Applied Catalysis B: Environmental 213 (2017) 136–146

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Fabrication of hollow mesoporous SiO_2-BiOCl@PANI@Pd photocatalysts to improve the photocatalytic performance under visible light

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ARTICLE INFO

Article history:
Received 18 February 2017
Received in revised form 2 May 2017
Accepted 7 May 2017
Available online 9 May 2017

Keywords:
Hollow mesoporous silica
Hybrid photocatalysts
LSPR
BiOCl
Polyaniline

ABSTRACT

A facile method was developed to synthesize a series of hollow mesoporous SiO_2-BiOCl@PANI@Pd (HBPP) photocatalysts with super adsorption performance, plasmonic effect and fast interfacial charge migration. The samples were characterized by XRD, FETEM, FT-IR, XPS, DRS, etc. Photocatalytic degradation of methyl orange (MO) by HBPP composites was investigated.

Results showed that the photocatalytic property of HBPP composite was superior to that of hollow mesoporous SiO_2-BiOCl@PANI (HBP) composite under visible light irradiation, and the $HBPP_{5wt\%}$ photocatalyst synthesized under 140 °C exhibits the highest photocatalytic activity. In this photocatalysis system, the orderly mesoporous opening structure of the hollow mesoporous SiO_2 sphere could effectively facilitate the transfer of reactant molecules, and the existence of the internal cavities would effectively prolong the action time of the irradiated light for the multiple reflections. Moreover, the formation of interacted interfaces between the semiconductor BiOCl and conducting polymer (polyaniline) could effectively improve the separation of the photogenerated electron-hole pairs, and the palladium nanoparticles (Pd NPs) with strong localized surface plasmon resonance (LSPR) absorption band in the near-UV region could effectively induce the generation of the photoexcited electron-hole pairs in BiOCl, thus the as-obtained photocatalyst exhibits superior photocatalytic activity under visible light irradiation. The work may set foundation for application of the new photocatalyst of HBPP-based LSPR and make an important step forward remedying environmental pollution.

1. Introduction

As a promising material, photocatalysts have attracted considerable attention in applications of remedying environmental pollution and dealing with energy crisis [1–5]. During the last two decades, the most widely TiO_2 has been developed in pursuit of high photocatalytic activity, high chemical stability, relative low-price and nontoxicity. However, the wide band gap (3.2 eV) and low quantum yield of TiO_2 limit its application in visible light range. Therefore, the work focused on TiO_2 modifications and the pursuit of better photocatalysts have attracted more attention in recent years. It's known that photocatalysis system can be generally classified as oxides (TiO_2, ZnO, NiO) [6–8], sulfides (CdS, ZnS) [9,10], and halides (AgCl, AgBr) [11–13], etc. Recently, lamellar BiOX (X = Cl, Br, I) as other species of bismuth-based materials have become a hotspot in photocatalysis field [14–17] for their unique properties of high dipole, indirect band gaps, high redox potential of holes and easily formed oxygen vacancies. However, some modification approaches to BiOCl semiconductor photocatalysts should be proposed to improve their photocatalytic property for their low visible-light response and low utilization efficiency of photon-generated carriers [3,18–20]. For instance, Yu et al. [21] developed a facile approach to synthesize the highly efficient $Bi_2O_2CO_3$/BiOCl photocatalyst. Di et al. [19] synthesized carbon quantum dots (CQDs) modified BiOCl ultrathin nanosheets photocatalyst via a facile solvothermal method. However, in previous studies, the electron was not excited from the valance band to the conductor band in the photocatalytic process of BiOCl.

In recent years, the applications of conducting polymer in photocatalysis field have been reported by many researchers [22–24]. It was demonstrated that introducing conducting polymer is an effective method to improve the photocatalytic performance of traditional semiconductor photocatalyst [25]. Polyaniline (PANI), a recognized promising conducting polymer, has attracted more and more attentions for the π-π conjugated electronic system, high absorption coefficients under visible light, high charge migra-

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http://dx.doi.org/10.1016/j.apcatb.2017.05.026
0926-3373/

tion and good environmental stability [26–28]. Zhang et al. [29] prepared TiO_2 photocatalysts modified with monolayer dispersed PANI via a facile chemisorption approach. Pei et al. [30] prepared PANI hybrid defective ZnO nanoparticles by a facile chemisorption method together with a cold plasma treatment technique. In these photocatalysis systems, the PANI acted as electron donor or hole acceptor to enhance the photocatalytic property under visible light irradiation.

Among numerous modification methods, the introduction of plasmonic nanoparticles (NPs) to traditional photocatalysis system has been extensively studied since it was firstly reported in 2008 [31]. On the one hand, plasmonic nanoparticles can accelerate the process of photoexited electron transferring to the substrate [13,32–35]. On the other hand, its strong interaction with electromagnetic fields also causes the localized surface plasmon resonance (LSPR) in the near-UV region, which is demonstrated to boost the excitation of electron-hole pairs in wide band semiconductor (i.e. TiO_2) and increase photocatalytic efficiency. Kowalska et al. [36] prepared hybrid photocatalysts composed of titania modified with plasmonic nanoparticles and ruthenium complexes for decomposition of organic compounds. Andreas et al. [35] reported a perfect palladium-based plasmonic perfect absorber at visible wavelengths and its application of hydrogen sensing. Moreover, it has not been reported that the palladium-based plasmonic renounce effect excites the electron-hole pairs in semiconductor. In this regard, we have proposed hybrid photocatalysts composed of plasmonic Pd NPs, BiOCl and PANI, as potential efficient materials for decomposition of organic compounds under solar radiation.

