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The preparation and photocatalytic activity of CdS/(Cal-Ta_2O_5-SiO_2) composite photocatalyst under visible light

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ABSTRACT

CdS/(Cal-Ta_2O_5-SiO_2) composite photocatalyst has been successfully fabricated via wet chemistry method. Ta_2O_5-SiO_2 with multi-step Ta_2O_5 deposition on SiO_2 has more Ta_2O_5 on SiO_2 to ensure the active sites. Trough multi-step calcination, Ta_2O_5 can load on SiO_2 with uniform and stable, which make it have high photocatalytic activity. The obtained samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), diffuse reflectance ultraviolet-visible spectroscopy (UV–vis) and photoluminescence spectroscopy (PL). Without any co-catalysts, the as-prepared CdS/(Cal-Ta_2O_5-SiO_2) exhibited remarkable photocatalytic activity and recyclability both in the degradation of rhodamine B and in the hydrogen production from water splitting under visible light.

1. Introduction

In recent years, the dye pollutants from wastewaters can cause threat to the health of human being and surrounding environment [1,2]. It is very necessary to develop faster treatment process to control their pollution. The photocatalytic degradation of dye pollutants has attracted widespread attention due to its low cost, simplicity, high efficiency and low secondary pollution [3–5]. Up to date, TiO_2-based photocatalysts are the fuse of the researches on photocatalysis [6–8]. The conduction band (CB) of Ta_2O_5 consisting of Ta 5d orbits is much more negative than that of TiO_2 consisting of Ti 3d orbits [9]. For the past few years, Ta_2O_5-based photocatalysts are widely paid attention to the researches on photocatalysis [10–13]. However, Ta_2O_5-based photocatalysts possess band gaps (3.9 eV or so) within the UV region. Approximately, less than 4% of solar spectrum includes the UV irradiation, while more than 50% is the visible light. As a result, Ta_2O_5 can't efficiently harness solar energy. In contrast, low band gap semiconductors may absorb the visible light, but they have low reduction potentials and weak photocatalytic stability that prevent their photocatalysis application.

Thus, in order to obtain the Ta_2O_5-based photocatalysts with high photocatalysis under solar light, we have made some efforts on synthesizing Ta_2O_5-based composites, such as 3D interconnected mesoporous In_2O_3/Ta_2O_5 [14], ordered mesoporous CdS/Ta_2O_5 [15] and silica reinforcement CdS/Ta_2O_5 composite [16], with enhanced photocatalytic activity on account of high advantages for separation of electron-hole pairs accompanying the extended light absorption. Especially CdS/Ta_2O_5 mesoporous composites have a remarkable visible photocatalytic activity for efficient interfacial charge transfer because of mesostructure characters.

CdS as a low band gap (2.4 eV) semiconductor has photocatalytic activity under visible radiation [17]. However, CdS is prone to photocorrosion because of the oxidation of lattice S^{2-} by photogenerated holes [18,19]. The recombination of Ta_2O_5 with CdS is done in order to improve the stability of CdS and increase the response of Ta_2O_5. In addition, when CdS combined with wide band gap semiconductors, the charge injection from the conduction band (CB) of the narrow band gap semiconductor to CB of wide band gap semiconductor can lead to efficient charge separation and decrease electron-hole recombination [20,21]. In addition to this, it is important to increase interaction between the reactant molecules and catalyst surface, especially photocatalytic dye degradation. However bulk Ta_2O_5 is easy to aggregate and the surface area is little. It will offer a large surface area, more surface-active sites and high dispersibility with SiO_2 nanospheres as supporter, because SiO_2 nanospheres have large surface area. How to make bulk Ta_2O_5 evenly dispersed on SiO_2 nanospheres to better improve the photocatalytic activity is an important problem.

In the study, we have prepared CdS/(Cal-Ta_2O_5-SiO_2) composite with high photocatalytic activity by wet chemistry method. Ta_2O_5-SiO_2 with multi-step Ta_2O_5 deposition on SiO_2 has more Ta_2O_5 on SiO_2 to

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ensure the active sites. Trough multi-step calcination, Ta_2O_5 can load on SiO_2 with uniform and stable, which make it has high photocatalytic activity. The greatly enhanced photocatalytic activity compared to CdS/(Ta_2O_5-SiO_2) and CdS/Ta_2O_5 commercial is attributed to the decreased recombination opportunity of photogenerated electron-hole pairs, resulting from their rapid velocity and short resident time from bulk to surface.

2. Experimental section

2.1. Catalyst preparation

In a typical synthesis, 30 ml anhydrous ethanol, 20 ml ethanol saturated with ammonium, a certain amount of ammonium hydroxide (0.5 M or 1 M) and deionized water (5 M or 10 M) were mixed in the reaction vessel and placed in a constant temperature bath. When the solution reached the temperature, the TEOS (0.17 M) was added quickly. After 3–8 h for the first addition of TEOS, TEOS and water were added to the suspension in a 1:2 mol ratio. Then the solution was kept for the temperature under stirring for 8 h. The product was separated from the liquid phase by centrifugation and dried at 80 °C overnight [22]. It was labeled as SiO_2.

Tantalum pentachloride ($TaCl_5$ 99.99%, Afaza) was used as a starting material to prepare the Ta_2O_5/SiO_2 precursor. A certain amount of $TaCl_5$ was added into a suitable amount of water-ethanol (V/V = 1:1) solution containing citric acid as a chelating agent for the metal ions. The molar ratio of metal ions to citric acid was 1:2. The pH value of the solution was about 2. After 2 h under 45 °C, silica particles as carrier were added under stirring. The product was obtained after stirring for 4 h, separated from the liquid phase by centrifugation and washed with deionized water and ethanol thoroughly. The final product was dried at 80 °C overnight, and labeled as Ta_2O_5-SiO_2. The obtained Ta_2O_5-SiO_2 as carrier was repeated three times according to the above process, in order to increase the thickness of Ta_2O_5 shell. While the prepared Ta_2O_5-SiO_2 in the first process was calcined at 500 °C for 2 h, the sample was labeled as calcined Ta_2O_5-SiO_2. The obtained calcined Ta_2O_5-SiO_2 as carrier was also repeated three times according to the above process.

