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Enhanced visible light photocatalytic performance of Ag_3PO_4 through doping by different trivalent Lanthanide cations

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ABSTRACT

To explore the efficacy of lanthanides doping on photocatalytic performance of silver orthophosphate, Gd-doped, Dy-doped and Er-doped Ag_3PO_4 nanoparticles were prepared by co-precipitation method. All synthesized samples were characterized systematically. The photocatalytic activity of pure and M-doped Ag_3PO_4 (M = Gd, Dy and Er) was compared in degradation of an Anthraquinone dye (Ractive Blue 19). In order to comprehensive comparison, photocatalytic processes by M-doped Ag_3PO_4 were individually optimized by Response Surface Methodology (RSM). At the optimal conditions proposed by RSM, the photocatalytic degradation efficiency by Gd-doped, Dy-doped and Er-doped Ag_3PO_4 were 80.4, 92.4 and 57.8%, respectively. Due to the considerable decrease in degradation efficiency in the presence of oxalate anion and *p*-benzoquinone, photogenerated holes and superoxide anion radicals were detected as the main reactive species in degradation of RB19. The main role of the trivalent lanthanide cations in Ag_3PO_4 photocatalytic activity enhancement was also discussed.

1. Introduction

Photocatalytic processes utilizing the semiconductors are promising technologies in photocatalytic degradation of persistent organic contaminants, conversion of water to hydrogen gas by water splitting, solar cells, etc. Most common semiconductors used in photocatalysis are the transition metal oxides such as TiO_2, ZnO, WO_3. Under ultraviolet or visible light irradiation, electrons in the valance band (VB) are excited to conduction band (CB) of a semiconductor remaining photogenerated holes in VB. The charge carriers (e^- and h^+) play the main role in producing active species such as hydroxyl or super oxide anion radicals [1–3]. However, photocatalysis by common semiconductor materials have indicated low quantum yield and high energy consumption because of their wide band gap energy and rapid charge carriers recombination. The lower quantum efficiency and activity of common photocatalysts in visible light irradiation range confine their photocatalytic performance for wide range of application. So, a considerable number of researches have been focused on the developing suitable and effective photocatalysts, especially visible light-responsive catalyst materials [4–6].

Silver orthophosphate (Ag_3PO_4) is recently taken into consideration as an active semiconductor material showing strong visible light absorbance with a narrow direct band gap of 2.4 eV. This semiconductor, which sensitized by visible light, has deeply attracted attention not only for its unique electronic structure but also for its great potential in water splitting and utilizing of solar energy full spectrum [7–10]. However, the large silver (noble metal) usage, large particle size and low photocatalytic stability are the major impediments of the pure Ag_3PO_4 in its practical applications [11,12]. To further increase of photostability and photocatalytic activity, introducing a heteroatom into the host semiconductor is one of the well-known methods. Doping of semiconductors by a suitable dopant caused to: (i) modify the surface structure, (ii) increase spectral response, (iii) considerable changes in the band gap energy, (iv) suppress the recombination of photoexcited electron- photogenerated hole and (v) form some crystalline defects [13–16,27].

Rare earth cations possess incompletely occupied 4f and empty 5d orbitals. The presence of a suitable lanthanide ion can significantly prevent the recombination of photoinduced e^- and h^+ in semiconductor and subsequently enhance the photocatalytic activity and photosensitivity. It has been reported that doping of

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semiconductors by lanthanides leads to formation of some crystalline defects [16]. These defects enhance visible wavelengths emission and hinder charge carriers recombination via trapping them from semiconductor. However, new crystalline defects could act as e^- and h^+ recombination centers resulting in decrease the photocatalytic activities and quantum efficiency. So, different lanthanide cations don't possess the same effect on the photocatalytic activity of a photocatalyst due to difference in their intrinsic properties [17].

Here in, we investigated the effect of doping by three different lanthanide cations on the photocatalytic performance of Ag_3PO_4. Gd-doped Ag_3PO_4, Dy-doped Ag_3PO_4, Er-doped Ag_3PO_4 and pristine Ag_3PO_4 nanoparticles were individually prepared by a facile co-precipitation method. The synthesized samples were characterized by X-ray diffraction pattern (XRD) analysis, Field emission scanning electronic microscopy (FESEM), transmission electron microscopy (TEM), diffuse reflectance UV–vis spectroscopy (DRS) and photoluminescence spectroscopy (PL). Energy dispersive X-ray spectroscopy (EDX) has been used to verify incorporation of dopants in the network of Ag_3PO_4. The photocatalytic efficiency of pristine Ag_3PO_4 and M-doped Ag_3PO_4 (M = Gd, Dy, and Er) samples was evaluated in the photocatalytic degradation of Reactive Blue 19 (RB19), as an organic sample pollutant. The effect of type and content of different lanthanide cations, RB19 concentration, photocatalyst dosage and their interactions on the RB19 degradation were investigated by Response Surface Methodology (RSM). The reusability tests were carried out for five runs in the optimal conditions proposed by RSM. Finally, the negative effect of various process inhibitor and radical scavengers on the photocatalytic activity was studied to understand the plausible role of lanthanide doping in photocatalytic performance enhancement of Ag_3PO_4.

