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Full Length Article

Intercorrelated Ag_3PO_4 nanoparticles decorated with graphic carbon nitride: Enhanced stability and photocatalytic activities for water treatment

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ABSTRACT

The method of decorating Ag_3PO_4 nanoparticles with carbon nitride material (g-C_3N_4) is demonstrated as an efficient pathway to remarkably improve the stability and photocatalytic performance of Ag_3PO_4 nanoparticles which have been widely used in photocatalysis, but limited by the instability. The improved material herein results in the largely enhanced photocatalytic performance for water purification under visible light irradiation, which was nearly 7 times as high as that of pure Ag_3PO_4. Meanwhile, the as-obtained materials show the unique stable property, mainly contributed by the protection effect of decorated g-C_3N_4 sheet. Additionally, the radical trapping experiments revealed that the introduction of g-C_3N_4 transformed the photocatalytic mechanism to some degree, where $^{\bullet}O_2{}^-$ played a more important role. The tremendous enhancement in catalytic performance may be attributed to the larger surface area, controllable particle size and the synergistic effect between Ag_3PO_4 and g-C_3N_4, promoting the separation efficiency of the photogenerated electron-hole pairs. The decorating system can in principle be broadly put into use for unstable photocatalysts.

1. Introduction

In recent years, semiconductor photocatalysis is considered as an efficient technology for converting photon energy into chemical energy. This technology offers the possibility to accomplish energy cycles without pollution to the environment in which one can use the sunlight as an energy source. [1,2] However, many widely used semiconductor photocatalysts, such as P25, [3,4] are merely active under UV-light irradiation, which is not economical and efficient compared to the photocatalysts using solar light. Therefore, it is essential to make an effort developing efficient visible light driven photocatalysts, improving and expanding the applications of the existed visible light photocatalysts through different ways.

Ag containing compounds, such as Ag_2CO_3, [5] AgX ($X = F^-$, Br^-, Cl^-, I^-), [6] and Ag_2O, [7] have attracted much attention and proved to be one of the promising photocatalysts for the photodegradation of organic pollutants and water splitting. Among which, Ag_3PO_4, with a quantum efficiency up to 90% at wavelength higher than that of those much known visible light photocatalysts, has been widely reported as an active visible light driven photocatalysts for degradation of organic pollutants and water splitting. [8–13] However, there are still some limitations in the Ag_3PO_4 system. Firstly, Ag_3PO_4 suffers from photocorrosion under prolonged light irradiation according to its light sensitivity that limits its stability. Secondly, Ag_3PO_4 with a relatively higher Ksp of 1.6×10^{-16} could slightly dissolute as Ag^+ and $PO_4{}^{3-}$ in aqueous solution. And thirdly, Ag_3PO_4 precipitated easily in the solution and the particle size remains relatively large due to the agglomeration in the synthesis process, which hinders its photocatalytic activity and practical application. [14] Hence, it is necessary to develop effective methods to improve the stability and activity of Ag_3PO_4 photocatalysts, such as designing various Ag_3PO_4 nanostructures considering its size and morphology effects or coupling Ag_3PO_4 with other semiconductor photocatalysts to form hybrid structures, like Ag_3PO_4/graphene, [15] Ag_3PO_4/SnO_2, [16] Ag_3PO_4/TiO_2, [17] Ag_3PO_4/CNT, [18] etc. In the previous work of our group, we have successfully synthesized Ag_3PO_4/MoS_2, [19] and Ag_3PO_4/HAP [20] with enhanced photocatalytic activities in water treatment. Also, Cui group synthesized Ag_3PO_4/RGO/Ag, which exhibited superior photocatalytic activity and stability to bare Ag_3PO_4, Ag/Ag_3PO_4 and Ag_3PO_4/GO in the degradation of Rhodamine B and phenol under visible light. [21] Ma and co-workers have dispersed nanophase of silver phosphate on an exfoliated bentonite (EB) to prepare the EB–Ag_3PO_4 photocatalyst. [22] Also, this group has

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further researched EB/g-C_3N_4/Ag_3PO_4 composite. [23] Liu et al. reported an Ag_3PO_4@PANI visible light-driven photocatalyst with core@shell structure prepared by a chemisorption method which showed enhanced photocatalytic performance for the degradation of phenol and 2,4-dichlorophenol significantly with increasing proportion of PANI. [24] Also, this group has researched Ag_3PO_4@g-C_3N_4 core shell composites via an ultrasonication method which exhibited better photocatalytic performance of MB degradation. [25] Fan group investigated the activities of photocatalytic composite, Ag_3PO_4/g-C_3N_4, in converting CO_2 to fuels under simulated sunlight irradiation for the first time. [26] Chai et al. deposited Ag_3PO_4 particles on the surface of C_3N_4 sheets and the composite showed improved photocatalytic activity. [27] Liu group reported the two-dimensional and porous C_3N_4/Ag_3PO_4 and the photocatalytic activity of the prepared nanocomposites is demonstrated by the degradation of 4-chlorophenol. [28] Zhang et al. reported a novel photofunctional graphic carbon nitride/silver phosphate bulk heterojunction. [29] Recently, Kumar et al. developed a facile and reproducible template free in situ precipitation method for the synthesis of Ag_3PO_4 nanoparticles on the surface of a g-C_3N_4 photocatalyst at room temperature. [30] From above, it can be observed that wide interests have been attracted in the field of Ag_3PO_4 based photocatalysts.

