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Microemulsion-mediated solvothermal synthesis of nanosized CdS-sensitized TiO_2 crystalline photocatalyst†

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Nanosized CdS-sensitized TiO_2 nanocrystals were successfully prepared by a microemulsion-mediated solvothermal method. The effectiveness of the new photocatalyst was demonstrated by the decomposition of an organic compound and the formation of Ti^{3+} on TiO_2 under visible-light irradiation.

Anatase TiO_2 is the most widely used photocatalyst for effective decomposition of organic compounds in air and water under irradiation with UV light with wavelength shorter than 387 nm.[1,2] The problem is that only about 3% of the solar spectrum falls in this UV range. The efficient use of sunlight becomes an appealing challenge for developing photocatalysis.[3] One approach for achieving this objective is to sensitize TiO_2 by using a narrow band gap semiconductor with a higher conduction band (CB) than that of TiO_2. In this sensitized TiO_2, charge injection from the CB of the semiconductor sensitizer to that of TiO_2 can lead to efficient and longer charge separation by minimizing the electron–hole recombination. For instance, CdS coupled TiO_2 colloids have been extensively studied in photoelectrochemistry and water splitting systems.[4–6] However, only bulk CdS mixed TiO_2 particles were developed for visible light photocatalysis.[7] This may decrease the sensitization ability of CdS due to its bulk nature. Utilization of nanosized CdS to couple with nanocrystalline TiO_2 could improve the efficiency of photocatalysis.

It would be desirable to directly prepare TiO_2 nanocrystalline particles with homogeneously dispersed CdS nanocrystals, because the direct formation of these two semiconductors would provide a strong coupling between them. This communication first describes a new approach to facilitate the direct formation of nanocrystalline TiO_2 coupled by highly dispersed CdS nanocrystals at a considerably lower temperature by combined microemulsion and hydrothermal methods. This method can avoid the oxidation of CdS in the CdS/TiO_2 nanocomposite during the process of post thermal treatment for the crystallization of TiO_2.[8]

A typical synthesis (CdS at 3%) involved cyclohexane (0.9 mol) as oil phase, Triton X-100 (0.028 mol) as surfactant and 1-hexanol (0.056 mol) as co-surfactant. Three microemulsions containing 1 mL of Millipore water (A), 1.5 mL of 0.3 M $Cd(NO_3)_2$ solution (B) and 2.5 mL of 20 wt% $(NH_4)_2S$ solution (C) were prepared. Titanium isopropoxide (14.55 mmol) was added into microemulsion (A) under continuous stirring. After titanium isopropoxide was gradually hydrolyzed and condensed in water nanodroplets for 30 minutes, microemulsion (B) was mixed with microemulsion (A) under vigorous agitation. Microemulsion (C) was then added into the mixture. This new microemulsion was stirred for 24 h at room temperature. In this process, cadmium sulfide was incorporated into the TiO_2 colloids by simultaneous coprecipitation of $Cd(NO_3)_2$ and $(NH_4)_2S$ in the water nanodroplets. 75 mL of the resulting microemulsion colloids containing CdS and TiO_2 was placed in a 100 mL Teflon-lined stainless steel autoclave and bubbled with Ar gas to remove air from the colloids, then solvothermally treated at 200 °C for 12 h. The yellow slurry obtained was centrifuged and washed with ethanol and water, and finally kept in a desiccator for drying. TiO_2 photocatalyst with CdS at 1 and 5 mol% (nominal values) were also synthesized by the same procedures.

