TEM images

For better understanding the morphology of as-prepared samples, SEM were tested, the morphology can be seen from Figure 2. In Figure 2a, it can be clearly seen that BiOCl was loaded on biochar. BiOCl was marked by blue circle with the diameter around 1~2um. Biochar could be seen with the red arrows marked, which is amorphous and a few microns in diameter. In Figure 2b, BiOCl looks like rose, it is assembled by ultrathin nanosheets with 200-300nm in width and the thickness at about 10-30nm. In EDS image, the peaks of C, O, Bi, Cl elements can be found, the existing of these elements has forceful proved that BiOCl loaded on modified pine needle biochar has

been succeed preparation. The biochar is marked with red arrow and BiOCl is yellow in Figure 2d, the structure of BiOCl looks like rose, which is consistent with the SEM

images. In Figure 2e, the ultrathin nanosheets are very thin and coincide with SEM image of Figure 2b.

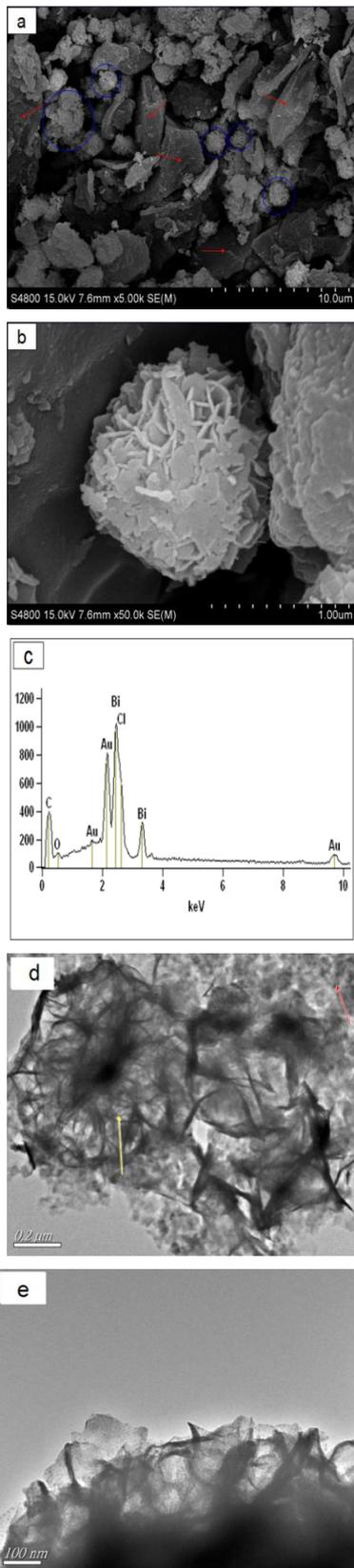


Figure 2 SEM and EDS pictures of BiOCl/C (3:4) (a-c), TEM pictures of BiOCl/C (d), BiOCl (e) XPS spectra

X-ray photoelectron spectroscopy (XPS) was taken to further prove the chemical states of each element mentioned above. From Figure S1a, we can find the peaks of the O, Bi, C, Cl elements, proved the existence of BiOCl and biochar. In Figure S1b, the peak of C 1s was individual illustrated. The peaks at 283.3eV, 286eV, 288eV are corresponding to C-C, C-O, C=O bond, respectively^[10]. During the synthesizing process, solvent was methanol and a certain amount of CA was added in, and biochar was treated by some organic reagents, so we could find the peaks of C-O and C=O in it.

DRS

The optical properties of the samples were measured by the diffuse reflectance spectroscopy. As known, BiOCl cannot be excitation under visible light irradiation on account of its broad band gap energy. From Figure S2, it can be seen that pure BiOCl and biochar have a strong response in the region of UV light area, but have no response in the region of visible light. After composited, absorbing boundary of BiOCl/C (3:4) has a red shift, photoresponse ability is obviously increased.

Photocatalytic activity test

From Figure 3, compared with different mass ratio, the BiOCl/C (3:4) composite photocatalyst showed the highest photocatalytic degradation efficiency at 91.33%. With the content of BiOCl increased, photocatalytic efficiency also improved, but when the ratio of BiOCl and biochar over 3:4, photocatalytic efficiency has decreased. Maybe when more BiOCl have been loaded on biochar, the active sites may be covered, then during the photocatalytic degradation, reactive species of which is conducive to the degradation cannot be generated.

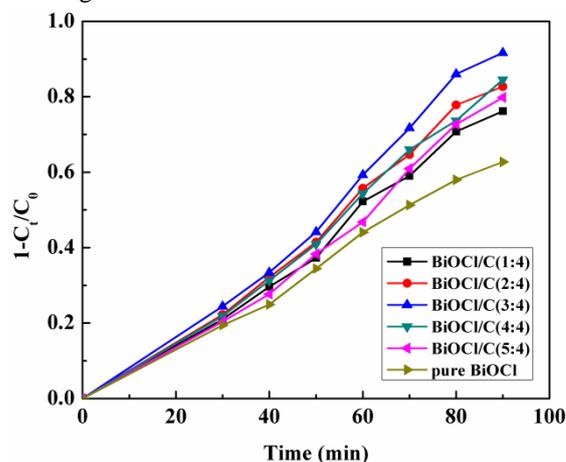


Figure 3. Degradation efficient of photocatalytic

Conclusions

In this work, the modified pine needle biochar loading rose-like BiOCl was successfully synthesized by hydrothermal method, and effectively enhanced the photocatalytic activity. In photocatalytic degradation 100ml 15mg/L RhB solution, the mass ratio of BiOCl and biochar at 3:4 showed the highest degradation efficiency at 91.33%.

Acknowledgments

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