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3D graphene aerogels-supported Ag and Ag@Ag_3PO_4 heterostructure for the efficient adsorption-photocatalysis capture of different dye pollutants in water

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ABSTRACT

In this paper, we successfully synthesized 3D graphene aerogels-supported Ag and Ag@Ag_3PO_4 heterostructure (3D Ag/Ag@Ag_3PO_4/GA) by the hetero-growth of Ag_3PO_4 on partly Ag nanoparticles in macroporous 3D graphene aerogels (3D GA), aiming for the efficient adsorption-photocatalysis capture of both cationic (RhB, MB, and NR) and anionic (MO) dyes from aqueous solutions. For the removal of different dyes, the contributions of adsorption and photocatalysis is different and the apparent removal sequence is NR > RhB > MB > MO on the prepared 3D Ag/Ag@Ag_3PO_4/GA. Compared with bare Ag_3PO_4 particles, Ag_3PO_4/GO, and Ag/Ag@Ag_3PO_4/GO, the prepared 3D Ag/Ag@Ag_3PO_4/GA exhibits the highest catalytic activities for the visible light degradation of RhB and MO. The possible mechanism for improved photocatalytic degradation of dyes by the 3D Ag/Ag@Ag_3PO_4/GA is proposed based on the active species trapping experiments. Moreover, the good stability and convenient recycling of the prepared 3D Ag/Ag@Ag_3PO_4/GA composite further make it have potential application prospect in eliminating organic contaminants.

1. Introduction

Visible light photocatalytic degradation method has attracted considerable attention to solve the aromatically structured organic dyes discharged from factories, with potential improvements in simplicity and cost-effectiveness over existing UV-employed photochemical technologies [1–3]. One of the key objectives in this field is to develop high-efficiency visible light active photocatalysts.

Recently, Ag_3PO_4 semiconductor has been demonstrated to possess excellent photooxidative capabilities for the photodecomposition of organic dyes under visible light irradiation [4,5]. However, there are still some inherent limitations for its practical applications, such as the slight solubility in aqueous solution, structural instability and the photocorrosion due to the absence of electron acceptors [6,7]. To further optimize its photocatalytic performances, various Ag_3PO_4 based hetero-photocatalysts, including TiO_2/ Ag_3PO_4 [8], AgX/ Ag_3PO_4 [9], $LaCO_3OH$/ Ag_3PO_4 [10], $BiOCl_{1-x}Br_x$/ Ag_3PO_4 [11], etc., have been synthesized and their synergistic behaviours have been studied in detail. Among them, Ag nanoparticles loaded on the Ag_3PO_4 semiconductor to form hetero-photocatalysts have attracted wide attention [12]. It is because Ag nanocrystals can not only effectively promote visible light absorption and facilitate the separation of photoexcited electron-hole pairs but also increase the O_2 adsorption, produce more active hydroxyl groups, and increase the catalytic activity [13].

It is well known that the surface adsorption properties of the catalysts, besides the structure and morphology, also play an important influence on its photocatalytic degradation performance. That is to say, increasing the intimate interface between the catalysts and pollutants would further lead to an improved efficiency of the photocatalytic degradation. Thus several studies have focused on the functionalized graphene-based semiconductor photocatalysts not only because of the good electron conductivity, large specific surface area and high adsorption of graphene, but also that graphene is very effective in enhancing light absorption in visible light wavelength range [14–16]. Meanwhile, like the Ag nanoparticles, the work function of graphene is also larger than that of bare Ag_3PO_4, and thus the schottky barrier formed on the interface of graphene/Ag/ Ag_3PO_4 ternary composite further reduces the recombination of free electrons and holes [17]. For example, Chen et al. have designed the reduced graphene oxide-based Ag/Ag_3PO_4 hetero-photocatalyst by coprecipitation and

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photoreduction [18]. Compared with Ag/Ag_3PO_4 and graphene/ Ag_3PO_4, the ternary composite exhibited greatly enhanced photocatalytic activity under visible light irradiation for photodegradation of not only cationic dye but also anionic dye. However, owing to the nanoscale morphology of these graphene-based Ag/ Ag_3PO_4 photocatalysts, it is difficult to carry out successive recycling in practical application.

