CdS Coating on TiO_2 Nanoparticles under Multibubble Sonoluminescence Condition

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In recent years, a large number of nano-size semiconductors have been researched for their potential applications in photovoltaic cell, optical sensor device and photocatalysts.[1-3] Nano-size semiconductor particles reveal many interesting properties due mainly to their size-dependant optical properties. In this sense, many kinds of nanomaterials have been prepared, such as CdS,[4] CdSe,[5] CuS,[6] and other composite materials. However, most of them were prepared with toxic reactants and/or complex multistep reaction process. To overcome such problems and to apply multilayered semiconductor nanoclusters, a lot of core/shell type nanocrystals are extensively studied through various methods, such as microwave and sonochemistry.[7,8] The sonochemistry is an application of sonoluminescence (SL) which is a light emission phenomenon associated with the catastrophic collapse of a gas bubble oscillating under an ultrasonic field. The intense local heating and high pressure inside the bubbles and liquid adjacent the bubble wall from such collapse can give rise to unusual effects in chemical reactions[9-12] and the sonochemical processing has been proven to be a useful technique to make novel materials with unusual properties. The estimated temperature and pressure in the liquid zone are about 1000 °C and 500 bar,[9] respectively, which make a high-energy chemical reaction possible. In case of multibubble sonoluminescence (MBSL) condition, a lot of transient bubbles can be generated by the irradiation of high intensity ultrasound in aqueous solution, providing unusual reaction conditions. In fact, methylene blue (MB) which is one of typical textile dyestuffs was degraded very fast at the MBSL condition while the MB was not degraded under simple ultrasonic irradiation.[13]

In this study, TiO_2 nanoparticles were tried to be coated with CdS through a one pot reaction under MBSL condition, which are very likely to be useful for the development of inorganic dye-sensitized solar cells.

Figure 1 shows an experimental apparatus for MBSL with a cylindrical quartz cell, into which a 5 mm diameter titanium horn (Misonix XL2020, USA) is inserted. This system was operated at 20 kHz and 220 W. The solution in the test cell was kept at 1.4 atm with argon gas and the temperature of the solution inside the cell was kept to around 40 °C by a water bath. These were found to be optimal conditions for the process.

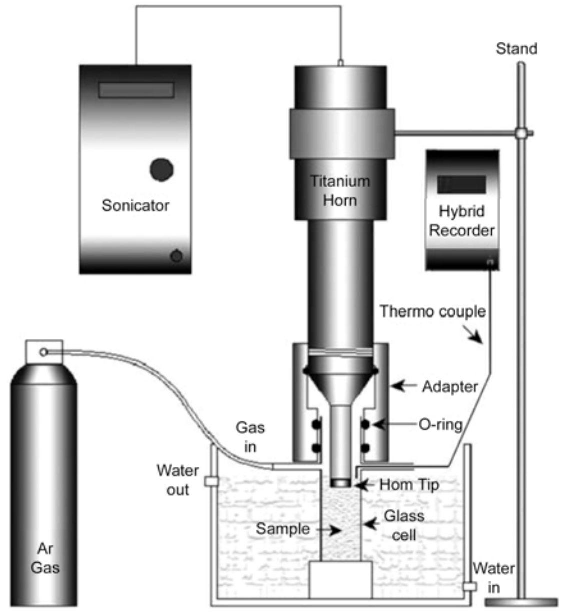

Figure 1. Experimental set-up for MBSL experiment.

Experimental details

For a typical experiment, cadmium chloride (Aldrich; 1.15 g, 6.3 mmol), thioacetamide (Aldrich; 0.473 g, 6.3 mmol) and TiO_2 (Degussa, P-25, 0.1 g, 1.25 mmol) in distilled water (13 mL) were sonicated at the MBSL condition with a high intensity ultrasonic horn. After 10 min later, the resulting powder was collected by centrifugation (Kontron, T-1180, Italy). After washing with water and ethanol, the product was dried at vacuum oven for 12 hr. The product was characterized by various instruments, such as X-Ray diffractometer (Scintag XDS-2000), energy dispersive X-ray spectroscopy (Philips XL 30S FEG), transmission electron microscope (JEOL, JEM-2000EXII), UV-VIS spectroscopy (JASCO U-550), and high resolution – transmission electron microscope (JEOL, JEM-3010).

