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Template-free synthesis of three-dimensional porous CdS/TiO_2 with high stability and excellent visible photocatalytic activity

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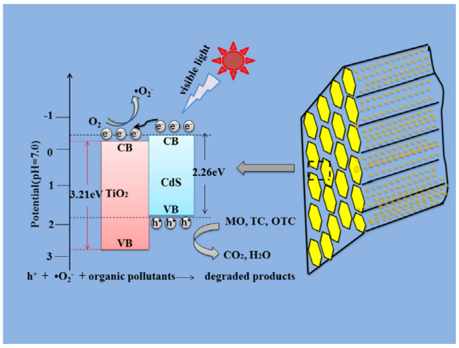
HIGHLIGHTS

- 3D porous CdS/TiO_2 heterojunction was fabricated in the absence of template.
- The prepared CdS/TiO_2 owned large specific surface area.
- Crystal phase was of changed from cubic into hexagonal.
- High stability of photocatalyst was achieved.
- Excellent photocatalytic activity of CdS/TiO_2 over MO, OTC and TC.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel stereo porous and highly stable photocatalyst CdS/TiO_2-400 (composite CdS/TiO_2 calcined at 400 °C) was synthesized by hydrolysis-hydrothermal-calcined method without the assistance of template. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), ultraviolet–visible diffuse reflectance spectra (UV–vis DRS), transient photocurrents, photoluminescence emission spectra (PL) and Brunauer-Emmett-Teller (BET) to study their crystallinity, morphologies, structure, optical properties and specific surface area. The experimental results validated that as-prepared CdS/TiO_2-400 could effectively improve the separation efficiency of photogenerated electron-hole pairs and displayed superior photocatalytic activity in the degradation process of methyl orange (MO), oxytetracycline (OTC) and tetracycline (TC). The promoted photocatalytic activity was attributed to the calcination procedure and high specific surface area. A possible photocatalytic mechanism of CdS/TiO_2-400 was proposed on the basis of trapping experiments.

1. Introduction

Titanium dioxide (TiO_2), as an important oxide material with low density, cheapness, harmless and high stability has been

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studied and used as photocatalyst for many years [1–3]. However, it showed lower light absorption capacity and fast electron hole recombination, which limited its photocatalytic activity and further application directly [4–6]. So far, various strategies were adopted to enhance the photocatalytic activity of TiO_2, such as noble metal surface modification [7–9], doping with metallic or non-metallic ion [10,11], semiconductors coupling [12–14], surface photosensitization [15,16], controllable synthesis of various nanostructures [17,18] and so on. Among them, developing particular morphologies of TiO_2 with large high specific surface area, good surface permeability and strong light absorbing ability were considered to be one of the most effective tactics for enhancing their photocatalytic performance. In the past few decades, a series of different morphologies and structures of TiO_2 have been prepared successfully such as nanorods [19], nanofibers [20], nanotube [21], nanoparticles [22], nanobelts [23,24], films [25], nanosheets [26], nanowire and so on. For example, Yu et al. synthesized hollow TiO_2 spheres with large specific surface area and improved their photocatalytic activity towards methyl orange (MO) due to the special nanoporous structure, which resulted in the effective transport process of reactant molecules to reach the active sites on the surface and promoted the photodegradation efficiency [27]. It was reported that a two-dimensional (2D) nanostructure of TiO_2 was prepared by Li et al. via thermal decomposition method [26]. The obtained TiO_2 nanosheets exhibit excellent adsorption capacities and photocatalytic activities over methylene blue (MB) and methyl orange (MO) degradation because of the tiny nanoparticles, large specific surface area ($360\,m^2\,g^{-1}$) and preferable dispersity in aqueous solution. Although the changed structure and increased large specific surface area could promote the light absorption ability and accelerate the transfer of charges to some extent, like many other photocatalysts, pure TiO_2 exhibited weak photocatalytic activity in visible light region owing to its wide band gap [28]. Therefore, it was still highly desirable to develop special morphologies and seek suitable cocatalyst for improving the optical properties of TiO_2 under sunlight for the practical large-scale application.