Recently, 3D graphene structures, such as graphene hydrogels (GH) and graphene aerogels (GA), have attracted much attention as a new type of porous material constructed by interconnecting 2D graphene sheets [19]. Due to its porous and interconnected network structure, 3D graphene exhibits large accessible surface area, excellent mechanical strength and good flexibility in addition to the inherent properties of 2D graphene [20]. The macroscopic porous structure of 3D graphene makes it an easy and convenient recycling support for semiconductor photocatalysts. Based on the excellent structure and properties of 3D graphene, it could be used as an electron capture agents to improve the charge transportation and separation. Therefore, if photocatalyst could be anchored on the surface of 3D graphene and utilized the combinative merits of photocatalyst and 3D graphene, a superior performance would be obtained. 3D Ag_3PO_4/ GH [21] and 3D AgX/GH [22] have been adapted to exhibit convenient recycling and improved charge separation, structural stability and photocatalytic activity.

In light of above two accomplishments and considering that, most of the plasmonic Ag nanocrystals are well dispersed in rGO sheets, rather than on the surface of Ag_3PO_4 particles or covered by Ag_3PO_4 particles, are reported to have better photocatalytic activity and stability than the former reported GO(rGO)-Ag_3PO_4@Ag nanocomposites [23,24]. Herein, we report a novel 3D Ag/Ag@Ag_3PO_4/GA structure, in which 3D Ag/GH with interconnected macroporous networks is first prepared via a facile one-step hydrothermal method, and then by introduction of the $[Ag(NH_3)_2]^+$ complex to activate the surface of Ag atoms of Ag nanoparticles, Ag_3PO_4 nanoparticles are hetero-grown on the surface of part of Ag nanoparticles in rGO sheets to form 3D Ag/Ag@Ag_3PO_4/GA. Combined with the unique adsorption of GA and the effective photocatalysis performance of Ag_3PO_4, such new prepared composite is proven effective in eliminating both cationic (RhB, MB, and NR) and anionic (MO) dyes. For the removal of different dyes, the contributions of adsorption and photocatalysis is different. Furthermore, the prepared 3D Ag/Ag@Ag3PO4/GA exhibit much higher visible light photocatalytic degradation activities than bare Ag_3PO_4 particles, Ag_3PO_4/GO, and Ag/ Ag@Ag_3PO_4/GO nanocomposites.

2. Experimental section

2.1. Materials

Native graphite flake was purchased from Alfa Aesar. Concentrated sulfuric acid (H_2SO_4), potassium persulfate ($K_2S_2O_8$), phosphorus pentoxide (P_2O_5), potassium permanganate ($KMnO_4$), sodium acetate (NaAc), Rhodamine B (RhB), methylene blue (MB), methyl orange (MO), neutral red (NR), disodium ethylenediaminetetraacetate (Na_2-EDTA), tert-butanol (TBA), p-benzoquinone (BZQ), ammonia (25 wt%), disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4{\cdot}12H_2O$), and silver nitrate ($AgNO_3$)were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

2.2. Preparation of samples

2.2.1. 3D Ag/Ag@Ag_3PO_4/GA composites

Graphene oxide (GO) was prepared from natural graphite according to the reported method [25]. GO solution was prepared by prolonged sonication of GO in deionized water, reaching a concentration up to 1.5 mg/mL. Next, $AgNO_3$ solution (15 mL, 0.4 mmol) was added to 15 mL of the GO dispersion to form a stable aqueous suspension with the aid of 30 min ultrasonic treatment. The mixture was then transferred into a Teflon-lined stainless-steel autoclave and kept at 180 °C for 12 h to form a graphene-based 3D hydrogel. In this way, Ag nanoparticles could nucleate and grow on the graphene surface. After the prepared 3D Ag /GH was washed with distilled water for several times, it was immersed into silver-ammino ($[Ag(NH_3)_2]^+$) complex aqueous solution (0.2 M) for 4 h. Then, the 3D Ag /GH was immersed into Na_2HPO_4 aqueous solution (0.15 M) again for another 24 h. The finally synthesized 3D Ag/Ag@Ag_3PO_4/GH was washed by deionized water for several times and treated by freeze-drying.