In Figure 2, the XRD pattern of the CdS-coated TiO_2 nanoparticles reveals that they are in hexagonal phase (JCPDS **1995** No. 06-0314) with most intense peaks at 2θ= 24.8°, 26.4°, 28.2°, 36.6°, 43.7°, and 51.9°, corresponding to (100), (002), (101), (102), (110), and (112) planes. It is quite

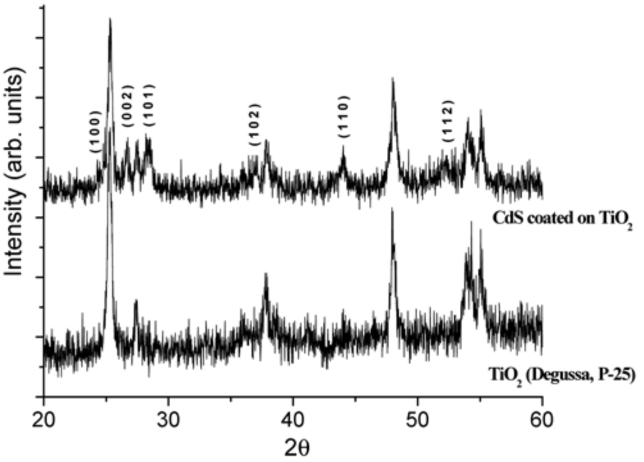

Figure 2. XRD patterns for bare TiO_2 nanoparticles and CdS coated TiO_2 nanoparticles by sonochemical reaction under MBSL condition.

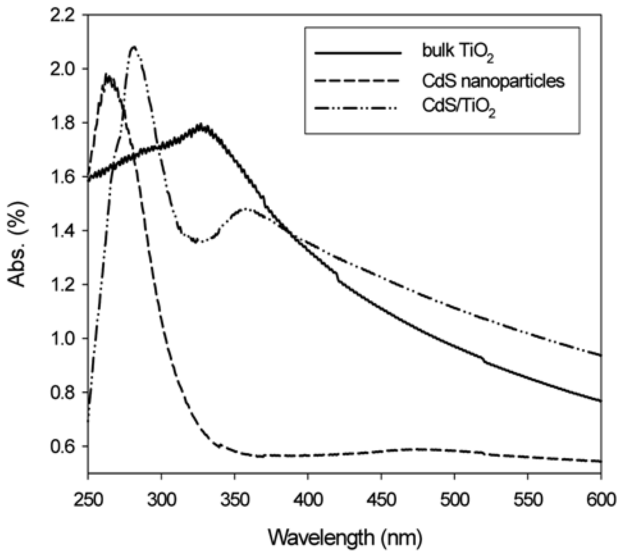

Figure 3. UV-VIS optical absorption spectra of nanoparticles; CdS, bare TiO_2, and CdS/TiO_2 prepared by sonochemical reaction under MBSL condition

