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Enhancement of visible-light-driven photoresponse of Mn-doped SnO_2 quantum dots obtained by rapid and energy efficient synthesis

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ABSTRACT

Mn-doped SnO_2 quantum dots (QDs) with different Mn concentrations were prepared by solution combustion synthesis. The crystallite size was under 5 nm was confirmed from XRD and HR-TEM. A considerable decrease in band gap energy was observed with the increase in Mn content. The PL spectra show orange emission at about 590 nm due to the ultra-small crystallite size and crystal defects of SnO_2 QDs. The photocatalytic degradation of MO dye was measured under visible light irradiation using the Mn-doped SnO_2 QDs as catalysts. 3 mol% Mn-doped SnO_2 QDs showed the 17 times higher photocatalytic performance than SnO_2 QDs within 240 min.

1. Introduction

Photocatalysis has been a proved phenomena to clean our environment from many harmful chemicals released from numerous different sources. So far, the scientific community developed many procedures to resolve the environmental issues by using photocatalysis [1]. The front row of photocatalysts is occupied by metal oxides particularly titanium dioxide (TiO_2), zinc oxide (ZnO), and tin oxide (SnO_2) due to their significant properties towards photocatalysis [2,3]. Among all, SnO_2 semiconductor nanomaterials have been gained the more recent interest for their applications in photocatalysis [4,5]. SnO_2 is a degenerate n-type semiconductor with a wide bandgap of 3.6 eV. It is thermally and chemically stable, non-toxic, abundant, and has relatively low cost. Its unique surface properties, high transmittance in the ultraviolet-visible region, and semi-conductivity make it one of the most useful multifunctional materials [6].

SnO_2 QDs show interesting properties of high surface-to-volume ratio and strong quantum confinement to achieve the best photocatalytic activity [7]. Bhattacharjee et al., prepared SnO_2 QDs by microwave method which exhibits the stronger absorption ability and higher larger surface areas to reach superior photocatalytic performance under direct sunlight [8]. Li et al., synthesized iodinated SnO_2 QDs to enhance the absorption of solar light for visible photocatalysis [9]. Liu et al., prepared SnO_2 QDs and achieved MB degradation rate of 90% in 240 min under visible light irradiation [10]. The large band gap energy of SnO_2 and the high recombination rate of photogenerated electron-hole pairs limit the usage of the solar spectrum and finally, the practical applicability of the pure SnO_2 material is limited. Therefore solar light-driven photocatalysis is still urging the new combination of materials with high photocatalytic efficiency prepared by environmentally friendly methods.

There are different strategies used in order to resolve the standing issues. In recent years, narrowing the bandgap of SnO_2 with transition metal (TM) doping has been considered as effective strategy owing to its major effect on particle size, surface area, tuning absorption into the visible region and retards the recombination of photogenerated electron-hole pairs [11,12]. The presence of oxygen vacancies in SnO_2 and dopant TM ions can modify and improve its optical and electrical properties [13–15]. Of the many transition metals, Mn is one of the suitable choices with multiple valence states (Mn^{2+}, Mn^{3+}, and Mn^{4+}) to replace Sn^{4+} ions in the SnO_2 host matrix due to the comparable ionic radii and large equilibrium solubility [16]. Adding Mn, increases the surface area and transport performance of the carriers and can be used to tune the band gap by the modifying energy levels [17]. Even the small amounts of manganese make possible to increase the oxygen vacancies resulting in enhanced photocatalytic activity of the SnO_2 semiconductor [18]. Therefore, the synthesis of TM-doped SnO_2 QDs is an enthusiastic area of optical materials, and more research is needed to explore simple and novel methods to prepare TM-doped SnO_2 QDs with low energy consumption in a short time [19].

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In the present work, we prepared Mn-doped SnO_2 QDs via solution combustion synthesis, which offers many advantages of molecular level mixing to obtain crystallite size less than 5 nm, as well as rapid process time to obtain the fine powder with large surface area. The results show that the Mn dopant plays a vital role in decreasing the crystallite size, increase in surface area, retards the recombination of charge carriers as well as decreasing the band gap to absorb visible light.

2. Experimental procedure

As precursors, 0.4 M of tin chloride pentahydrate ($SnCl_4{\cdot}5H_2O$) and 1.2 M of urea ($CO(NH_2)_2$) were used to prepare undoped SnO_2 QDs. The tin precursor and urea were mixed with different concentrations (1, 2, and 3 mol%) of manganese nitrate with respect to tin chloride pentahydrate and dissolved in 50 mL of distilled water. The mixture was magnetically stirred at room temperature for 20 min to obtain a uniform, homogeneous solution.

