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Invited feature article

Facile hydrothermal synthesis of carbon dots (CDs) doped ZnFe₂O₄/TiO₂ hybrid materials with high photocatalytic activity



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ABSTRACT

In this study, a novel and highly efficient ternary photocatalytic ZnFe₂O₄/TiO₂/CDs nanocomposite was successfully synthesized by a hydrothermal method. The properties and structures of the samples were characterized by X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Fourier transform infrared spectrometry (FT-IR), and photoluminescence spectrum (PL). The UV–vis diffuse reflectance spectrum was used to demonstrate that carbon quantum dots could increase the absorption of visible light wavelengths. When compared with TiO₂/3.00 wt%CDs and ZnFe₂O₄/TiO₂ nanocomposites, the ternary photocatalysts exhibited the enhanced photocatalytic activity under solar-spectrum irradiation. A low CDs content of 3.00 wt% in the ternary photocatalysts possessed excellent performance in the decomposition of Rhodamine B (RhB). Act as donor and receiver, CDs can efficiently improve the ability of electron transfer and separate the electron-hole pairs. *OH and O₂*⁻ were confirmed to be involved in the photocatalytic degradation of RhB base on the Electron spin resonance (ESR) tests, and the photocatalytic mechanism of the ZnFe₂O₄/TiO₂/3.00 wt%CDs was proposed. After four sequential operational cycles, the ZnFe₂O₄/TiO₂/CDs maintained its photocatalytic efficiency, indicating its high photocatalytic stability. Therefore, our results provide a high efficient photocatalytic nanocomposite that synthesized by a facile method, and have implications in the removal of environmental persistent pollutants under ternary photocatalysts mediated solar degradation

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1. Introduction

With the advantages of cost-effectiveness, environmental compatibility, stability and high efficiency, TiO₂ nanomaterials are considered to be a superior photocatalyst for air pollutant degradation, organic sewage reduction, and household waste sterilization [1,2]. Nevertheless, there are numerous elements limit the photocatalytic efficiency of titanium dioxide including limited reusability, the requirement of UV light for activation, rapid recombination and possession of wide band gap (3.2 eV). Furthermore, particle agglomeration could cause photocatalytic material to deactivate easily in photodegradation process [3]. Hence, it cannot be widely used in practical applications [4]. In order to enhance the photocatalytic activity of TiO₂ nanomaterials,

multiple studies have proposed to dope TiO₂ composite, which has been widely considered. Doping metals and non-metals into TiO₂ nanomaterial is a practicable way to narrow the band gap energy, which makes electronic transition of catalysts active from the valence band under sunlight [5–7]. Therefore, improving the photocatalytic efficiency of TiO₂ powders demands to modify nanocomposite photocatalysts appropriately. Possessing a low band gap (1.92 eV), good magnetic separation characteristics, with chemical stability at low-cost, spinel zinc ferrite nonmaterial (ZnFe₂O₄) is regarded as an excellent candidate for photocatalytic activities under light irradiation [8,9]. As a well-known photocatalytic material, ZnFe₂O₄ nanomaterials are compounded in hydrothermal synthesis [10], solvothermal [11], and sol-gel process [12], etc. Although electrons are easily excited in the ZnFe₂O₄ material exposure to sunlight, rapid electron-hole pair recombination in ZnFe₂O₄ results in poor photocatalytic performance [13,14].

It is acknowledged that carbon dots (CDs) not only have chemical stability and sensitivity to visible light, but also possess the advantages of unique photoluminescence (PL) upconversion

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property and non-toxicity [15]. Recently, carbon dots have been widely investigated as an excellent candidate for photo-induced processes, and integration into nanocomposite photocatalysts [16]. It was observed by Duo that CDs/BiOBr composites demonstrated higher photocatalytic activity than did pure CDs or BiOBr, due to the upconversion effect of the CDs [17]. The incorporation of CDs can improve photocatalytic activity, while accommodating the adsorption of longer photocatalyst wavelength [18]. CDs may generate additional electrons and decrease the recombination of electron-hole pairs, which is beneficial for the photocatalytic activity [15]. Therefore, the application of CDs for the doping of photocatalysts toward the degradation of dye contaminants is a promising prospect for water purification.

Concurrent with continuously expanding economic and social development, the issue of water pollution, particularly dye pollution, has gained increased attention in recent years [19]. It has been reported that over 70,000 tons of dyes are discharged into industrial wastewaters annually [20]. Moreover, it is difficult to degrade dye-infused waste-water due to the high concentrations of dyes and their chemical complexity [21]. More importantly, stable dyes have a significant negative influence on ecological balance and myriad biological life forms, including human beings; causing cancer and other diseases, when they are discharged into the aqueous environment [20]. The discovery of solutions to dye contamination is urgent and critical [22,23]. Many researchers are dedicated to the development of photocatalytic technologies, which are well-known for their utility in the degradation of dye-permeated wastewater.

In the present work, we synthesized CDs-doped $\text{ZnFe}_2\text{O}_4/\text{TiO}_2$ samples for the purpose of improving the photocatalytic degradation of RhB. To the best of our knowledge, this is the first paper describing the preparation of $\text{ZnFe}_2\text{O}_4/\text{TiO}_2/\text{CDs}$ nanocomposites. This work not only aimed to address the drawbacks of ZnFe_2O_4 and TiO_2 (P25) nanomaterials, but also to demonstrate and verify the superior performance of CDs. The optimal mass ratio of CDs-doped $\text{ZnFe}_2\text{O}_4/\text{TiO}_2$ nanocomposites content for the Rhodamine B photodegradation activity was determined. Further, the structures, morphologies, and properties of the $\text{ZnFe}_2\text{O}_4/\text{TiO}_2/\text{CDs}$ nanocomposites were systematically evaluated by state-of-the-art characterization techniques. Finally, the potential photocatalytic mechanism of the $\text{ZnFe}_2\text{O}_4/\text{TiO}_2/\text{CDs}$ was proposed.

