



Mesoporous graphitic carbon nitride and carbon–TiO₂ hybrid composite photocatalysts with enhanced photocatalytic activity under visible light irradiation



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ABSTRACT

The mesoporous g-C₃N₄/C–TiO₂ composites with efficient visible light photocatalytic activity were prepared by a facile heating method. The as-prepared g-C₃N₄/C–TiO₂ composites were thoroughly characterized by X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy, N₂ adsorption–desorption analysis, UV–vis diffuse reflectance spectroscopy and X-ray photoelectron spectroscopy. As evaluated by the degradation of methylene blue under visible light irradiation, g-C₃N₄/C–TiO₂ composites exhibit much higher photocatalytic activities than pristine g-C₃N₄ and C–TiO₂, respectively. Moreover, the prepared composite catalysts retain good stability; their photodegradation efficiency hardly changes after four cycles. The significant enhancement in photodegradation activity over the g-C₃N₄/C–TiO₂ catalyst could be ascribed to the combined effects coming from the enhanced visible light absorption, enriched adsorption of the dye on the photocatalyst and subsequent efficient separation of photogenerated charge carriers. A tentative mechanism for the photodegradation process was proposed.

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1. Introduction

With increasing environmental problems, photocatalytic degradation of organic pollutants over a photocatalyst becomes one of the most important remediation technologies utilizing solar light [1]. Recently, a polymer photocatalyst named graphitic carbon nitride (g-C₃N₄) has attracted intensive attention for hydrogen and oxygen evolution via water splitting, photocatalytic degradation of organic pollutants, and photosynthesis under visible light illumination [2–5]. The band gap of g-C₃N₄ is about 2.7 eV, which can absorb visible light up to 460 nm. Furthermore, the CB minimum (–1.12 eV vs. NHE) of g-C₃N₄ is extremely negative, and photo-generated electrons should have high reduction capability [6]. However, the photocatalytic efficiency of single g-C₃N₄ is limited due to the high recombination probability of photogenerated electron–hole pairs [7,8]. In order to improve photocatalytic activity, many strategies such as doping and coupling g-C₃N₄ with other semiconductor materials or metal and nonmetal have been

applied to modify g-C₃N₄ [9–17]. These strategies involve the g-C₃N₄-based heterojunction which could remarkably enhance the photocatalytic activity through extending the photoresponding range and increasing the charge separation efficiency [18]. To date, the combination of g-C₃N₄ and TiO₂ into a heterostructure presents a feasible and inspiring route towards improved charge separation in the electron transfer process [19–25]. Miranda et al. reported the preparation of g-C₃N₄–TiO₂ composites with different g-C₃N₄ loadings by a simple impregnation, giving good photoactivities for the degradation of phenol under UV irradiation [26]. Yu et al. [27] synthesized g-C₃N₄–TiO₂ nanocomposites by a facile calcination route using P25 and urea, resulting in higher photoactivity for the decomposition of HCHO than that of single-phase C₃N₄ and bare TiO₂. Cao et al. reported a new photocatalyst of meso-TiO₂/g-C₃N₄ hybrids exhibited higher photodegradation of methyl orange and phenol under visible light irradiation, which can be ascribed to the adequate separation of photogenerated electrons at the heterojunction interfaces and dominant contribution of photoinduced holes mainly caused by the well-constructed nano-architectures [28]. Above studies have clearly proved that graphitic carbon nitride is formed from urea on the surface of TiO₂ during the process of calcination. Moreover, combining TiO₂ with g-C₃N₄ to

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form composite photocatalysts seems to be a possible way to construct heterojunction structure leading to enhanced photoactivity. However, for most reported $g\text{-C}_3\text{N}_4\text{-TiO}_2$ composites, their specific surface areas are less than $100\text{ m}^2\text{ g}^{-1}$ owing to a heating process to form $g\text{-C}_3\text{N}_4$ over TiO_2 . It is widely accepted that large surface area provides more surface activity sites for the adsorption of reactant molecules and mesoporous structure is beneficial to the transportation of reactant molecules and products, making the photocatalytic process more efficient [29]. The mesoporous TiO_2 contains special pore network, which is favorable for the diffusion of reactants and products, and a large surface area, which offers more active sites [30]. In the present study, a novel ternary composite of heterostructured mesoporous $g\text{-C}_3\text{N}_4/\text{C-TiO}_2$ material was prepared by a facile calcination approach with commercially available urea and synthesized amorphous TiO_2 precursors, and its composition, morphology and optical properties were well characterized. This novel mesoporous carbonous titania covered with $g\text{-C}_3\text{N}_4$ exhibits significantly enhanced visible-light-driven photocatalytic activity for degradation of methylene blue dye (MB). The enhanced photoactivity of the $g\text{-C}_3\text{N}_4/\text{C-TiO}_2$ catalyst results from its good adsorption to dyes due to its large surface area as well as the high migration efficiency of photoinduced electron-hole pairs. A tentative mechanism for dye degradation over the developed composite photocatalyst was thereby proposed. The facile preparation process, low cost, and the uniform hybridization make the synthesized nanocomposites hold great potential in the fields of sustainable energy and environment.

