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Short communication

Enhancing the photocatalytic activity of CdS nanorods for selective oxidation of benzyl alcohol by coating amorphous TiO_2 shell layer

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ABSTRACT

One dimension (1D) core–shell structural CdS@TiO_2 was fabricated by a modified sol–gel method. The thickness of amorphous TiO_2 (a-TiO_2) layer was adjusted by changing the amount of ammonia. Although a-TiO_2 shell layer diminishes the visible light absorption in a certain extent, it largely increases the surface area of photocatalyst and effectively promotes the separation rate of photogenerated electron–hole pairs. It was revealed that a-TiO_2 shell layer can effectively enhance the photocatalytic activity of CdS NRs for benzyl alcohol (BA) to benzaldehyde (BAD) transformation. Moreover, the core–shell structural CdS@a-TiO_2 showed high stability and reusability for the selective oxidation of BA.

1. Introduction

In the recent years, core–shell composite photocatalysts have attracted much attention because the hetero-junction structure can facilitate the separation of photo-generated electron–hole pairs by creating a staggered band-gap offset and thus enhances photocatalytic performance [1–8]. As a kind of core–shell structures, 1D core–shell structure has been received much research attention due to its unique advantages in light absorption, electron transportation, and surface properties [1,3–6].

As two important and classical semiconductor photo-catalysts, CdS and TiO_2 have been extensively used as coupling materials in recent years because of their suitable energy level structures [1–3,9]. However, most researches are focused on coupling CdS with crystalline TiO_2, the studies on combining with amorphous TiO_2 (a-TiO_2) are infrequent. However, compared with TiO_2 crystallites, a-TiO_2 has some distinct advantages: Firstly, it can be easily prepared without calcination [10,11]. Secondly, it has a porous structure, thus leading to a higher adsorptive property [10,11]. Thirdly, a-TiO_2 can be used as a protection layer to alleviate the corrosion of substrate material, such as CdS [12–15].

Here, we successfully fabricated 1D core–shell structural CdS@a-TiO_2 NRs with tunable shell layer thickness by a modified sol–gel method. The selective oxidation of benzyl alcohol (BA) to benzaldehyde (BAD) was employed as a probing reaction to study the photo-catalytic performances of the samples. On the basis of the above experiment results, the influences of a-TiO_2 shell layer on the photocatalytic activity were systematically discussed.

2. Experimental section

2.1. Fabrication of core–shell structural CdS@a-TiO_2 NRs

The CdS NRs were synthesized by a hydrothermal method [16] (see the Supporting information). The CdS@a-TiO_2 NRs were fabricated by a kinetics-controlled sol–gel method as follows [17]: 25 mg of CdS NRs was added into 100 mL of ethanol solution (99.5%) and ultrasonicated for 15 min at room temperature. Next, a desired amount of ammonia (0.22, 0.24, 0.26, 0.28 mL, respectively) was injected in mixture solution. Afterward, 0.75 mL of TBOT was added drop-wise in 5 min, and the reaction was allowed to proceed for 24 h at 45 °C under continuous mechanical stirring. Finally, the obtained product was washed with absolute ethanol and deionized water for several times, and dried at 60 °C for 8 h. The obtained samples were denoted as CAT-x, in which "x" stands for the additional amount of ammonia.

2.2. Characterization

The samples were analyzed by the following characterization means and instruments: X-ray diffraction pattern (XRD, Rigaku D/max 2550 VB/PC), transmission electron microscopy (TEM, JEOL JEM2000EX), UV–Vis diffuse reflectance spectrum (DRS) (SHIMADZU UV-2450), X-ray photoelectron spectrum (XPS, Thermo Fisher ESCALAB 250Xi), N_2 adsorpton–desorption isotherm (Micromeritics ASAP2020), Inductively

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coupled plasma spectrum (ICP, Agilent 725ES), and Photoluminescence spectrum (PL, EDINBURGH FLS980).