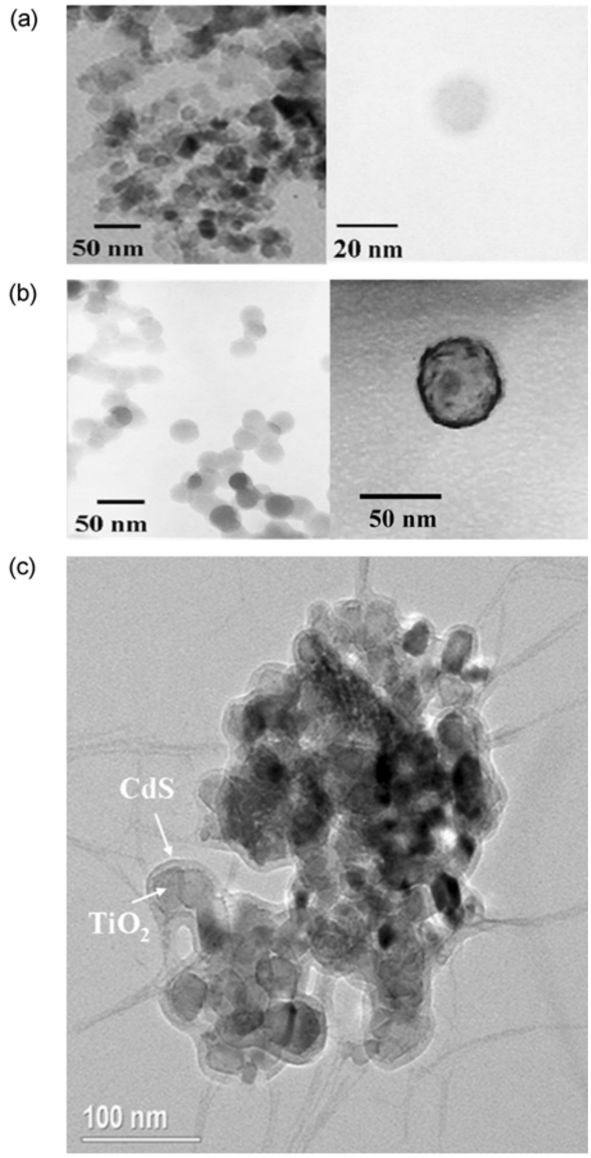

Figure 4. Typical TEM images of (a) bare TiO_2, (b) CdS-coated TiO_2 particles, (c) HR-TEM image of CdS-coated TiO_2 particles prepared under MBSL condition.

interesting to note that CdS particles are typically in cubic phase when they are prepared over 450 °C.[14,15] This means that the actual reaction temperature in this system is supposed to be at least over 450 °C, which is possible in the liquid layer at the bubble wall around the bubble collapse. The relatively low intensities of peaks are assumed to arise from the fact that the particles are nano-sized and the CdS is thinly coated on TiO_2. In addition, EDX analyses show that the atomic percents of Cd, S, and Ti are 12.19, 14.43, and 72.09%; this result means that the ratio of Cd/S is nearly 1 : 1, and that of CdS/TiO_2 1 : 5.

For a comparative study, a series of UV-VIS optical absorption spectra for CdS nanoparticles fabricated from sonochemical reaction under MBSL, bare TiO_2 nano-particles, and CdS-coated TiO_2 particles were examined. In the case of bulk CdS, the absorption band characteristically appeared at 500 nm.[16,17] However, as shown Figure 3, those of CdS nanoparticles and CdS-coated TiO_2 nanoparticles appears at about 290 nm. This result is in good agreement with the reports that as the particles become small to nano-size, their optical absorption band shows a drastic blue shift compared to that of bulk CdS powder.[17,18]

Figure 4 shows the typical transmission electron microscopic images of the bare TiO_2 nanoparticles and CdS-coated TiO_2 nanoparticles. They are nearly spherical in shape, indicating that CdS is evenly coated on the surface of TiO_2. The average size of the bare TiO_2 nanoparticles is about 20 nm in diameter and those of CdS-coated TiO_2 nanopartcles at the described condition were found to be about 25-30 nm range. But they were found to be controlled to about 30-50 nm by adjusting reaction conditions; simply by controlling the amount of reactants and/or the sonication time, various CdS-coated TiO_2 nanoparticles with different coating depths were able to be produced in this system.

Thus, CdS-coated TiO_2 nanoparticles were produced by a one pot sonochemical reaction at the MBSL condition using $CdCl_2$, thioacetamide, and TiO_2. The crystalline phase of CdS in the resulting particles is hexagonal and the average particle size of CdS coated on TiO_2 nanoparticles was 25-30 nm in diameter.

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