Graphite-like carbon nitride (g-C_3N_4), one of the π-conjugated semiconductor materials, has been demonstrated to be a promising photocatalyst for decomposing organic pollutants and splitting water under solar energy. [31,32] This metal free polymeric material possesses high thermal and chemical stability as well as great electronic properties. Nevertheless, for pure g-C_3N_4, the high recombination rate of the photoinduced electron-hole pair limits its photocatalytic performance. Thus, g-C_3N_4 was widely used to couple with other semiconductor photocatalysts due to its appropriate band position [33–35] (the theoretical calculated potentials of conduction band and valence band are −1.12 and 1.57 eV, respectively). Meanwhile, the characteristics of g-C_3N_4 such as its surface area depending on the synthesis way are beneficial in the process of photocatalysis, so it is very important to develop and choose a suitable synthetic method for g-C_3N_4.

In the present work, we report a template free in situ precipitation method to deposit the Ag_3PO_4 semiconductor nanoparticles on the surface of the large-surface-area porous g-C_3N_4. Meanwhile, the synthesis method contributed to the formation of junctions between Ag_3PO_4 and g-C_3N_4, and the results displayed that the size of Ag_3PO_4 nanoparticles could be adjusted in the synthesis process. The optimal weight ratio of the g-C_3N_4 to Ag_3PO_4 is obtained. In addition, the stability and photocatalytic activity of Ag_3PO_4 were enhanced under visible light irradiation. With the help of various characterizations, the relationship between the specific structure and the enhancement of stability and the admirable photocatalytic activity was also investigated.

2. Experimental

2.1. Catalyst preparation

All the reagents purchased from Sinopharm Chemical Reagent Co., Ltd. were of analytical purity and used as received, unless otherwise specified.

Synthesis of pure g-C_3N_4: Porous g-C_3N_4 was synthesized by thermal treatment of 20 g of urea in a crucible with a cover under ambient pressure in air. The precursor was heated to 550 °C at a heating rate of 10 °C/min in a tube furnace for 2 h in air and then the as-prepared powder was crushed into fine powder.

Synthesis of Ag_3PO_4/g-C_3N_4: Ag_3PO_4 nanoparticles decorated with different amount of g-C_3N_4 were prepared through a facile in situ precipitation method. Typically, an appropriate amount of g-C_3N_4 was dispersed in 20 mL water and ultrasounded for 30 min. To this mixture, $AgNO_3$ solution were added dropwise and stirred at room temperature for 2 h, followed by dropwise addition of $Na_3PO_4 \cdot 12H_2O$ solution. The mixture was stirred for 4 h. The as-obtained solid product was centrifuged, washed with water and vacuum-dried at 80 °C for 12 h.

Herein, we use Ag_3PO_4/g-C_3N_4-10%, Ag_3PO_4/g-C_3N_4-30%, and Ag_3PO_4/g-C_3N_4-50% to represent the Ag_3PO_4 nanoparticles decorated with the weight ratio of 10%, 30% and 50% g-C_3N_4 (the weight percentage of g-C_3N_4 is determined by ICP method).

Ag_3PO_4/g-C_3N_4-10%, Ag_3PO_4/g-C_3N_4-30%, and Ag_3PO_4/g-C_3N_4-50% were obtained using the same method. The pure Ag_3PO_4 crystals were also prepared for comparison following the same method without the addition of g-C_3N_4.

2.2. Catalyst characterization

The XRD patterns were collected on a Bruker D8 Advance X-ray diffractometer using nickel-filtered Cu *K*α radiation (λ = 0.154 nm) with a scanning angle (2θ) range of 20–90°, a scanning speed of $2^\circ\,\mathrm{min}^{-1}$, and a voltage and current of 40 kV and 40 mA, respectively. Specific surface areas were calculated by nitrogen adsorption–desorption method at −196 °C (Micromeritics Tristar ASAP 3000) using Brunauer–Emmett–Teller (BET) method. TEM micrographs were obtained on a JOEL JEM 2010 transmission electron microscope. The samples were supported on carbon-coated copper grids for the experiment. The FT-IR spectra were obtained on a Nicolet Avatar-360 FT-IR spectrometer. The optical properties of the samples were analyzed by UV–vis diffuse reflectance spectroscopy (DRS) using a UV–vis spectrophotometer (Cary-500, Varian Co.), using $BaSO_4$ as the reference. X-ray photoelectron spectroscopy (XPS) experiments were carried out with a RBD 147 upgraded Perkin–Elmer PHI 5000C ESCA system equipped with a hemispherical electron energy analyzer. The Mg *K*α ($h\nu$ = 1253.6 eV) anode is operated at 14 kV and 20 mA. The spectra were recorded in the constant pass energy mode with a value of 46.95 eV, and all binding energies were calibrated using the carbonaceous C 1s line at 284.6 eV as reference. The experimental errors were within ±0.2 eV.

2.3. Evaluation of photocatalytic activity

The photocatalytic performance of the samples was first evaluated through the photodegradation of RhB under visible light irradiation with a 300W Xe arc lamp (Ceaulight, CEL-HXF300) equipped with a 420 nm cut-off filter provided visible-light irradiation. The photoactivity of MB, MO and 4-CP degradation was also tested. In a typical process, 100 mL of RhB (10 mg/L) aqueous solution and 0.025 g photocatalyst were mixed in a 250 mL photoreactor. Before the irradiation process, the suspension was stirred in the dark for 30 min to reach an adsorption –desorption equilibrium. At a given time interval, 3 mL suspensions were collected and centrifuged to remove the photocatalyst. The degradation efficiency is calculated using the following equation:

$$\text{Degradation efficiency} = (C_0 - C)/C_0 \times 100\% = (A_0 - A)/A_0 \times 100\%$$

Where C_0 and A_0 are the initial concentration and absorbance of RhB solution under 550 nm while C and A are the concentration and absorbance of RhB solution after a certain illumination time period t (min).