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Superior nanoporous graphitic carbon nitride photocatalyst coupled with CdS quantum dots for photodegradation of RhB

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ABSTRACT

Nanoporous graphitic carbon nitride (npg-C_3N_4) shows much higher photocatalytic activities than bulk g-C_3N_4. Npg-C_3N_4 was used to couple with CdS quantum dots (QDs) by a simple deposition method to further increase the photocatalytic activities of the photocatalyst. The obtained photocatalyst was characterized by XRD, FT-IR, and XPS techniques; nitrogen adsorption isotherms, SEM and TEM images; and UV–vis DRS and Photoluminescence spectra. Results showed that the CdS QDs had been successfully deposited onto the surface of npg-C_3N_4 with a good dispersion, and the two components formed stable composites because the CdS QDs can be anchored by the rolled and curled edges of npg-C_3N_4. The as-prepared CdS QDs/npg-C_3N_4 composites not only exhibited extended optical absorptions of visible light (up to 600 nm) and enhanced photocatalytic activity for the photodegradation of Rhodamine B than each of the components, but also showed good catalytic stability.

1. Introduction

The extensive use in many fields and unintended release into the environment of synthetic dyes cause considerable environmental pollution and serious health-risk to human. As the pollutants of synthetic dyes in wastewater are chemical stable, a wide range of methods has been developed for the removal of these pollutants [1]. Photocatalysis using semiconductors, as one of the most effective methods, has received considerable attention during the past decades [2–4]. TiO_2 is the most widely studied photocatalyst due to its non-toxicity, good stability and excellent photocatalytic activity. But TiO_2 is not a visible light active photocatalyst because of its wide band gap (3.2 eV) [5]. Exploring new photocatalytic materials with photocatalytic activity under visible light is of great interest. Recently, a polymeric graphitic carbon nitride (g-C_3N_4) composed of carbon, nitrogen, and some minor hydrogen content only, was introduced as a metal-free photocatalyst for solar-driven applications, such as organic pollutant degradation [6], water splitting [7–9], and CO_2 reduction [10–12] in the visible light region. This organic semiconductor offers new opportunities for photocatalysis due to its cheap availability, high stability, and visible light response. However, the photocatalytic activities of pristine g-C_3N_4 are seriously limited by its intrinsic drawbacks, including relatively low surface area, fast charge recombination, and poor mass diffusion/transfer [13,14]. Many methods have been developed to enhance its photocatalytic performance, including texture modification [15–19], element doping [20–22] and noble metal deposition [23], and constructing heterojunctions with other materials [24–27]. Among these methods, introducing nanoporous [28–31] in g-C_3N_4 has been demonstrated a facile and efficient pathway to promote charge migration and separation, as well as the mass diffusion/transfer during photoredox reactions, greatly enhancing the photocatalytic performance. Our recent study [32] also revealed that nanoporous g-C_3N_4 (npg-C_3N_4) with large surface area exhibits much higher photocatalytic activity than pristine g-C_3N_4. Considering combining with other semiconductors has been demonstrated an effective way to inhibit the recombination of photogenerated electron–hole pairs, it was supposed that introducing another visible light response semiconductor to the texture modified npg-C_3N_4 can further improve the photocatalytic activity of the catalyst.

CdS, as a well-known II–IV semiconductor, has been attracting increasing attention as a visible-light catalyst due to its narrow band gap of 2.4 eV [33]. However, several drawbacks still limit the photocatalytic efficiency on pure CdS nanoparticles. For example, small CdS particles can easily aggregate into large particles,

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resulting in smaller surface area and higher recombination rate of photogenerated electrons and holes. Additionally, CdS seriously suffers from photocorrosion as S^{2-} in CdS tends to be self-oxidized by photogenerated holes during the photocatalytic reaction [34]. Several approaches have been developed to solve these problems. For instance, CdS was coupled with various semiconductors (TiO_2 [35], ZnO [36], MoS_2 [37], etc.) or noble metals [38,39] to promote the separation of photogenerated charge carriers. By coating with polymeric materials (such as polyaniline [40] and resin [41]) or carbon films [42] to form core/shell nanostructure, the problem of CdS photocorrosion can be mostly inhibited. Recently, several works have reported that the photocatalyst coupled by CdS and g-C_3N_4 shows better photocatalytic performance than the pure g-C_3N_4 and CdS for H_2 generation because of the high efficiency of the separation of photogenerated charge carriers [43–47]. Therefore, the combination of g-C_3N_4 and CdS can deal with the drawbacks of each other simultaneously [48]. But the reported CdS/g-C_3N_4 composites synthesized by using the pristine g-C_3N_4 with low surface area to couple with CdS exhibited relatively low photocatalytic activity. Very recently, Zheng et al. [49] used hollow carbon nitride spheres (HCNS) to synthesize CdS/g-C_3N_4 composites, which showed excellent photocatalytic activity and stability. But the use of g-C_3N_4 with nanostructures to construct CdS/g-C_3N_4 composites is still limited.