2.3. Photo-catalytic activity measurements

The photo-catalytic selective oxidation of BA was performed in a 50 mL three-necked flask at room temperature and oxygen atmosphere. For each measurement, 50 mg of as-synthesized catalyst was dispersed in the mixed solution of acetonitrile (20 mL) and BA solution (2 mmol) and then stirred for 1 h in the dark to attain the adsorption–desorption equilibrium. The photo-catalysis reaction was performed under visible light for 4 h, using a 300 W Xenon arc lamp with a UV-cutoff filter (λ ≥ 420 nm) as the light source. After the reaction, the concentrations of BA and BAD in the solution were measured with a SHIMADZU SPD-M20A high-performance liquid chromatograph (HPLC). The conversion rate of BA, the yield of BAD, and reaction selectivity were calculated with the equations as displayed in the Supporting information.

3. Results and discussion

Fig. 1A–E shows the TEM images of CdS and CdS@a-TiO_2 NRs prepared with different additional amount of ammonia. It can be seen that an amorphous TiO_2 shell is homogeneously coated on the entire surface of the CdS NRs to form a distinct core–shell structure. Additionally, the thickness of the TiO_2 layer exhibits an increase trend with the augment of ammonia dosage (Table S1), indicating that the thickness of a-TiO_2 layer can be conveniently adjusted by altering the additional amount of ammonia.

Fig. 1F presents the XRD patterns of bare CdS and different CdS@a-TiO_2 NRs samples. All the diffraction peaks can be indexed tohexagonal CdS (JCPDS card, No. 41-1049). Notably, almost no diffraction peak ascribed to TiO_2 can be distinguished in all CdS@a-TiO_2 samples, due to the relatively low crystallinity of TiO_2 in core–shell composites (Fig. S1).

The XPS spectra of the representative sample CAT-0.24 are presented in Fig. S2. In Fig. S2A, there exist two symmetric peaks at 458.8 eV and 464.5 eV, which should be ascribed to Ti^{4+} $2p_{3/2}$ and Ti^{4+} $2p_{1/2}$, respectively, of TiO_2 [18,19]. The O1s peak in Fig. S2B is asymmetric and broad, indicating that there exist at least two different kinds of O species: the fitted peak at 530.4 eV can be assigned to the lattice oxygen (O_L) of TiO_2 and the other smaller peak at 531.9 eV can be attributed to hydroxyl groups (O_H) at TiO_2 surface [18–20]. Fig. S2C shows the Cd 3d XPS spectrum, in which the two peaks at 405.3 eV and 412.0 eV can be ascribed to Cd^{2+} $3d_{5/2}$ and Cd^{2+} $3d_{5/2}$, respectively [21,22]. The XPS spectrum of S element is shown in Fig. S2D. The two symmetric peaks located at 161.6 and 162.8 eV can be assigned to the S^{2-} $2p_{3/2}$ and S^{2-} $2p_{1/2}$, respectively [21,22].

Fig. 2 shows the nitrogen adsorption–desorption isotherms of the CdS and CAT-0.24. Both samples exhibit a type IV isotherm, indicating the presence of mesopores [23,24]. The higher relative pressure at the closure point of the hysteresis loops indicates bigger pore diameter [25], meaning that the pore diameter of CAT-0.24 is much smaller, which is confirmed by the pore diameter distribution in Fig. S3. What's more, the introduction of a-TiO_2 leads to a significant improvement of specific surface area (S_{BET}) from 19.5 m^2 g^{-1} for CdS NRs to 143.8 m^2 g^{-1} for CAT-0.24, which indicates that the CdS@a-TiO_2 should have a higher adsorption capacity than bare CdS NRs. The S_{BET} and average pore sizes for different CdS@a-TiO_2 samples are summarized in Table S2. As the thickness of a-TiO_2 shell layer increases, the surface area of sample augments gradually, along with the decease of pore size.