2. Experimental section

2.1. Materials and reagents

ZnFe_2O_4 , TiO_2 (P25) and Citric acid (analytically pure), were purchased from Aladdin Co. Ltd. (Shanghai, China); Ethanediamine (98% purity) was purchased from Tianjin TaiMau Co. Ltd. (Tianjin, China); Alcohol (95% purity), was purchased from Guangzhou Chemical Co. Ltd. (Guangzhou, China); Ultra-pure water used in all experiments was generated by a dedicated pure water system (Smart 2 MilliQ apparatus, TKA, Germany).

2.2. Synthesis of $\text{ZnFe}_2\text{O}_4/\text{TiO}_2/\text{CDs}$

2.2.1. Preparation of CDs

In this experiment, CDs were synthesized via a hydrothermal method [24], where 0.50 g citric acid was dissolved in a measured volume (30.00 mL) of ultra-pure water under magnetic stirring. Following 60 min of stirring, 2.50 mL of ethanediamine was added to the beaker, which again underwent magnetic stirring for 60 mins. The mixed solution was subsequently transferred to a 100.00 mL sealed Teflon-lined stainless-steel autoclave and allowed heat for 300 min at 180 °C. The obtained CDs solution was separated with a centrifuge, after cooling to room

temperature, in order to remove molecular particulates. The concentration of CDs was 15 mg/L.

2.2.2. Synthesis of $\text{ZnFe}_2\text{O}_4/\text{TiO}_2/\text{CDs}$

The $\text{ZnFe}_2\text{O}_4/\text{TiO}_2/\text{CDs}$ were prepared by a hydrothermal method [25]. In a typical procedure, 500.00 mg TiO_2 , 15.00 mg ZnFe_2O_4 , and certain quantities (0.5 mL, 1 mL, 2 mL, 3 mL, 4 mL) of CDs were put into 30.00 mL ethanol. Subsequently, the solution was mixed by magnetic stirring for 6 h before undergoing evaporation at 70 °C to dry. The mixture was then transferred to a muffle furnace at a heating rate of 1.5 °C/min. and maintained at 300 °C for 2 h. Once the muffle furnace naturally cooled to room temperature, the resulting catalysts were obtained by grinding for 30 min using an agate mortar. The added contents of CDs to the $\text{ZnFe}_2\text{O}_4/\text{TiO}_2/\text{CDs}$ hybrid nanomaterials were 1.16 wt%, 3.00 wt%, 5.80 wt%, 8.70 wt%, and 11.6 wt%, which were marked ZTC1.16, ZTC3.00, ZTC5.80, ZTC8.70, and ZTC11.6, respectively. The $\text{ZnFe}_2\text{O}_4/\text{TiO}_2$ and $\text{TiO}_2/3.00\text{ wt}\%\text{CDs}$ nanoparticles were synthesized using the same process without the addition of CDs and ZnFe_2O_4 .

2.3. Catalyst characterization

For the purpose of characterizing the phase structures and particle dimensions of all samples, X-ray power diffraction (XRD) was performed using a Rigaku D/max-Ultima X-ray diffractometer (Cu K α radiation ($\lambda = 1.54156\text{ \AA}$)), operating at 40 kV and 40 mA, at a scan rate of 8°/min., from 10° to 80°. The UV-vis diffuse reflectance spectra (UV-vis DRS) of samples were determined with a UV-vis absorption spectrometer (UV-2550, Shimadzu); The infrared spectra of the as-prepared samples were recorded by Fourier Transform Infrared Spectrometers (FT-IR) (ThermoFisher Nicolet 6700) in the scan range of between 400 and 4000 cm^{-1} ; Additionally, a scanning electron microscope (FESEM; Hitachi S-4800, Japan) was employed to observe the morphologies of the catalysts, whereas a high-resolution transmission electron microscope (HRTEM, JEOL JEM-2100F, Japan) was used to examine the structure of the samples. Further, Energy Dispersive X-ray spectroscopy (EDS) (HORIBA EX-250) was also used to examine the samples during the FESEM measurements. X-ray photoelectron spectroscopy (XPS) was utilized to measure functional groups, and the chemical composition was elucidated with a spectrometer (Thermo, ESCALAB 250Xi). The PL spectra of the photocatalysts were also surveyed by Fluorescence Spectroscopy (F97 PRO, Lengguang Tech). The ESR spectra of the $\text{ZnFe}_2\text{O}_4/\text{TiO}_2/3.00\text{ wt}\%\text{CDs}$ were validated by Electron Spin Resonance spectroscopy (Bruker, E500).

2.4. Photocatalytic experiments

The photocatalytic activities of the prepared nanocomposites were examined via the photocatalytic degradation of RhB in an aqueous solution. The experiment was carried out using the photoreactor (XPA-7, Nanjing Xuj Co. Ltd.). Pyrex and quartz tubes were vertically placed in the photoreaction device, which included a quartz cooling jacket [26]. The light source employed was a 350W Xe lamp, which possessed full spectral distribution, with a 290 nm cut off filter so as to simulate sunlight irradiation. For each experiment, 50.00 mg of as-synthesized catalysts was dispersed in a 50.00 mL RhB aqueous solution (10.00 mg/L) in a cylindrical quartz tube under ultrasonication. In order to ensure the attainment of adsorption-desorption equilibrium between the RhB and the prepared nanomaterials, the resultant solution was magnetically stirred in the dark for 30 mins. Subsequently, the light was turned on and the photoreactor was illuminated under magnetic stirring (1000 rpm). At certain time intervals (15 min),

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