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Original Research Paper

A fast and facile microwave irradiation method for the synthesis of $ZnO@ZrO_2$ core-shell nanocomposites and the investigation of their optical properties

Md. Obaidullah[a,*], Takeshi Furusawa[a], Iqbal Ahmed Siddiquey[b], Newaz Mohammed Bahadur[c], Masahide Sato[a], Noboru Suzuki[a]

[a] Department of Innovation Systems Engineering, Utsunomiya University, 7-1-2 Yoto, Utsunomiya 321-8585, Japan
[b] Department of Chemistry, Shahjalal University of Science and Technology, Sylhet 3114, Bangladesh
[c] Department of Applied Chemistry and Chemical Engineering, Noakhali Science and Technology University, Noakhali 3814, Bangladesh

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ABSTRACT

$ZnO@ZrO_2$ core-shell nanocomposites (NCs) were prepared by a novel and accessible path employing microwave (MW) irradiation to regulate photocatalytic property of ZnO. The synthesized $ZnO@ZrO_2$ NCs were further examined to discern their optical and chemical properties by FT-IR, XPS, XRF, XRD, FE-SEM, EDX, TEM, UV–vis, and PL analysis. XPS data analysis confirmed the presence of zirconium and oxygen on the coated surface. An almost similar zeta potential curve was observed for the pure ZrO_2 and ZrO_2 coated ZnO NCs, predicting the presence of the ZrO_2 layer on ZnO. Photoluminescence studies show the enhanced intensity of $ZnO@ZrO_2$ nanostructure compared to uncoated ZnO. Photocatalytic activity of ZnO could be controlled by the amorphous ZrO_2 layer, which was guaranteed by the photo mineralization of methylene blue under UV irradiation at room temperature.

1. Introduction

Core-shell nanomaterials have prompted great fascination because of the distinctive characteristics of nanoparticles and diverse potential applications based on the enhanced optical, electrical and mechanical properties [1]. Surface modification of semiconductor oxide with inorganic oxide materials has been proved to show unique attributes due to the integrated electronic structure [2]. Moreover, the coated shell issues enhancement to the core accompanying passivation, extra functionalities, protection from damage of high energy laser pulses, and resistance to possible chemical reactions of the core part with its environment [3]. Zinc oxide nanoparticles have been widely used in the sunscreen formulation due to the high transparency in the visible spectral region and broad optical absorption in both UVA (spectral ranges 400 nm–315 nm) and UVB (315 nm–280 nm) to protect against radiation skin damage [4]. But nanosized ZnO generates highly reactive oxygen species in the presence of solar light, which can degrade other ingredients present in the cosmetics [5–8]. Moreover, bare ZnO gets dissolved in highly acidic solutions, so it is quite impossible to keep the multifunctional properties of nanosized bare ZnO in the extremely acidic formulated method. On the other hand, ZrO_2 is a renowned ceramic material due to its high dielectric constant, refractive index and high oxygen ion conduction. It strengthens more mechanical, chemical, and thermal stability of ZnO. Therefore, $ZnO@ZrO_2$ core-shell matrix can eliminate the adverse impacts of nanostructured bare ZnO, and this array can be used in pyroelectric, piezoelectric ceramics, oxygen sensors, and a variety of functional ceramic products [3]. Moreover, ZrO_2 coating on ZnO nanoparticles (NPs) can restrain the photocatalytic activity of ZnO with keeping UV absorbing and visible light transmitting properties, making it an ideal component for pragmatic applications [9,10]. Numerous research groups have reported a variety of methods to prepare nano core-shell matrix for getting enhanced multifunctional properties, which mainly araise from the interfacial interaction. These include sol-gel method [11–15], hydrolysis [16,17], stober method [18], reduction method [19,20], hydrothermal method [21], etc. Compared to the above-stated methods, microwave (MW) assisted nano core-shell structure synthesis is a time-saving and easy process. Moreover, uniform layers with the different thicknesses are possible within short reaction times by raising the desired temperature quickly and fixing the percentage of MW irradiation [8–10,22,23]. In this study, $ZnO@ZrO_2$

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* Corresponding author.
E-mail address: dt167102@cc.utsunomiya-u.ac.jp (Md. Obaidullah).