The UV–Vis diffuse reflectance spectroscopy (DRS) was used to analyze the light absorption properties of as-prepared samples. As shown in Fig. 3, as the increase of TiO_2 shell thickness, the light absorption of CdS@a-TiO_2 exhibits a downtrend in the range of 350–500 nm and increase trend in the range of 200–320 nm. Due to quantum size effect, amorphous TiO_2 only can absorb short-wavelength UV light while CdS can absorb the light below 500 nm. Thus, the light absorption variation is well consistent with the change of TiO_2 shell thickness.

The HPLC and GC–MS analyses proved that part of benzyl alcohol has been successfully converted into benzaldehyde over CAT-0.24 (Figs. S4–S6). Fig. 4 shows the BA conversion rates and BAD yields over different

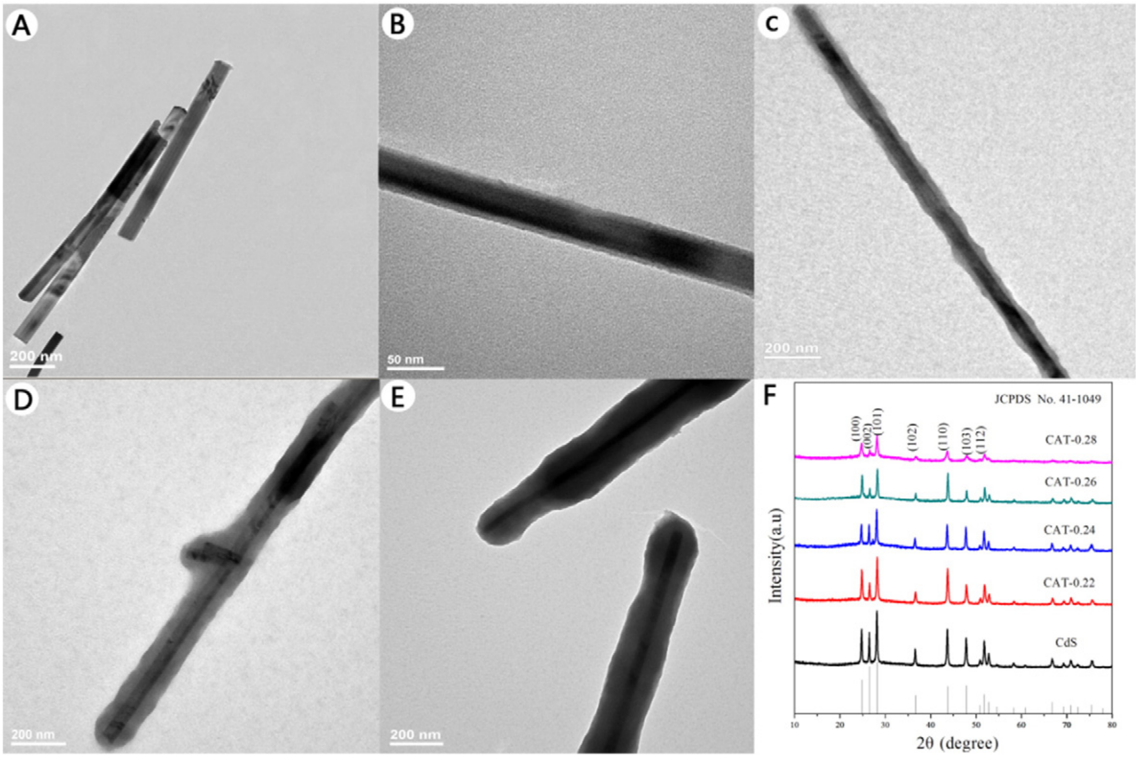

Fig. 1. (A–E) TEM images of CdS and different CAT samples: (A) CdS; (B) CAT-0.22; (C) CAT-0.24; (D) CAT-0.26; and (E) CAT-0.28. (F) XRD patterns of CdS and different CAT samples.