To the best of our knowledge, hollow mesoporous silica submicrospheres (H-mSiO$_2$), which can fulfill the multiple scattering of the irradiated light in the internal cavity, can efficiently prolong the action time of the irradiated light and promote the generation of the photoexcited electrons. Simultaneously, the orderly mesoporous opening structure can facilitate the transfer of reactant molecules [37–39]. Based on aforementioned consideration, a novel visible-light-driven (VLD) HBPP photocatalyst was successfully synthesized by loading the nanosheet BiOCl semiconductor, PANI conducting polymer and Pd plasmonic nanoparticles on the surface of amino-functionalized H-mSiO$_2$. Subsequently, MO was chosen as the target organic pollutant, and the photocatalytic activity of the HBPP photocatalyst for degrading MO in water system under the visible light irradiation was investigated, and the possible photocatalytic mechanism was also discussed.

2. Experimental section

2.1. Reagents and materials

All of the reagents were analytical pure. Absolute ethanol (EtOH), ammonia solution (25 wt%), tetraethoxysilane (TEOS), cetyltrimethylammonium bromide (CTAB), anhydrous sodium carbonate (Na_2CO_3), ammonium nitrate (NH_4NO_3), bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), 3-triethoxysilylpropylamine (APTES), potassium chloride (KCl), methyle orange (MO), aniline, $Pd(OAc)_2$, hydrochloric acid(HCl, 1 mol/L), Ammonium persulfate (APS), polyvinyl pyrrolidone (PVP), potassium iodide (KI), isopropyl alcohol (IPA), *p*-benzoquinone (BQ), $AgNO_3$ and P25 were purchased from J & K Chemical. Deionized water was used throughout the work.

2.2. The preparation of HBPP

2.2.1. Preparation of amino-functionalized H-mSiO$_2$

The preparation process was obtained by modifying a reported method [38] (Supplementary Note 1). The solid silica sub-microspheres were prepared by traditional Stöber hydrolysis method. Subsequently, in the presence of CTAB, the core-shell silica sub-microspheres were prepared by coating the silica on the surface of solid silica sub-microspheres. Moreover, the hollow silica sub-microspheres were prepared by the selective alkaline-tailored method under the protection of CTAB. After that, the mesoporous structure was prepared by calcination at 500 °C. Finally, aforementioned H-mSiO$_2$ was modified by the APTES at an acetonic system containing a small amount of ammonia solution (25 wt.%).

2.2.2. Preparation of H-mSiO$_2$-BiOCl@PANI@Pd photocatalyst

The Bi^{3+} ions and Pd^{2+} were anchored on the surface of amino-functionalized H-mSiO$_2$ under the complexation, and they transform into BiOBr nanosheet and Pd NPs on the surface of H-mSiO$_2$ by the hydrothermal synthesis. 0.3 g PVP, 0.3 g amino-functionalized H-mSiO$_2$, 0.5 g $Bi(NO_3)_3{\cdot}5H_2O$ and 0.025 g $Pd(OAc)_2$ were sonicated in 300 mL water for 10 min, and stirred for 1 h. In this stirring system, HCl was added to adjust the pH of solution, and 0.5 mL aniline was dissolved in the as-obtained solution. After blending uniformly, 0.01 g/mL 60 mL APS was dissolved in this system until the temperature rising to 40 °C, and the as-obtained mixed system was stirring slowly at 40 °C for 8 h. After the reaction finished, the sample was separated by centrifugalization at the speed of 10000 rpm and washed 2–3 times with distilled water. Subsequently, aforementioned sample was redispersed into 80 mL deionized water containing 0.3 g KCl. Then the mixture in the teflon liner was sealed in a stainless steel autoclave and maintained at 140 °C for 3 h. After cooled naturally to ambient temperature, the resultant products were washed several times with water and ethanol then dried for 12 h via the vacuum freeze-drying technology. To study the effect of the weight percent of Pd (Pd: BiOCl) on the photocatalytic performance of the products, HBPP photocatalysts with different weight percent of Pd (10 wt.%, 7 wt.%, 3 wt.%, 2 wt.% and 0 wt.%) were synthesized via the similar process.

2.3. Characterization

Fourier transform-infrared (FT-IR) spectra of the samples was recorded on a Perkin-Elmer 580BIR spectrophotometer using the KBr pellet technique. X-ray powder diffraction (XRD) analysis was performed on a Bruker AXS D8-advance X-ray diffractometer with Cu Kα radiation. The morphologies and sizes of the samples were characterized using a JEOL JEM-2100F field emission transmission electron microscopy (FETEM). X-ray photoelectron spectroscopy (XPS) datas were collected to examine the chemical states of the multi-component photocatalyst with an Axis Ultra instrument (Kratos Analytical, Manchester, U.K.) under ultrahigh vacuum condition ($<10^{-6}$ Pa) and using a monochromatic Al Kα X-ray source (1486.6 eV). N_2 adsorption/desorption isotherms were obtained on a TriStar II 20 apparatus. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area based on the adsorption branches. UV–vis diffuse reflectance spectra (DRS) was obtained using a Shimadzu UV-3600 spectrometer by using $BaSO_4$ as a reference at room temperature.

2.4. Evaluation of photocatalytic properties

The photocatalytic activities of the as-prepared HBPP photocatalyst were evaluated respectively by catalyzing the photodegradation of MO in aqueous solution at room temperature under the visible light irradiation with one 500 W xenon lamp (CHF-XM500, light intensity = 600 mW/cm^2) located at 20 cm away from the reaction solution. To make sure that the photocatalytic reaction was really driven by visible-light, all the UV lights with the wavelength less than 420 nm were removed by a glass filter (JB-420). In a typical reaction, 0.1 g of as-prepared supported photocatalyst was