As shown in Table 1, CdS was successfully incorporated into TiO_2 at 1.07, 2.80 and 5.36 mol%, as confirmed by X-ray photoelectron spectroscopy (XPS)‡ results. This microemulsion-mediated solvothermal method can generate nanocomposite particles with high surface areas of 156–263 $m^2\ g^{-1}$ and with anatase crystal sizes ranging from 5.5 to 9.8 nm. All CdS-sensitized TiO_2 nanocrystalline samples absorb in the visible range with estimated absorption onset at about 550 nm, which corresponds to band gap energy of 2.25 eV. For comparison, the absorption onsets for anatase TiO_2 and CdS are 410 and 556 nm, respectively (Fig. 1 in ESI†), corresponding to band gap energies of 3.02 and 2.23 eV. X-Ray diffraction (XRD)§ patterns confirm that the obtained TiO_2 is pure anatase and CdS has a cubic phase (Fig. 2 in ESI†). Characteristic XRD patterns from both TiO_2 and CdS are observed. Five distinctive TiO_2 peaks are found at 25.43°, 37.92°, 48.09°, 54.58°, and 62.81° corresponding to the anatase (101), (103, 004 and 112), (200), (105 and 211), and (204) crystal planes, respectively (JCPDS 21–1272). Meanwhile, three additional peaks at 26.5° (d = 3.355 Å), 43.9° (d = 2.055 Å) and 52.1° (d = 1.752 Å) are also present, which can be assigned to the CdS cubic phase (111), (220), and (311) crystal planes, respectively (JCPDS 89–0440). Uniform nanoparticles with size about 8 nm were observed in the transmission electron microscopy (TEM)¶ image of S2 (Fig. 1), in agreement with that obtained from XRD. It is also found that this preparation method produces highly crystalline nanoparticles, as shown in high-resolution transmission electron microscopy (HRTEM)¶ (right in Fig. 1). The fringes appearing in the micrographs allow for the identification of the crystallographic spacing of the TiO_2 and CdS nanocrystallites. The fringes of d = 3.7 Å and d = 3.2 Å observed in Fig. 1 match that of the (101) and (111) crystallographic planes of anatase TiO_2 and CdS cubic phase, indicating the existent of CdS/TiO_2 coupling between the distinct phase domain.

Visible-light photocatalytic activities of the CdS-sensitized TiO_2 samples as well as pure CdS and TiO_2 were measured by

Table 1 CdS molar percentage, surface area and anatase crystal size of prepared samples

Sample	CdS (mol%) N_1[a]	CdS (mol%) N_2[b]	S_{BET}[c]/$m^2\ g^{-1}$	Anatase crystal size[d]/nm
S1	1	1.07	263	5.6
S2	3	2.80	201	8.8
S3	5	5.36	156	9.8

[a] N_1 as nominal value. [b] N_2 as value measured by XPS. [c] BET surface area measured by nitrogen adsorption–desorption isotherm at 77 K. [d] Calculated by XRD using the Scherrer equation.

† Electronic supplementary information (ESI) available: UV-visible absorption spectra, XRD patterns and EPR spectrum. See http://www.rsc.org/suppdata/cc/b3/b302418k/

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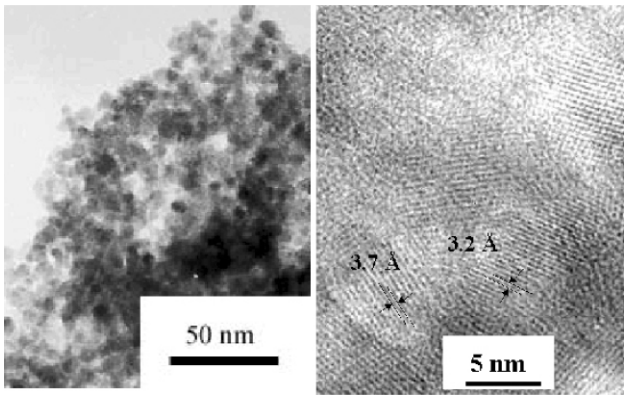

Fig. 1 TEM and HRTEM (right) images of S2.

the decomposition rate of methylene blue in an aqueous solution. Air was bubbled into the solution throughout the entire experiment. A 300 W tungsten halogen lamp with a 400 nm cut off filter was used as visible light source. 0.15 g of photocatalyst (pure CdS is 8 mg which is the same amount of CdS present in S2) was suspended in a 200 mL aqueous solution of 2.2×10^{-5} M methylene blue and the absorption peak at 660 nm was monitored. Results are shown in Fig. 2. S2 and S3 exhibit the highest visible-light photocatalytic activity and no degradation of methylene blue was observed on pure TiO_2. Obviously, nanosized CdS-sensitized TiO_2 nanocrystalline photocatalyst shows high visible-light activity.