2.2.2. Ag/Ag@Ag_3PO_4/GO nanocomposites

$AgNO_3$ solution (15 mL, 0.4 mmol) was added to 15 mL of the GO dispersion to form a stable aqueous suspension with the aid of 30 min ultrasonic treatment, followed by stirring for 30 min at 100 °C. In this period, the Ag nanoparticles were deposited on the surface of the GO sheets to form Ag/GO nanocomposites. After the prepared Ag/GO was washed with distilled water for several times, it was immersed into silver-ammino ($[Ag(NH_3)_2]^+$) complex aqueous solution (0.2 M) for 4 h. Then, the Ag/GO nanocomposites were immersed into Na_2HPO_4 aqueous solution (0.15 M) again for another 4 h. The finally synthesized Ag/ Ag@Ag_3PO_4/GO was washed by deionized water for several times and treated by freeze-drying.

2.2.3. Ag_3PO_4/GO nanocomposites

$AgNO_3$ solution (15 mL, 0.2 mol/L) was added to 15 mL of the GO dispersion to form a stable aqueous suspension with the aid of 30 min ultrasonic treatment. Then Na_2HPO_4 aqueous solution (0.15 M) was added drop by drop into the above suspension with vigorous magnetically stirring in dark condition at room temperature. The brown precipitate of Ag_3PO_4/GO was collected by centrifugation and then rinsed repeatedly with deionized water and absolute ethanol for several times. Finally, the precipitate was dried in a vacuum oven at 50 °C for 2 h.

2.2.4. Ag_3PO_4 powder

The bare Ag_3PO_4 powder sample was prepared under the same condition as Ag_3PO_4/GO, but no GO was added in the reaction.

2.3. Measurements of adsorption and photocatalytic degradation activities

The adsorption and photocatalytic activities of prepared 3D Ag/ Ag@Ag_3PO_4/GA were evaluated by the photodegradation of four different organic dyes, RhB, MB, MO, and NR, under the same conditions. In all catalytic activity of experiments, the as-obtained 3D Ag/ Ag@Ag_3PO_4/GA samples were put into 40 mL of dye aqueous solution (15 mg/L). The solution was magnetically stirred for some time without light first to ensure the establishment of an adsorption-desorption equilibrium between the catalysts and dyes. Then the solutions were irradiated with a 400 W Xe arc lamp equipped with an ultraviolet cutoff filter to provide visible light $\lambda \geq 420$ nm. At given time intervals of irradiation, 2 mL of aliquots were collected and variations in the concentration of dyes were monitored using UV–vis spectrophotometer. Active species involved in RhB degradation were identified by applying Na_2-EDTA as hole scavenger, TBA as quencher for $\cdot OH$ radicals, and BZQ as scavenger for $\cdot O_2^-$, respectively. Typically, 1 mg 3D Ag/ Ag@Ag_3PO_4/GA catalysts with 2 mL Na_2-EDTA, TBA or BZQ with concentration of 1 mM were firstly dispersed in RhB solution (40 mL, 15 mg/L) before the photocatalytic process.

For comparison, other photocatalysts, such as Ag/Ag@Ag_3PO_4/GO nanocomposites, Ag_3PO_4/GO, and bare Ag_3PO_4 particles, was added into cationic RhB and anionic MO aqueous solution to test the photocatalytic performance under the same condition.