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nanocomposites were synthesized by MW irradiation method to avoid time-consuming and tedious processes, and also to get the uniform ZrO_2 layer on ZnO nanoparticles. Furthermore, we investigated the crystallinity, morphology, interfacial interactions, optical properties of the prepared nanocomposites by X-ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM), fourier transform infrared spectroscopy (FT-IR), photoluminescence (PL) spectroscopy.

2. Materials and methods

2.1. Materials

The ZrO_2 coating was accomplished on commercial ZnO (MZ-500) with a surface area of 38.4 m^2/g provided by Tayca Corporation, Japan. Zirconium sulfate tetrahydrate ($Zr(SO_4)_2{\cdot}4H_2O$), methylene blue, and ethanol (99.5%) were obtained from Kanto Chemical Co. Inc., Japan. Ammonia solution (28%) was purchased from Wako Pure Chemical Industries Ltd., Japan. All chemicals were of reagent grade and used without further purification.

2.2. Synthesis of $ZnO@ZrO_2$ core-shell nanocomposites

At first, 1.0 g of ZnO nanoparticles were dispersed in 20 mL water followed by pulverization in a zirconia pot with 73.5 g of zirconia ball (5 mm in diameter) by a planetary ball mill (Pulverisette-7, Fritsch GmbH, Germany) at 370 rpm for 10 min. Then the dispersed ZnO NPs were shifted into a three-necked 300 mL round bottom flask followed by further addition of 60 mL H_2O, and different amounts of ammonia solution (pH = 12) to maintain moderate basicity. This ZnO dispersion is introduced as solution A. Solution B was prepared by dissolving the different amount of zirconium sulfate tetrahydrate (0.5 g, 1.0 g, and 1.5 g) distinctly in 20 mL water. Solution B was then added to the solution A dropwise during moderate stirring. Then the final mixture was irradiated under microwave (MW) at 70 °C for 5 min in a batch type MW apparatus (SMW-064, 2.45 GHz, Shikoku Keisoku, maximum power 500 W) containing a built-in magnetic stirring system. The temperature was measured by inserting an optical fiber into the flask during irradiation. Finally, the $ZnO@ZrO_2$ suspension was washed with ethanol by centrifugation for at least three times followed by vacuum drying at 110 °C for two hours. The samples prepared for the amount of 0.5 g, 1.0 g and 1.5 g of zirconium sulfate tetrahydrate will be described in the further sections as $ZnO@ZrO_2$–0.5, $ZnO@ZrO_2$–1.0, and $ZnO@ZrO_2$–1.5, respectively, where the amount of ZnO was 1.0 g in each case.

2.3. Characterizations

Fourier transform infrared spectral (FT/IR-4100, Jasco corp., Japan) study was carried out in transmission mode in the frequency range of 4000–400 cm^{-1} with 64 scans of each sample to confirm the prediction of Zn—O—Zr bond. The UV shielding and the visible light transmittance property of the core-shell $ZnO@ZrO_2$ nanocomposites were justified by UV–Vis spectrophotometer (V-660, Jasco Corp., Japan). The photoluminescence (PL) characterizations of bare and zirconia coated ZnO were determined at room temperature by a spectrofluorometer (FP-8200, Jasco Corp. Japan). The crystalline structure and phase of the synthesized core-shell nanomaterials were analyzed by a powder diffractometer (Ultima IV, Rigaku Corp., Japan) at a speed of $4^\circ\ min^{-1}$ in the range of 20°–80° with Cu-Kα radiation. The morphology of the synthesized core-shell nanocomposites was observed by a field emission scanning electron microscope (FE-SEM S-4500, Hitachi Ltd., Japan) and a transmission electron microscope (JEM-2010, JEOL Ltd., Japan). XPS measurements were carried out by PHI 5000 Versaprobe II (ULVAC-PHI INC.) with an energy resolution of 1.0 eV for the survey scans and 0.25 eV for the high-resolution scans of the individual characteristic peaks. X-ray fluorescence spectroscopy (SEA-2010, SEIKO Instruments Inc.) was used to determine the chemical compositions of the core-shell nanomaterials. The surface zeta potential of the core-shell nanocomposite was examined by Zetasizer Nano ZSP (Malvern Inst. Ltd., UK). 0.02 g of each sample was dispersed in 50 mL distilled water by sonicating for 20 min. The pH of the solution was modulated by the addition of 0.1 M NaOH or 0.1 M HCl aqueous solution.