2. Materials and methods

2.1. Chemicals

Gadolinium (III) nitrate hexa-hydrate ($Gd(NO_3)_3{\cdot}6H_2O$), Dysprosium(III) nitrate hydrate ($Dy(NO_3)_3$. H_2O), and Erbium(III) nitrate pentahydrate ($Er(NO_3)_3$. $5H_2O$) were obtained from sigma Aldrich-USA. Sodium hydrogen phosphate (Na_2HPO_4), Silver nitrate ($AgNO_3$), *tert*-butanol, benzoquinone and ammonium oxalate were purchased from Merck-Germany. Reactive Blue 19 as an anthraquinone dye was purchased from Solar Fine Chemical Co., and its specifications are given in Table S1. All chemical reagents used in our study were of analytical grade and were used without further purification.

2.2. Preparation of pure Ag_3PO_4 and M-doped Ag_3PO_4 photocatalysts

Ion-exchange, colloidal method, hydrothermal, electrochemical oxidization, and co-precipitation methods have been successfully introduced to produce Ag_3PO_4 with different morphology and sizes [18–22]. Co-precipitation method is not only simple and low cost but also produces large scale of products [22,23]. M-doped Ag_3PO_4 (M = Gd, Dy, and Er) photocatalysts with variable Lanthanide cations contents (1–9 mol%) were prepared by co-precipitation method. The proper amounts of lanthanide cation (depending on lanthanide mole fraction) and $AgNO_3$ were dissolved in 20 mL distilled water under the agitation, and then the warm solution of Na_2HPO_4 was added dropwise to the aforementioned solution. As-synthesized M-doped Ag_3PO_4 nanoparticles were collected and washed with distilled water and absolute ethanol three times in order to remove residual impurities, and then dried at 80 °C for 5 h.

2.3. Characterization

To determine the structure, phase composition and real size of the Ag_3PO_4 and M-doped Ag_3PO_4 nanoparticles, Powder XRD investigations were performed at room temperature using Siemens X-ray diffraction ((D5000, Germany), with Cu $K\alpha$ radiation (1.54065 °A and θ = 5–75°)). The Scherrer formula [24] was also used to estimate the average particles sizes of prepared photocatalysts. The surface state and morphology of the prepared nanoparticles were observed by TEM (JEOL, JEM 2200) and FESEM (MIRA3 FEG-SEM, Tescan) equipped with EDX. DRS and PL spectra were recorded with a Perkin-Elmer, Lambda 25 and JASCO FP-6200, respectively. The specific surface area determination and pore size were determined by the Brunauer-Emmett-Teller (BET) theory from the N_2 adsorption–desorption measurements using Belsorp-mini ii.

2.4. Experimental design

In this work, four key factors have been selected as the RSM input variables. The experimental ranges of input variables in coded and actual values are given in Table S2. The coded values were calculated by following equation [25].

$$Coded\ value = \frac{z_i - z_0}{\Delta z} \quad (1)$$

where z_i, z_o and Δz (dimensionless value)are the coded level of the variable, center point of the variable and interval variation, respectively.

Central Composite Design (CCD), as a useful experimental design in RSM, was utilized to investigate the individual and interactive effects of four variables on the degradation efficiency (X) (output response). Based on the CCD, 31 experiments (Table S3) including 8 axial points (as $\pm\alpha$, where α=2), sixteen orthogonal, two levels, full factorial design points (coded as $\pm$1), and seven replications must be carried out. The experimental design and analysis of experimental data were performed by Design Expert 7 software. The proposed experiments by CCD were individually implemented using all three doped catalyst i.e. Gd-doped Ag_3PO_4, Dy-doped Ag_3PO_4 and Er-doped Ag_3PO_4 to obtain optimum operational conditions for obtaining maximum degradation efficiency.

2.5. Photocatalytic activity evaluation experiments

In each experimental run, the photocatalytic performance of the doped samples was evaluated by photocatalytic degradation of RB19 under visible light irradiation. The source of visible light was 50W fluorescent lamp in which irradiated light intensity on the surface was 11.35 W/m^2. Light irradiated from compact fluorescent visible lamps was passed from cutoff filter for providing visible light illumination (λ > 420 nm). The concentration of RB19, catalyst amount, doping level, and time are adjusted in each run to the values proposed in Table S3 (according to CCD). The reaction system including RB19 and M-doped Ag_3PO_4 with known concentration was prepared and stirred in the dark to eliminate the photocatalysis reaction effect and to reach the adsorption/desorption equilibrium. Then, the solution was irradiated. At the different irradiation times (according to Table S3), 2 mL of the RB19 solution was sampled and centrifuged. The degradation efficiency (X) of RB19 was calculated by determining the concentration of remaining RB19 was determined using a Thermo Helios Alpha UV spectrophotometer at λ_{max} = 594 nm.