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Homogeneous ZnS coating onto TiO_2 nanoparticles by a simple one pot sonochemical method

Seung Soo Lee[a], Ki-Taek Byun[b], Jong Pil Park[a],
Sin Kyu Kim[a], Jong Chan Lee[a], Suk-Kyu Chang[a],
Ho-Young Kwak[b], Il-Wun Shim[a,*]

[a] *Department of Chemistry, Chung-Ang University, Seoul 156-756, Republic of Korea*
[b] *Department of Mechanical Engineering, Chung-Ang University, Seoul 156-756, Republic of Korea*

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Abstract

TiO_2 nanoparticles were easily coated with ZnS in nano-scale through a simple one pot reaction under multibubble sonoluminescence (MBSL) conditions which can provide a very powerful and efficient coating system. The coating depths of ZnS shell were in 2–5 nm range in a core/shell type nanostructure which is very likely to be useful for the development of inorganic dye-sensitized solar cells. The ZnS-coating depths on TiO_2 in this system were found to be easily controlled in nano-scale by adjusting the amount of reactants and/or the sonication time. The ZnS-coated TiO_2 nanoparticles were characterized by XRD, UV–vis, EDS, and HR-TEM.

Keywords: Sonochemistry; ZnS-coated TiO_2 nanoparticles

1. Introduction

In recent years, a wide variety of nano-size semiconductors have been investigated for their potential applications in photovoltaic cell, optical sensor device and photocatalysts [1–3]. Semiconductor nanoparticles reveal many interesting optical properties due to their size-dependent absorption and/or emission. It is most correct to write many kinds of nanomaterials have been prepared, such as CdS [4], CdSe [5], CuS [6], and other composite materials. ZnS, a group II–VI semiconductor having a large direct band gap of 3.6 eV in near UV region and a refractive index of 2.35, is well known to be an important device material, which can be used for detector, emitter, modulator in optoelectronics, and blue light emitting laser diode. Also, it can be applied to a transparent dielectric material, and a cadmium free buffer layer of CIGS-based solar cell [7]. However, most of them were prepared with toxic reactants and/or complex multistep reaction process. To overcome such problems and to apply for multilayered semiconductor nanoclusters, various core/shell type nanocrystals are extensively studied through different methods, such as hydrothermal synthetic method, microwave and sonochemistry [8–10]. Sonochemistry is an application of sonoluminescence which is a light emission phenomenon associated with the 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 [11] and the sonochemical process has been proven to be a useful technique to make novel materials with unusual properties. For an example, methylene blue (MB) which is one of typical textile dyestuffs was degraded very fast at the specific sonochemical conditions, while it was not decomposed under simple ultrasonic irradiation [12].

Recently observed results [13] of the peak temperature and pressure from the sonoluminescing gas bubble in sulfuric acid solutions turned out to be predicted [14] accurately by the hydrodynamic theory for the sonoluminescence phenomena [15–17]. The estimated temperature and pressure in liquid zone around the collapsing bubble with equilibrium radius 5 μm, generated in a sonochemical reactor at a driving frequency of 20 kHz with an input power of 179 W [18] are about 1000 °C and 500 atm, respectively [14]. A lot of transient bubbles which are generated

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* Corresponding author. Tel.: +82 2 820 5201; fax: +82 2 825 4736.
E-mail address: iwshim@cau.ac.kr (I.-W. Shim).

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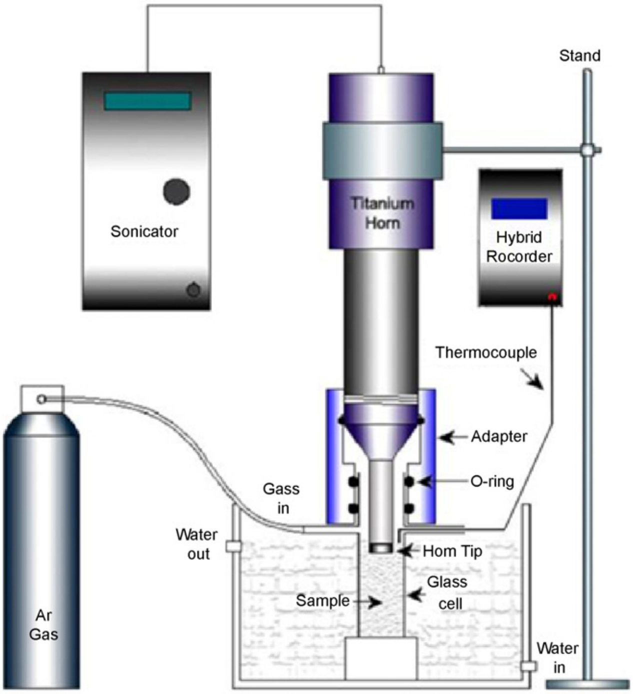

Fig. 1. Experimental set-up for sonochemistry experiment.

and collapsed synchronizingly with the applied ultrasound facilitate transient supercritical state [19] in the liquid layer where rapid chemical reactions can take place.