Cadmium sulfide (CdS) has been proved to be a visible light sensitizer with the narrow band gap (about 2.4eV) and exhibited strong response to sunlight [29]. Over the years, CdS was found to be a cocatalyst and widely applied in energy, biology and environment fields, such as hydrogen production [30,31], degradation of organic matter [32], sterilization [33] and so on. CdS was an appropriate material for practical application, but the photogenerated electron-hole pairs were not effectively separated unless suitable electron acceptor exists. It was known to all that combining CdS with other support semiconductor materials was recognized as a useful way to suppress the recombination of electron-hole pairs (e^-_{CB}-h^+_{VB}) and improve their photocatalytic activity. Recently, CdS/TiO_2 photocatalysts with various morphologies (such as nanorods [34], nanotubes [35], nanosheet [36], etc.) were synthesized to reform the optical performance of TiO_2 and reduce the recombination rate of electron-hole pairs (e^-_{CB}-h^+_{VB}), in which TiO_2 was used as electron acceptor. However, the stability of these composites, as a crucial standard for practical application, were barely investigated and the reason may be the photocorrosion, which was an inevitable weakness for CdS and CdS-based composites exposed to visible light according to previous reports [37,38]. Therefore, it is highly desirable to construct novel CdS-based nanocomposites with enhanced charge separation efficiency, as well as promoted stability.

In this context, three-dimensional mesoporous and highly stability CdS/TiO_2-400 was prepared with hydrolysis-hydrothermal-calcined method in the absence of template. Compared to pure TiO_2, the as-prepared composite possessed large specific surface area, abundant mesoporous, enhanced optical absorption capacity and excellent photocatalytic activity under visible light. Most importantly, the stability of CdS/TiO_2-400 was improved effectively with the treatment of calcination due to the change of crystal structure. MO, OTC and TC were used as target pollutants to estimate the photocatalytic property and stability of samples. Furthermore, the trapping experiments were carried out to research the mechanism and the possible photocatalytic mechanism toward CdS/TiO_2-400 was proposed and discussed in detail.

2. Experimental

2.1. Materials

Tetrabutyl titanate (TBOT), cadmium nitrate ($Cd(NO_3)_2$), thiourea (CH_4N_2S), commercial titanium dioxide (P25), MO, OTC and TC were all purchased from Sinopharm Chemical Reagent Co. All reagents were analytical pure and without further purification. Deionized water and ethanol were used as solvent in all experiments.

2.2. Preparation of samples

TiO_2 was prepared by simple hydrolyzed-calcined method according to previous reports [39]. Briefly, 20 mL TBOT was added dropwise to 200 mL deionized water, and then the mixture was placed for 30 h without stirring at room temperature. Subsequently, the white precipitate was collected and washed with deionized water and ethanol. In the end, the samples were dried in vacuum drying oven at 60°Cfor 12 h. The pure TiO_2 used for contrastive study was calcined in a muffle furnace at 400°Cfor 1 h.

CdS was synthesized via hydrothermal method. 1.5 mmol $Cd(NO_3)_2$ and 3 mmol CH_4N_2S were dissolved in 40 mL deionized water, and stirred for 1 h. Then, the solution was transferred to a sealed teflon-lined autoclave and kept at 140°Cfor 24 h. The synthesized CdS was filtered and dried at 60°Cfor 12 h. Finally, the prepared CdS was calcined at 400°Cfor 1 h [40] and the achieved sample was marked as CdS-400.

CdS/TiO_2-400 was synthesized by simple hydrothermal-calcined method. Firstly, 3 mmol as-prepared TiO_2 was dispersed in 40 mL deionized water, then 1.5 mmol $Cd(NO_3)_2$ and 3 mmol CH_4N_2S were dissolved in the above mixed solution. After stirring for 1 h, the solution was transferred to a sealed teflon-lined autoclave at 140 °C for 24 h. Secondly, the collected samples was calcined at 200 °C,300 °C,400°Cand 500°Cfor 1 h. The CdS/P25-400 was prepared with the same mole ratio and conditions. All products were separately marked as CdS/TiO_2-200, CdS/TiO_2-300, CdS/TiO_2-400, CdS/TiO_2-500 and CdS/P25-400 according to calcination temperature.

2.3. Characterization methods

The X-ray diffraction patterns (XRD) of samples were measured by a Bruker D-8 advance X-ray diffractometer using Cu Ka radiation ($\lambda = 0.15406$ nm) in the range of $2\theta = 5–80°$. Electron microscope (SEM, Hitachi S-4800), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were used to analyze the morphology, structure and lattice plane of prepared samples. The photogenerated electron-hole pairs (e^-_{CB}-h^+_{VB}) separation efficiency was analyzed via a PerkinElmer LS-55 spectrofluorimeter with the excitation wavelength at 322 nm. The UV–vis diffuse reflection spectra of the samples were examined by a UV–vis spectrophotometer (Hitachi U-4100) in the range of 200–800 nm with $BaSO_4$ as reference. Nitrogen adsorption–desorption method was adopted to measure the