From electron paramagnetic resonance spectrum (EPR)‖ shown in Fig. 3, visible-light irradiation on S2 at 77 K in the presence of oxygen produced an obvious signal at a *g*-tensor value of 1.991, indicating the presence of Ti^{3+} on irradiated TiO_2.[9] Meanwhile, no EPR signal of Ti^{3+} can be detected on pure TiO_2 under the same measurement conditions (Fig. 3 in ESI†). This suggests an effective transfer of photo-generated electrons from the conduction band of CdS to that of TiO_2 and provides evidence to the mechanism of sensitisation.

The experiments described here demonstrate the feasibility of direct preparation of highly crystalline nanosized CdS-sensitized TiO_2 particles using microemulsion-mediated solvothermal method. The obtained samples also exhibit high efficiency for decomposition of methylene blue under visible light irradiation. The efficient separation of charges through interaction of CdS and TiO_2 results in the formation of Ti^{3+} as observed in the EPR spectrum. It should be noted that the actual application of CdS-sensitized TiO_2 photocatalyst for wastewater treatment might not be highly desirable due to the

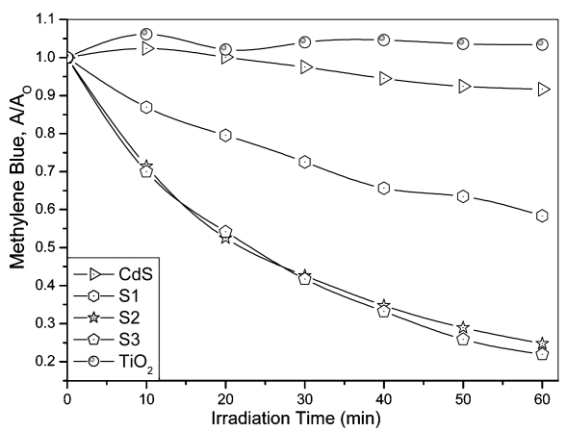

Fig. 2 The methylene blue reduction in UV–vis absorption spectra at 660 nm as a function of visible-light irradiation time in the prepared photocatalysts.

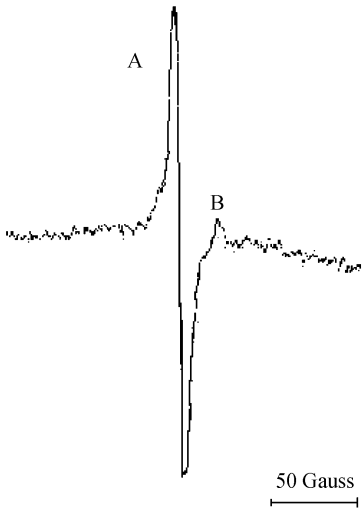

Fig. 3 EPR spectrum of S2

potential leaching of cadmium ions into the effluent. Nevertheless, practical solar energy activated air purification systems may be designed utilizing an immobilized CdS/TiO_2 photocatalyst. Preparation and photocatalysis of other chalcogenide semiconductor sensitized TiO_2 nanocrystalline materials are currently under investigation in our laboratory.

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Notes and references

‡ XPS were recorded on a PHI Quantun 2000 XPS System with Al–Kα radiation as the exciting source.

§ XRD patterns were obtained on a Bruker D8 Advance X-ray diffractometer with Cu–Kα radiation.

¶ TEM image was taken on a Philips CM-120 electron microscopy instrument and HRTEM image was taken on a JEOL 2010 transmission electron microscopy.

‖ The EPR spectrum was recorded on an X-band EPR spectrometer (JEOL, JES-TE100) at 77K. The sample was irradiated by a 500 W superhigh-pressure mercury lamp (Ushio, USH500D) equipped with a bandpass filter of 424 nm (Toshiba, Y-44).

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