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Photocatalytic degradation of ciprofloxacin by a novel Z-scheme CeO_2–Ag/AgBr photocatalyst: Influencing factors, possible degradation pathways, and mechanism insight

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In this study, CeO_2–Ag/AgBr composite photocatalysts with a Z-scheme configuration were fabricated by in situ interspersal of AgBr on CeO_2 and subsequent photoreduction process. The CeO_2–Ag/AgBr composites exhibited enhanced photocatalytic activity for the photodegradation of ciprofloxacin (CIP) under visible light irradiation. The effects of initial CIP concentration and various inorganic salts were investigated in detail. Three-dimensional excitation–emission matrix fluorescence spectra were used to further monitor the CIP molecule degradation. Plausible degradation pathways for CIP were proposed based on LC-MS instruments. Photoluminescence, electrochemical impedance spectroscopy, and photocurrent tests indicated the rapid transfer and migration of electrons–holes can be achieved in this ternary photocatalytic system. The enhanced photocatalytic performances of CeO_2–Ag/AgBr could be credited to the accelerated interfacial charge transfer process and the improved separation of the photogenerated electron–hole pairs. The existence of a small amount of metallic Ag is conducive to the formation of a stable Z-scheme photocatalytic system. This work would pave the route for the design of novel Z-scheme photocatalytic systems for application in solar-to-fuel conversion and photocatalytic water treatment.

1. Introduction

The large-scale use of antibiotics has posed a great threat to ecosystems and human health [1]. Ciprofloxacin (CIP), a typical second-generation fluoroquinolone (FQ) antibiotic, is extensively used in human and veterinary medicine because of its broad activity against bacteria and good oral intake properties [2]. Frustratingly, the CIP that enters the human or animal body can be partially broken down by metabolism and largely exist in the natural environment in a pharmacological form [3]. Today, CIP has been detected in different environmental matrices [4,5]. Worse, most wastewater treatment plants would not eliminate it effectively. Therefore, seeking an efficient strategy to eliminate CIP from wastewater is still imperative.

Semiconductor-based photocatalysis has been proven to be a promising technology for purifying water and wastewater [6,7]. Therefore, the search for suitable photocatalysts has become intensively pursued. Over the past few decades, researchers have sought visible-light-driven (VLD) photocatalysts [8–10]. Various VLD semiconductor materials, such as rare earth metal oxides, bismuth-based semiconductors, noble-metal-based semiconductors, and even non-metal-based graphitic carbon nitride have been exploited [11–13]. CeO_2, a rare earth metal oxide, is broadly used for catalysts, fuel cells, oxygen sensors, and luminescent materials due to its excellent characteristics [14–16]. Nevertheless, a single CeO_2 only slightly absorbs visible light and suffers from poor capability to separate electron–hole pairs. Great efforts have been devoted to overcoming these drawbacks and maximizing its catalytic performance. Among various methods, fabricating heterojunction structures have recently attracted the most interest from researchers [17,18]. For instance, fabricating of $BiOX/CeO_2$ (X = Br, I) p-n junctions can greatly improve the catalytic performance of CeO_2 [19,20]. Moreover, many kinds of semiconductors have been chosen to couple with it to form heterojunction structures, such as Ag_3PO_4 [21], C_3N_4 [22], or CdS [23]. Although traditional heterojunctions can effectively promote the separation of electron–hole pairs, the reduction and oxidation potentials of the composites are also reduced with the transfer of electron holes,

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leading to poor photocatalytic performance for refractory pollutants [24]. In contrast, Z-scheme photocatalysts can overcome this shortcoming. The photogenerated electrons in one photocatalyst with a lower conduction band (CB) can recombine with the holes in another photocatalyst with a higher valence band (VB) though the electron mediator. As a consequence, the holes can be retained at a higher oxidative level and react with H_2O molecules to produce $\cdot OH$ or oxidize organic pollutants directly; the generated electrons can be retained at a higher potential and further react with the O_2 to form the reactive superoxide radical [25]. Thus, the whole system not only promotes the effective separation of electrons and holes, but also maintains strong redox ability. Therefore, it is meaningful to fabricate CeO_2 photocatalysts based on a Z-scheme heterostructure that can have excellent photocatalytic properties for the elimination of refractory pollutants.

Recently, AgBr has been reported as a promising VLD photocatalyst for pollutant degradation or inactivation of bacteria due to its excellent optical properties and catalytic activity [26,27]. Furthermore, when it was exposed to light, the Ag^+ ions in AgBr can be easy to reduce to Ag due to its photosensitivity. With noble metal Ag nanoparticles (NPs) coexisting on the AgBr, on one hand, the visible light absorption of the catalysts would be greatly improved via the surface plasmon resonance (SPR) of the Ag nanoparticles (NPs); on the other, noble metal Ag NPs can also be used as electron mediators in Z-scheme heterostructural photocatalysts, such as Ag_3VO_4/AgBr/Ag [28], Ag–AgBr@$Bi_{20}TiO_{32}$ [29], AgI/Ag/AgBr [30], and Ag@AgBr/g-C_3N_4 [31]. Anchoring Ag/AgBr onto CeO_2 seems to be an ideal way to enhance the photocatalytic activity of CeO_2.