In this study, TiO_2 nanoparticles were coated with ZnS, leading to a core/shell type nanocrystals, through a simple one pot sonochemical reaction under MBSL conditions.

2. Experimental details

The fabrication of ZnS-coated TiO_2 nanoparticles was carried out with an experimental apparatus (Fig. 1) for sonochemistry system consisting of a cylindrical quartz cell into which a 5 mm diameter titanium horn (Misonix XL2020, USA) is inserted.

The sonochemical reaction system in this study was operated at 20 kHz and 220 W, which is quite intensive compared to other typical ultrasound irradiation processes [20–22]. 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 50 °C by a circulating water bath, which was found to be optimal condition for the coating process [23].

All reagents were used from Sigma–Aldrich Corporation, and ethanol was refluxed over molecular sieves 3 Å (pellets, 3.2 mm) to remove water molecules and distilled before using them.

For the coating of ZnS onto TiO_2 nanoparticles, $ZnCl_2$ (Aldrich; 0.859 g, 6.3 mmol), thioacetamide (Aldrich; 0.473 g, 6.3 mmol) and TiO_2 (Degussa, P-25, 0.079 g, 1.25 mmol) in distilled water (13 ml) were sonicated at the aforementioned conditions. After a 10 min sonication reaction, gray colored ZnS-coated TiO_2 nanoparticles were obtained. They were washed by DI-water, alcohol, acetone in order and dried at vacuum oven at 60 °C for 12 h. The products were characterized by various techniques, such as X-ray diffraction (Scintag XDS-2000), transmission electron microscopy (JEOL, JEM-2000EXII), UV–vis spectroscopy (JASCO U-550), high resolution-transmission electron microscopy (JEOL, JEM-3010), and energy dispersive X-ray spectroscopy (Philips XL 30S FEG).

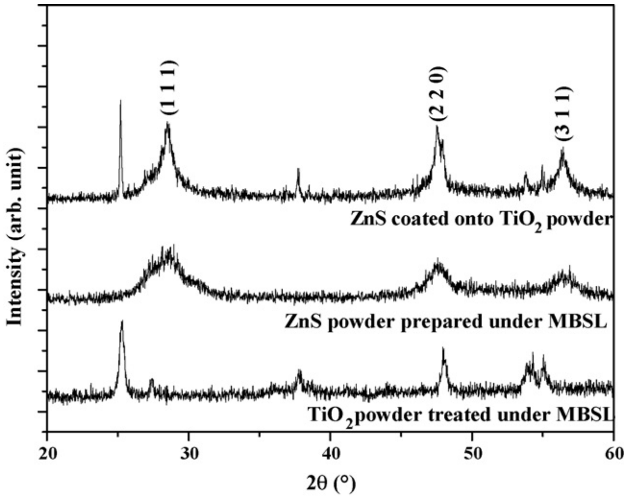

Fig. 2. XRD patterns for TiO_2, ZnS, and ZnS-coated TiO_2 nanoparticles fabricated by sonochemical reaction under MBSL conditions.

In case of the same sonochemical reaction without TiO_2 particles, pure ZnS nanoparticles were obtained and its XRD pattern can be seen in Fig. 2. Their average size was about 4 nm, but their size distribution was quite wide.

3. Results and discussion

The X-ray diffraction spectra (Fig. 2) of the ZnS-coated TiO_2 nanoparticles indicates that the coated ZnS on is in a cubic phase [24] with most intense peaks at $2\theta = 28.5°$, 47.4°, 56.4° corresponding to (1 1 1), (2 2 0), (3 1 1) planes. It should be mentioned that they were found to be very critical optimum conditions for our coating process. In other milder sonochemical conditions without light emission, no appreciable ZnS coating onto TiO_2 nanoparticles was observed. This result reveals that our MBSL coating process, leading to the preparations of various core/shell nanocystals, is a very powerful method which can be operated only around 50 °C for 10 min. The relatively low intensities and broadness of X-ray diffraction peaks are assumed to arise from the fact that the particles are nano-sized and the ZnS is thinly coated on TiO_2. In addition, EDX analyses show that the atomic percents of Zn, S, and Ti are 2.47, 2.14, and 26.09%; this observation means that the ratio of Zn/S is nearly 1:1, and that of ZnS/TiO_2 is about 1:10.