A certain amount samples (Ta_2O_5-SiO_2 or calcined Ta_2O_5-SiO_2 or commercial Ta_2O_5) were immersed in 0.2 M $Cd(AC)_2$ solution under stirring for 2–3 min, then separated by centrifugation and washed with deionized water. The above process was repeated three times to obtain the products. The final products were dried at 80 °C overnight, and labeled respectively as CdS/(Ta_2O_5-SiO_2), CdS/(Cal Ta_2O_5-SiO_2), CdS/Ta_2O_5 commercial.

2.2. Characterization techniques

The thermogravimetric-differential thermal analysis apparatus (TG-DTA)of sample was recorded on TA SDT-Q600, scavenging for helium gas, heating rate of 10 °c/min, the sample quality of 0.01 g.

The X-ray diffraction (XRD) patterns of samples were recorded on a Bruker D8 ADVANCE powder diffractometer using Cu-Kα radiation (λ = 0.1542 nm) at a scanning rate of 12° min^{-1} in the region of 2θ = 20–80°.

The morphologies and composition of samples were examined on a field emission scanning electron microscope (FE-SEM, Hitachi S-4800).

Transmission electron microscopy (TEM) images were taken on a Philips Tecnai G^2 20 S-TWIN electron microscope at an acceleration voltage of 200 kV. A few drops of alcohol suspension containing the sample were placed on a carbon-coated copper grid, followed by evaporation at ambient temperature.

Diffuse reflectance ultraviolet-visible (UV–vis) spectra were recorded in the air against $BaSO_4$ in the region of 200–700 nm on a Varian Cary 300 UV–vis spectrophotometer.

Photoluminescence (PL) spectra of samples were recorded on a Spex FL201 fluorescence spectrophotometer.

Infrared spectra of samples were recorded on Bruker Tensor 27. Scan range was 4000–800 cm $^{-1}$, The resolution was 4 cm $^{-1}$.

2.3. Photocatalytic evaluation

The photocatalytic degradation of RhB was performed in a top-irradiation-type double-walled quartz cell cooled by water with a mercury lamp (200 W, wavelength: 320–780 nm) as the light source. In each experiment, the catalyst of ca. 0.1 g was dispersed in the 200 ml of RhB solution (10 mg/L) in the quartz cell under stirring. The suspension was stirred in the dark for 30 min until the concentration of RhB did not change any more, indicating the adsorption equilibrium of RhB. After the start of photocatalytic reaction, samples were taken at regular time intervals and analyzed by UV–vis spectrometer (Varian Cary 300).

Photocatalytic reforming of methanol (also-known as photo-catalytic water splitting with methanol as sacrificial agent) was performed in a top-irradiation-type Pyrex reaction cell connected to a closed gas circulation and evacuation system under the irradiation of Xe lamp with filter (wavelength: 320–400 nm). In a typical experiment, a catalyst sample of ca. 100 mg was put in 100 ml 10% methanol aqueous solution in the reaction cell. After evacuated for 30 min, the reactor cell was irradiated by the Xe lamp at 200 W under stirring. The evolved gas product, e.g. hydrogen, was analyzed by an on-line gas chromatograph (Varian CP-3800) equipped with thermal conductivity detector.

3. Results and discussion

3.1. Physico-chemical properties of as-prepared samples

In order to obtain the calcination temperature, TG-DTA of as-prepared Ta_2O_5-SiO_2 is done. Fig. 1 shows the TG-DTA curve of the product. As is shown above, there are four different steps of weight in TG curve under the atmosphere of air. The main mass loss is the physical adsorption of water and residual organic matter decomposition before 250 °C [23–25]. The main mass loss is the molecules of water decomposition in 250–400 °C. There has a very prominent endothermic peak between 500 and 550 °C on the differential thermal analysis curve, which due to crystallization peak of glass. The little absorption peak around 490 °C should attribute to the crystallization peak with the combination of Ta_2O_5 and silica, which is consistent with the mass loss between 450 and 550 °C on TG curve. When the temperature reaches 600 °C, the silicon ball begins to gather, melt, and can't keep the morphology of silicon ball. So there are many endothermic peaks on DTA curve, and mass loss on TG curve.

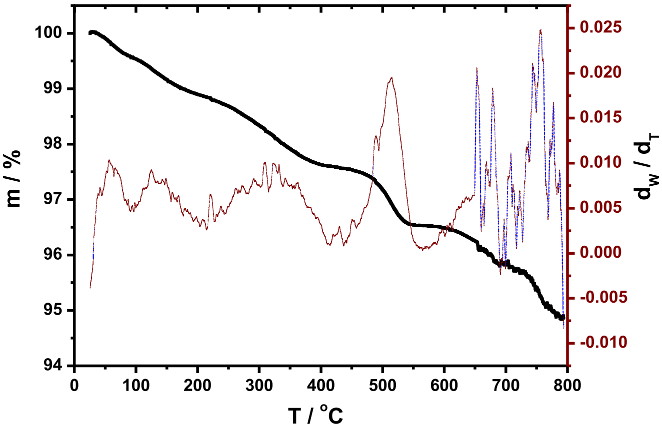

Fig. 1. The TG-DTA curves of the as-prepared Ta_2O_5-SiO_2.