The photocatalytic efficiency of the uncoated ZnO NPs, as well as the synthesized core-shell nanocomposites, was measured by the photodegradation of methylene blue at ambient temperature and pressure. In a typical experiment, 0.02 g of sample was added to 100 mL of 1.0×10^{-5} M methylene blue aqueous solution and kept on stirring in the dark for 30 min to confirm adsorption-desorption equilibrium of methylene blue on the ZnO surface. Then the heterogeneous solution was irradiated with UV lights (15 W × 5). After that, the photo illuminated solution was collected at a regular time interval, and the absorbance of methylene blue solution was monitored at 664 nm using a UV–Vis spectrometer (V-630, Jasco Corp.) to determine the residual concentration.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FT-IR) analysis

Fig. 1 shows the schematic diagram for the formation of ZrO_2 coating on the ZnO particles through the Zn—O—Zr bond. FT-IR was used to identify the functional groups present in the prepared samples. Fig. 2 represents the FT-IR spectra of pristine ZnO, ZrO_2, and as prepared $ZnO@ZrO_2$ core-shell nanocomposites. The bands at 3434 cm^{-1} and 1632 cm^{-1} are the stretching and bending vibratons of H—O—H, which typically comes from the residual water molecule or physically adsorbed water [2,3,6,24]. For pure ZrO_2, the peak at 746 cm^{-1} corresponds to the Zr—O vibrational mode [25]. From Fig. 2, the spectrum of pure ZnO can be differentiated from the spectra of the $ZnO@ZrO_2$ core-shell nanocomposites. A few new bands such as 619 cm^{-1}, 1120 cm^{-1}, and 1402 cm^{-1} arise after modification of ZnO by ZrO_2. The band at 619 cm^{-1} and 1120 cm^{-1} implies the Zn—O—Zr stretching vibration, and the band at 1402 cm^{-1} predicts that the molecule on the surface contains O—H group [25,26]. Using the change in FTIR spectra of $ZnO@ZrO_2$ nanocomposites compared to the uncoated ZnO, we can predict that the hydrolyzed ZrO_2 covers the ZnO nanoparticles.

3.2. X-ray photoelectron spectroscopy (XPS) analysis

XPS analysis was carried out for the uncoated ZnO, pure ZrO_2, and ZrO_2 coated ZnO core-shell nanocomposites to explore the interfacial interaction between ZnO and ZrO_2. A wide scan was conducted (binding energy range: 0–1249.3 eV, pass energy: 58.7 eV) for detecting desired elements on the surface and a narrow scan was carried out for each element of C 1s, Zn $2p_{3/2}$, O 1s, and Zr 3d with the same pass energy. C 1s peak at the binding energy of 284.8 eV was employed as the reference. Fig. 3 depicts the wide scan XPS spectra and shows the presence of characteristic peaks of ZrO_2 (Zr 3d) and ZnO (Zn $2p_{3/2}$) in the synthesized $ZnO@ZrO_2$ nanocomposites. From Fig. 3, it can also be discerned that the intensity of Zn $2p_{3/2}$ decreases and Zr 3d peak intensity escalates with the increasing of ZrO_2 precursor. These signify the coating of ZnO surface by ZrO_2 [27–31]. The relative surface compositions of the zirconia coated samples, as derived from XPS peak

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