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Preparation and photocatalytic properties of visible light driven Ag-AgBr-RGO composite

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ABSTRACT

A visible light responsive photocatalyst (Ag-AgBr-RGO) consisting of Ag-AgBr composite dispersed over reduced graphene oxide (RGO) was synthesized via a facile method. The as-prepared samples were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Nitrogen adsorption-desorption measurements, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectrum measurements (FTIR), and UV–visible diffused reflectance spectra (UV–vis DRS). The photocatalytic activity of the composite was evaluated by degradation of rhodamine B (RhB) and p-nitrophenol (PNP) under visible light irradiation. The results indicated that the Ag-AgBr-RGO catalyst showed more enhanced photocatalytic activity and stability than the pure Ag-AgBr. The excellent photocatalytic activity of Ag-AgBr-RGO catalyst could be attributed to the heterojunctions among three materials (Ag^0, AgBr and RGO). Finally, a possible photo-degradation mechanism was postulated based on the tests of photoactive radicals.

1. Introduction

Water pollution caused by organic dyes and aromatic compounds has a negative impact on human health and ecosystem. However, it is difficult to degrade them completely by conventional physical, chemical or biological techniques because of their structural stability and resistance to biodegradation [1,2]. Therefore, developing a highly-efficient and cost-effective clean technology for decomposition of the harmful organics has always been the pursuit of environmental remediation [3]. In recent years, the semiconductor-aided photocatalysis using solar energy has been recognized as one of the most effective and green technologies to solve the existing environmental problems [4]. Of the well-known photocatalysts, Although TiO_2 has proven to be one of the most excellent and most cost-effective materials for the degradation of organic pollutants due to its relatively high reactivity, innocuousness, chemical and biological stability [5–7], its practical industrial application is significantly limited by widely-accepted two bottleneck factors, including a poor absorption of visible light with a wide band gap and low quantum efficiency arising from the rapid recombination of photo-induced electrons and holes [8,9].

Recently, it was demonstrated that Ag-AgX (X = Cl, Br, I) could work as a prospective photocatalyst under visible light irradiation, which originates from the surface plasmon resonance of metallic Ag^0 and its synergistic effect together with the photosensitive characteristic of AgX [10–12]. Unfortunately, the semiconductor had no stable activity under visible light irradiation because the transformation of Ag^+ to Ag^0 was usually accompanied during the photocatalytic process. In addition, the reported Ag-AgX photocatalysts often have larger size and wider size distribution. Therefore, it is rather necessary to further improve the photocatalytic activity and stability of Ag-AgX composite.

Graphene, with a single layer sp^2-bonded carbon atoms arranged in a honeycomb lattice, has been suggested to be a promising supporting material to disperse and stabilize inorganic nanoparticles for potential applications in the catalysis fields. Coupling with graphene and graphene derivatives, such as graphene oxide (GO) and reduced graphene oxide (RGO), has been proved to be an effective strategy to improve the quantum yield of a semiconductor photocatalyst [13,14]. What's more, GO could provide abundant opportunities for the construction of GO-based photocatalysts because of its large specific surface area, high optical transmittance, and unique electronic properties caused by the locally conjugated aromatic system [15–17]. Furthermore, GO are decorated with diverse oxygen-containing functional groups, including carbonxyl, hydroxyl, epoxide, which increases its solubility and provide fertile opportunities for the construction of GO-based hybrid composites [18,19]. Therefore, in virtue of the excellent properties of GO, promising results can be expected from coupling GO with Ag-AgX as it is expected to improve the efficiency of photocatalytic activity and fabricate the Ag-AgX species with controlled size and shape.

Herein, considering the broad interests of GO and the significant concerns of visible light driven plasmonic photocatalysts, we developed

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a facile solution route to synthesize a kind of Ag-AgBr-RGO composites. Here, the hybridized RGO sheets serve as acceptors of the generated electrons of semiconductors and then effectively suppress the charge recombination. Moreover, the Ag-AgBr-RGO catalyst exhibited excellent activity and stability for the photodegradation of organic pollutants under visible light irradiation. Finally, a possible enhanced photocatalytic mechanism was investigated and presented on the basis of our experimental tests and modern spectra characterizations. This work should provide an easy avenue and open new opportunities for an in-deep investigation on graphene-based photocatalysts for their practical applications.

2. Experimental section

2.1. Materials

Silver nitrate ($AgNO_3$) and Hexadecyl trimethyl ammonium bromide (CTAB) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Graphene oxide aqueous solution (12.35 mg/mL) was supplied by Shanxi Coal Chemical Research Institute, China. Polyvinyl pyrrolidone (PVP) and absolute ethanol were obtained from Tianjin, P. R. China. All chemicals were of analytical grade without further purification. Distilled water was used in the whole experiments.