Herein, the npg-C_3N_4 with rolled layer edges and excellent photocatalytic activity [32] was used to couple with CdS quantum dots for further improving the photocatalytic activity. The unique structure of npg-C_3N_4 not only can provide more catalytic active sites, but also can direct a good dispersion of the CdS QDs and inhibit the aggregation of CdS QDs. The CdS QDs/npg-C_3N_4 composites were characterized in terms of chemical structure, morphology, optical and electronic properties. The photocatalytic activity of the obtained samples was tested by evaluating the degradation of Rhodamine B (RhB) dye under visible light illumination, and the CdS QDs optimum content was investigated.

2. Experimental

2.1. Synthesis of npg-C_3N_4

All chemicals were of analytical grade without further treatment. Npg-C_3N_4 was synthesized by a template-induced method as we have reported before [32]. In a typical synthetic procedure, 5.0 g melamine and 2.5 g Triton X-100 were added into 100 mL distilled water, and then the mixture was heated in an oil bath at 100 °C with stirring for 1 h under refluxing. Then 2 mL concentrated sulfuric acid (98 wt%) was added to the solution dropwise while the white precipitate gradually formed, and the mixture was stirred at 100 °C for another hour. After naturally cooling down to room temperature, the precipitate was filtrated and washed several times with distilled water to remove Triton X-100, then dried in an oven at 80 °C overnight. The obtained sample was put into an alumina crucible with a cover and then heated to 500 °C in a muffle furnace for 2 h with a heating rate of 2 °C min^{-1}, and further heat treatment was set at 580 °C for another 2 h.

2.2. Synthesis of CdS QDs

CdS QDs were prepared in the aqueous phase with TGA (thioglycollic acid) as stabilizer by adding 0.5 mL TGA to a 17.5 mmol $CdCl_2{\cdot}2.5H_2O$ (200 mL) solution with at pH 10 adjusted by the addition of 1 mol L^{-1} NaOH solution. The Na_2S solution obtained by dissolving 0.84 g $Na_2S{\cdot}9H_2O$ in 10 mL water was added to the solution, and then the mixture was stirred at 60 °C for 1 h. Subsequently, the solution was centrifuged, and the CdS QDs were extracted and rinsed with distilled water. The obtained sample was redispersed in distilled water to obtain a pure CdS QDs aqueous solution.

2.3. Synthesis of CdS QDs/npg-C_3N_4 composites

CdS QDs/npg-C_3N_4 composite photocatalysts were prepared as following: the as-prepared npg-C_3N_4 powder (0.3 g) was added to 20 mL CdS QDs solutions containing different amounts of CdS QDs and stirred for 1 h. Then 10 mL acetone was added to the solution to make CdS QDs deposit onto the surface of npg-C_3N_4. After being stirred for 24 h, the product was collected by centrifugation, followed by drying in an oven at 80 °C overnight. Finally, the samples were heated at 300 °C in a muffle furnace for 1 h. Thus, CdS QDs/npg-C_3N_4 composites with weight percentages of CdS QDs of 2.5, 5, 10, 15, and 20 wt% were prepared, denoted as CdS/CN-2.5%, 5%, 10%, 15%, and 20%, respectively. For comparison, the pure CdS QDs also treated by the same route.

2.4. Characterization

X-ray diffraction (XRD) patterns were collected in a Bruker D8FOCUS powder diffractometer with Cu Kα irradiation (λ = 0.15406 nm). X-ray photoelectron spectroscopy (XPS) data were measured by an ESCALAB-250 with monochromated Al Kα radiation. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken with Tecnai G220 microscope and JEOL-3010 microscope, respectively. Scanning electron microscopy (SEM) images Hitachi S4700 and the elemental compositions were analyzed by the energy dispersive spectrometer (EDS) (INCA Energy, OXFORD). Nitrogen sorption measurements were accomplished with N_2 at 77 K after degassing the samples at 300 °C under vacuum for 3 h using a Quantachrome Quadrasorb SI-MP porosimeter. The specific surface area was calculated by applying the Brunauer–Emmett–Teller (BET) model to analyze the adsorption data. UV–vis absorption spectra were measured using a Shimadzu UV3600 spectrophotometer. The photoluminescence (PL) spectra were performed on a Hitachi F7000 fluorescence spectrophotometer with photomultiplier tube voltage of 400 V and scanning speed of 1200 nm min^{-1}.

2.5. Photocatalytic evaluation

The photocatalytic activity of the samples was evaluated by degradation of RhB under visible light irradiation. A 500 W Xenon lamp (Institute of Electric Light Source, Beijing) with 400 nm cut-off filter was chosen as a visible light source. The temperature of the reaction solution was kept at 20 °C by means of a cooling water sleeve surrounding the lamp. The distance between the light source and the surface of the reaction solution was 15 cm. In a typical experiment, 0.1 g photocatalyst was suspended in RhB aqueous solution (100 mL, 10 mg L^{-1}), and then stirred in the dark for 1 h to reach the adsorption–desorption equilibrium. During the visible light irradiation, an aliquot of 5 mL containing the sample was taken from the reaction suspensions at given time intervals, and then centrifuged to remove the photocatalyst particles. Subsequently, the solutions were measured with the UV–vis spectrophotometer at wavelength of 554 nm. The concentration changes were described by C/C_0, where C_0 is the initial concentration of RhB (after subtraction of the concentration of RhB which was adsorbed to the catalysts) and C is the remained concentration of RhB. The RhB degradation percent (Dp) was determined by $Dp = [1 - (C/C_0)] \times 100\%$.