In this paper, novel Z-scheme CeO_2–Ag/AgBr heterostructural photocatalysts with CeO_2 spindles decorated by Ag/AgBr NPs were prepared by a facile in situ co-precipitation method followed by a photoreduction process. The photocatalytic activities of the obtained photocatalysts were evaluated via the photodegradation of CIP under visible light irradiation. LC-MS was applied to analyze the possible intermediates formed in the photodegradation process. 3D EEMs was used to further monitor the CIP molecule degradation. Photoluminescence (PL), electrochemical impedance spectroscopy (EIS), and photocurrent tests were used to investigate the charge separation and migration behaviors. Diffuse reflectance spectra (DRS) and Mott–Schottky tests (MS) were applied to confirm the band structure of the pure catalysts. Active species trapping experiments and the electron spin resonance (ESR) technique were used to identify reactive species that participated in the photocatalytic degradation process. Based on an energy band determination, photoelectrochemical investigations, the ESR test, and an active-species-trapping experiment, a plausible mechanism is also proposed and discussed in detail.

2. Experimental

2.1. Chemicals and reagents

Silver nitrate ($AgNO_3$), polyvinylpyrrolidone K30 (PVP), potassium bromide (KBr), isopropyl alcohol (IPA), sodium oxalate ($Na_2C_2O_4$), sodium hydroxide (NaOH), cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$), polyvinyl alcohol (PVA), benzoquinone (BQ), ciprofloxacin (CIP), and urea were all purchased from Shanghai Chemical Reagents Co. All ultrapure water used in all the experiments was obtained from a Milli-Q ultrapure (18.25 MΩ cm) system.

2.2. Fabrication of CeO_2–Ag/AgBr photocatalyst

CeO_2 spindles were prepared via urea hydrolysis and calcination according to the previously reported method [32]. CeO_2–Ag/AgBr photocatalysts were prepared via a facile in situ coprecipitation method with the assistance of photoreduction. In brief, 0.20 g CeO_2 was ultrasonically dispersed in 60 mL of distilled water to get a uniform solution A. Then 5.0 mL 0.1 M silver nitrate solution was added dropwise to solution A under vigorous stirring. The mixture was further stirred for 30 min at room temperature. Afterward, 5.0 mL of 0.1 M KBr solution was added dropwise to the above solution and stirred for 1 h in the dark. Eventually, the suspension solution was irradiated for 1 h under a 300 W Xe lamp. The precipitate was collected by vacuum filtration and washed several times with ultrapure water and alcohol. CeO_2–Ag/AgBr composites with 21.26 wt% of Ag (denoted as CAB-21.26) were obtained after drying in a vacuum oven at 60 °C for 12 h. Similarly, by changing the volume of $AgNO_3$ (1.00 mL, 3.00 mL, 5.00 mL), CeO_2–Ag/AgBr hybrids with different Ag mass ratios of 5.12, 13.94, and 27.43 wt% (denoted as CAB-5.12, CAB-13.94, and CAB-27.43) were obtained. Pure Ag/AgBr was prepared according to the same procedure as above without the addition of CeO_2. For comparison, an Ag/CeO_2 sample (Ag/CeO_2 weight ratio = 21.26 wt%) was prepared according to the same procedure as above in the absence of KBr.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance instrument in a 2θ range of 10–80°. The morphologies were examined using field emission scanning electron microscopy (SEM, Hitachi S4800). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were acquired with a JEOL 2100 transmission electron microscope. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250X. UV–vis diffuse reflectance spectra (DRS) were measured on a Hitachi U-4100 with $BaSO_4$ as a reference material. Fluorescence spectra were monitored with a fluorescence spectrophotometer. Three-dimensional excitation–emission matrix fluorescence spectra (3D EMMs) and PL spectra were recorded using a FluoroMax-4 fluorescence spectrophotometer. The Brunauer–Emmett–Teller (BET) specific surface area of the powders was analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). A Shimadzu total organic analyzer (TOC-L series) was used to perform TOC analysis. The electron spin response (ESR) signals of radicals spin-trapped by the reagent 5, 5-dimethyl-l-pyrroline N—oxide (DMPO) were examined on a Bruker ER200-SRC spectrometer under visible light irradiation (λ > 420 nm). Electrochemical measurements were carried out via a CHI660E electrochemical workstation with a standard three-electrode probe. The details are provided in the Supplementary Information.

2.4. Photocatalytic activity tests

CIP was used to evaluate the photocatalytic activity of the obtained samples. The visible light source was a 300 W Xe lamp (Zhong jiao jin yuan, CEL-HXF300) equipped with a UV cutoff filter(UVCUT420). Briefly, 50 mg of catalyst was added into CIP (50 mL, 10 mg/L) solutions. Before the light was switched on, the suspensions were stirred for 30 min in the dark to reach adsorption–desorption equilibrium. During the irradiation, an approximately 3.0 mL suspension was taken out and separated at given time intervals to obtain the supernatant liquids. The concentration of the pollutants was measured with a UV–vis spectrophotometer at their maximum absorption wavelength (277 nm for CIP). Determination of the photodegradation intermediates of CIP was carried out on a LC–MS system. The details are provided in the Supplementary Information.