2. Experimental

2.1. Catalyst preparation

A 20 wt% resol ethanolic solution was first synthesized according to a previously reported protocol [31]. The 1.6 g of triblock copolymer F127 was dissolved in 30 mL of anhydrous ethanol, then 2.3 mL acetic acid and 0.74 mL hydrochloric acid were added slowly with stirring for 30 min at room temperature (solution A), and 3.5 mL tetrabutyl titanate was dissolved into 10 mL anhydrous ethanol (solution B). After that, solution B was added drop-wise to solution A under magnetic stirring. The resultant mixture was stirred at room temperature for 2 h until the transparent sol was obtained. 2.0 g of 20 wt% resol ethanolic solution was added into the transparent sol with stirring for another 2 h. The resulting mixture was then transferred into the Petri dishes and dried at 40°C for 24 h in an oven to form the orange transparent membranes, and the membranes were heated at 100°C for another 24 h. After that, the membranes were scraped from the Petri dishes and ground into powders. The powders were mixed with the designed stoichiometric urea (1:0.8, 1.0:1.0 and 1.2:1.0, mass ratio of powder to urea) into the agate mortar, and grinded uniformly. Calcination was carried out in a tubular furnace under N_2 atmosphere at a flow rate of 50 mL/min. The heating programs started from ambient temperature to the 350°C at a rate of $1^\circ\text{C}/\text{min}$, held for 4 h at 350°C , and then heated to 600°C at a rate of $5^\circ\text{C}/\text{min}$, then maintained for 1 h. Following that, the as-prepared powder was cooled to room temperature and washed several times with distilled water. Finally, the as-obtained material was dried in air at 60°C . The as-synthesized materials with different C_3N_4 mass percentage loadings are denoted as $g\text{-C}_3\text{N}_4/\text{C-TiO}_2\text{-1}$, $g\text{-C}_3\text{N}_4/\text{C-TiO}_2\text{-2}$ and $g\text{-C}_3\text{N}_4/\text{C-TiO}_2\text{-3}$, corresponding to the mass ratio of powder to urea of 1.0:0.8, 1.0:1.0 and 1.0:1.2, respectively. For comparison, free $g\text{-C}_3\text{N}_4$ sample was also prepared by the same procedure without adding urea, which is denoted as C-TiO_2 . TiO_2 sample was prepared by the same method in the absence of 20 wt% resol ethanolic solution, calcined at 500°C for 3 h under air atmosphere. Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) was

synthesized by a facile heating method [32]. In a typical synthesis run, 6 g of urea was placed in a semi-closed alumina crucible with a cover. The crucible was heated to 520°C for 4 h under N_2 atmosphere to obtain $g\text{-C}_3\text{N}_4$ powder. The yellow-colored product was washed with nitric acid (0.1 M) and distilled water to remove residual alkaline species adsorbed on the sample surface, and then dried at 80°C overnight.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the powders were recorded at room temperature by a Bruker D8 X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418\text{ nm}$). Thermogravimetric analysis was conducted on an NETZSCH STA 449F3 instrument. The experiment temperature ranged from 25°C to 1000°C at a constant heating rate of $10^\circ\text{C}/\text{min}$ in air. Optical properties were analyzed with a spectrophotometer (Shimadzu SolidSpec-3700DUV) and converted from reflection to absorbance by the standard Kubelka-Munk method. Raman spectra were recorded on a microscopic confocal Raman spectrometer (LabRAM HR Evolution) with an excitation of 514.5 nm laser light. Fourier transform infrared (FT-IR) spectra were measured using PerkinElmer spectrometer in the frequency range of $4000\text{--}450\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . The morphologies and structure of the obtained samples were examined by field emission scanning electron microscopy (FESEM; ZEISS SUPRA55VP) and transmission electron microscopy (TEM; JEOL-JEM 2100). X-ray photoemission spectroscopy (XPS) was recorded with PerkinElmer PHI 5000C ESCA System with $\text{Al K}\alpha$ radiation operated at 250 W. The shift of binding energy due to relative surface charging was corrected using the C 1s level at 284.6 eV as an internal standard. The nitrogen adsorption-desorption isotherms at 77 K were investigated using a nitrogen adsorption apparatus (QUADRASORB IQ, Quantachrome Instrument Corp.). The ESR spectra were recorded at 100 K (Bruker E500-10/12). The electrochemical measurements were performed on an IM6e electrochemical workstation (ZAHNER Elektrik, Kronach, Germany) based on a conventional three-electrode system consisting of samples as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl (3 N KCl) as the reference electrode. The electrochemical measurements were performed in a 0.5 mol L^{-1} NaSO_4 solution over the frequency range from 0.01 Hz to 100 kHz at 0.24 V, and the amplitude of the applied sine wave potential in each case was 5 mV. The working electrode was prepared on fluoride tin oxide (FTO) glass substrates. First, 50 mg powder was mixed with 2 mL of acetone under sonication for 30 min to get slurry. The slurry was then spread onto the FTO. After air-drying, the electrode was annealed at 300°C for 30 min in air to improve the adhesion.

2.3. Photocatalytic activity test

The photocatalytic activities of the samples were measured by the degradation of aqueous methylene blue under visible light. About 100 mg of a sample photocatalyst was first added to an aqueous solution of methylene blue (100 mL , 50 mg L^{-1}) in a beaker. The pH value of mixture was kept at 7.0. The solution was sonicated for 10 min and stirred for 2 h in the dark to reach the adsorption-desorption equilibrium. This is followed by irradiation of visible light obtained from 400 W Xe lamp with a cutoff filter ($\lambda > 420\text{ nm}$). At certain time intervals, 3 mL aliquots were sampled and centrifuged to remove the photocatalyst particles. Then the filtrates were analyzed by recording variations in the absorption band maximum (663 nm) in the UV-vis spectra of MB. The reproducibility was checked by repeating the measurements at least three times and was found to be within the acceptable limit ($\pm 5\%$).

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