2.2. Preparation

Ag-AgBr-RGO composite was synthesized via a facile and fast solvothermal-photoreduction method. In a typical procedure, GO was added to polyvinyl pyrrolidone (PVP) ethanol solution with vigorous stirring for 10 min, the $AgNO_3$ ethanol solution was then added drop by drop. The mixture was then ultrasonicated with probe ultrasonic for 30 min and marked as solution A. Next CTAB solution was added to solution A at a rate of 0.4 mL/min. Subsequently, the mixture was transferred into a Teflon-lined stainless steel autoclave, and kept at 100 °C for 30 min. After cooling the mixture down to room temperature, the samples were collected, washed with distilled water and absolute ethanol for three times. The samples were then dried at 70 °C to obtain AgBr-RGO composite. The reduction of some Ag^+ ions to Ag^0 was carried out via irradiation by a 300 W UV–vis light source for 30 min. The precipitate was then collected and dried in air to obtain the Ag-AgBr-RGO composite. Reference AgBr and Ag-AgBr were prepared using the same procedures without the irradiation steps and introduction of GO, respectively.

2.3. Characterization

The structural information of the as-synthesized powders was collected by X-ray diffraction (XRD) performed on a D8 ADVANCE A25 using Cu Kα radiation (λ = 1.5406 Å). The morphologies were further examined with scanning electron microscopy (SEM, JSM-7001F) and transmission electron microscopy (TEM, JEM-2100F) operated at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was carried out by using a Kratos Analytical AXIS Ultra DLD spectrometer using a monochromatic Al Kα source. The Brunauer-Emmett–Teller (BET) surface area and porosity were measured on a Quantachrome Autosorb-1 (USA) automated sorption system. Fourier transform infrared spectra (FTIR) were recorded from KBr pellet in a Thermo Nicolet 380 spectrophotometer. The optical properties of the samples were studied by the UV–visible diffuse reflectance spectroscopy (DRS) using a UV–vis spectrometer (UV2550, Shimadzu, Japan) in the range of 250–700 nm, in which $BaSO_4$ was used as the reflectance standard material. The concentration of Ag ions in remaining solutions was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo iCAP6300, USA).

2.4. Evaluation of photocatalytic activity

The photocatalytic performance of the as-prepared photocatalyst was evaluated by decomposing RhB and PNP under visible light irradiation. A 300 W Xe lamp was used as the light source with a 400 nm cutoff filter to ensure complete removal of radiation below 400 nm. The photodegradation experiments were carried out at room temperature as follows: aqueous suspensions of RhB (100 mL, 10 mg/L) or PNP (100 mL, 5 mg/L) with the as-prepared catalyst were placed in the beaker. Prior to irradiation, the dispersions were magnetically stirred in the dark for 30 min to disperse the photocatalyst sufficiently. At given irradiation time intervals, about 6 mL dispersions were collected and centrifuged to remove the particles. The absorption UV–vis spectrum of the centrifugated solution was then recorded using an UV–visible spectrophotometer (Unico UV-2102PC). The photocatalytic degradation efficiency was calculated using the formula as follows:

$$D\% = [(C_0 - C_t)/C_0] * 100\% = [(A_0 - A_t)/A_0] * 100\% \quad (1)$$

where C_0 and A_0 denotes the initial concentration and absorption balance value, respectively. C_t and A_t is the concentration and absorption balance value of t time.

3. Results and discussion

3.1. Formation mechanism

Fig. 1 displays the graphical illustration for the formation mechanism of the synthesized Ag-AgBr-RGO composite. The GO can be well dispersed in water to form a homogeneous and stable light-brown solution owing to the existence of oxygenous groups, such as hydroxyl group, carboxyl group, oxygen-containing groups [20]. In the GO solution, the negative functional groups can easily combined with Ag^+ to form Ag^+ -GO by an electrostatic attraction interaction after the addition of $AgNO_3$ solution. The well dispersion of Ag^+ ions leads to the formation of AgBr crystal nucleus. What's more, in the process of AgBr grain growth, the wrap of GO sheets can strain the diffusion of Ag^+ and Br^- ions, thus slowing down the growth rate of AgBr. Following the solvothermal and photoreduction process, GO was reduced to RGO and certain amounts of Ag^+ ions were reduced to Ag^0 nanoparticles under laboratory light conditions, leading to the final formation of Ag-AgBr-RGO composite.

3.2. XRD analysis

XRD was applied to detect the phase composition and phase structure of the as-prepared samples. The XRD peaks observed at 26.7°, 30.9°, 44.3°, 52.5°, 55.1°, 64.5° and 73.2° can be perfectly indexed to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0) and (4 2 0) planes coinciding with the standard face centered cubic AgBr phase (JCPDS No. 06-0438). The peak at 38.2° can be indexed to (1 1 1) reflection of Ag^0 (JCPDS No. 65-2871). However, no peak attributed to RGO was observed in the XRD pattern because the trace amount of loaded RGO with a low atomic number could not be resolved by XRD. Besides, the addition of GO did not change the diffraction peak position of AgBr in the composite when compared with the JCPDS standard data of AgBr, which indicated that RGO was not incorporated into the lattice of AgBr.

3.3. SEM and TEM images

To further obtain the microscopic morphology and structure information, the SEM and TEM analysis of the as-prepared samples were investigated. As shown in Fig. 3a, the pure Ag-AgBr particles exhibited the irregular and aggregated grains with size of several micrometers. In contrast, when the GO was added to the reaction system, the Ag-AgBr particles were well dispersed on the surface of RGO sheets, and the average size of Ag-AgBr decreased to ca. 0.6 μm. This could be due to