For a comparative study, a series of UV-VIS optical absorption spectra for ZnS nanoparticles fabricated from sonochemical reaction, bare TiO_2 nanoparticles, and ZnS-coated TiO_2 particles were examined. In case of bulk ZnS, the absorption band characteristically appears at 500 nm. However, as shown in Fig. 3, those of ZnS and ZnS-coated TiO_2 nanoparticles appears at about 275 and 320 nm, respectively. 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

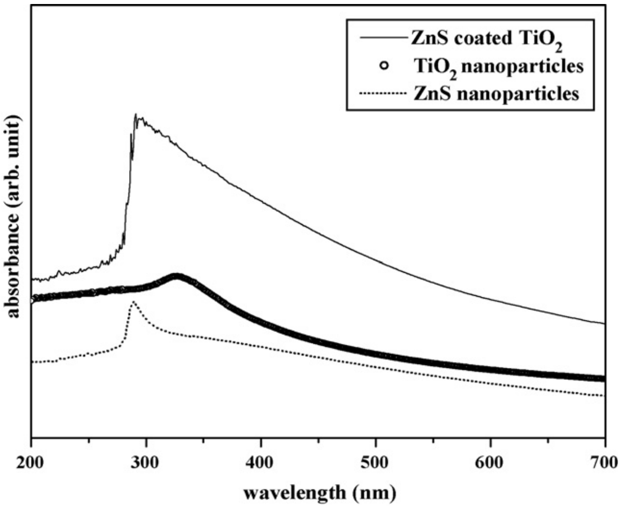

Fig. 3. UV–vis spectra for TiO_2, ZnS, and ZnS-coated TiO_2 nanoparticles fabricated by sonochemical reaction under MBSL conditions.

shift compared to that of bulk ZnS powder [25,26]. Also, the absorption band at 275 nm for the prepared ZnS nanoparticles can be explained by their smaller size of about 4 nm in diameter.

Fig. 4 shows the high resolution-transmission electron microscopic images of the ZnS-coated TiO_2 nanoparticles. They indicate that ZnS is uniformly coated on the surface of TiO_2. The average size of the bare TiO_2 nanoparticles was about 20–30 nm in diameter and that of ZnS-coated TiO_2 nanoparticles was found to be about 22–35 nm range. But the particle sizes were found to be easily controlled to about 30–50 nm by simply controlling the amount of reactants and/or the sonication time; for an example, if the concentrations of $ZnCl_2$ and thioacetamide were increased to twice at the same MBSL conditions, the particle sizes were in 25–40 nm range, indicating that the ZnS-coating depths are 5–10 nm. Thus, various TiO_2 nanoparticles with different ZnS-coating depths were able to be produced in this system.

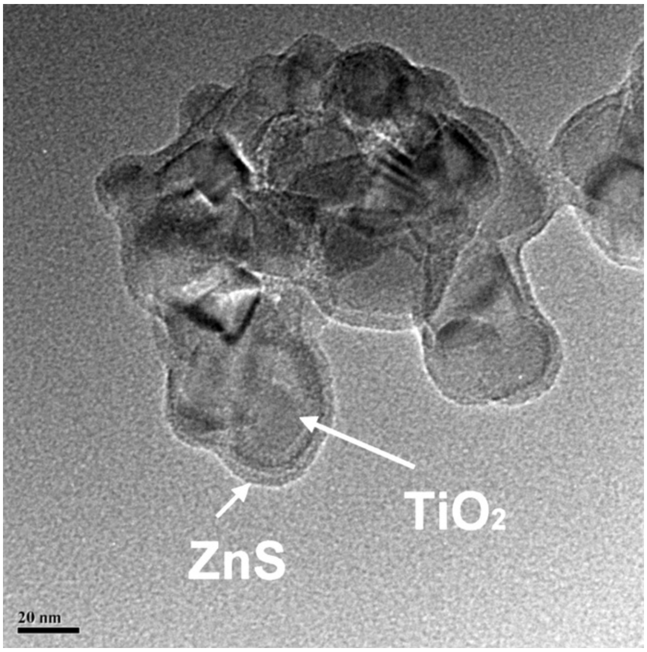

Fig. 4. HR-TEM image of ZnS-coated TiO_2 particles prepared.

It should be noted that rapid syntheses with very homogeneous size of ZnS and subsequent coating of the particles onto TiO_2 nanoparticles under the described sonochemical conditions might be attributed to the existence of transient supercritical state in the liquid layer adjacent to the bubble wall around the collapse point. This result can be referred to the report [27]: the rate of the hydrolysis reaction of *p*-nitrophenyl acetate became highly accelerated by several orders of magnitude in the presence of specific ultrasound, suggesting that there was a similar development of the supercritical state of water during the bubble collapse.

4. Conclusions

ZnS-coated TiO_2 nanoparticles were produced by a one pot reaction at the described sonochemical conditions using $ZnCl_2$, thioacetamide, and TiO_2. The crystalline phase of ZnS in the resulting particles was cubic and the depth of coated ZnS onto TiO_2 nanoparticles was found to be controlled in nano-scale on demand by this method.

Acknowledgments

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