The solution was placed in a pre-heated muffle furnace and kept at a temperature of 450 °C. During the process, the mixed solution became viscous and formed a gel. The gel slowly swelled, burned by itself, and produced a powder. The powder was cooled down to room temperature naturally and then gently ground using an agate mortar. 1, 2, and 3 mol % Mn-doped SnO_2 nanopowders were named as Mn-1, Mn-2, and Mn-3, respectively.

2.1. Photocatalytic experiment

The photocatalytic activities of pristine SnO_2 QDs and Mn-doped SnO_2 QDs were evaluated for the degradation of methyl orange as a model organic pollutant under visible light. All photodegradation experiments were performed at ambient temperature. A halogen lamp (100 W, 220 V H-PAR30) with a 410 nm cut-off filter (UV L41 Kenko Tokina Japan) was fitted just below the lamp which served as a visible-light source to trigger the photocatalytic reaction. To maintain the constant temperature, a quartz photoreactor with a water circulation jacket was fixed in a steel container along with a magnetic stirrer. The lamp was kept 6 cm above the dye solution, and 50 mg of photocatalyst was added to an aqueous solution of methyl orange (100 mL, 10 ppm).

In a typical experiment, prior to light illumination, the dye solution was stirred for 30 min in the dark to ensure adsorption–desorption equilibrium between the dye solution and the photocatalyst. After a certain time interval, 4.0 mL aliquots were collected from the photoreactor and centrifuged to remove the small particles of the photocatalyst. A UV–vis–NIR double-beam spectrophotometer was used to monitor the concentration of the dye during the photoreaction. The absorbance of the clear solution was recorded at λmax of 464 nm. To confirm that the photocatalytic activity is due to the photocatalyst only, we carried out blank experiments without a catalyst under light (photolysis) with a catalyst in the dark (adsorption).

2.2. Characterization

Powder X-ray diffraction patterns of the prepared samples were recorded on a Shimadzu 6100 X–ray diffractometer with CuK(alpha) radiation. High-resolution transmission electron microscope (HRTEM) images were recorded on a Tecnai G2 F 20 S-Twin TEM at an accelerating voltage of 200 kV. Optical absorption spectra were obtained by a Cary 5000 UV–vis–NIR spectrophotometer. X-ray photoelectron spectroscopy was done using a Thermo Scientific K-alpha surface analysis instrument. The EPR spectrum was obtained using a JEOL JES-TE 100 EPR spectrometer operating at X-band frequencies with 100-kHz field modulation. A Shimadzu IRAffinity-1S FT-IR spectrophotometer was used to record the IR spectrum of the samples in the region of 400–4000 cm^{-1}.

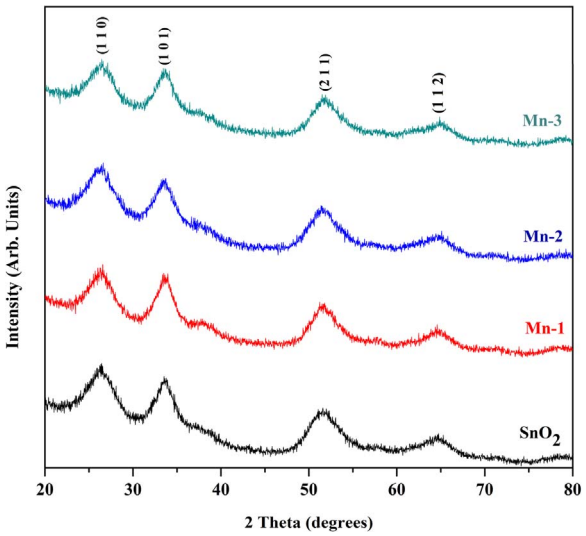

Fig. 1. XRD patterns of undoped and Mn-doped SnO_2 QDs.

3. Results and discussion

3.1. XRD

The structural properties of the undoped and Mn-doped SnO_2 QDs were investigated by X-ray diffraction patterns, as shown in Fig. 1. The prominent diffraction lines of each sample located at 26.4°, 33.7°, 51.6°, and 64.6° were indexed to the (1 1 0), (1 0 1), (2 1 1), and (1 1 2) diffraction planes of the tetragonal rutile structure of SnO_2 [20]. The diffraction planes of both the doped and undoped QDs agreed well with the standard JCPDS data (41-1445). Primarily, the broad diffraction peaks indicate a very small crystallite size of the QDs. No diffraction lines related to Mn or its oxides were detected. The crystallite size of the samples was evaluated using the Debye-Scherrer formula, $D = 0.9\lambda / \beta \cos\theta$. The crystallite size decreased slightly with increasing Mn concentration. The crystallite size ranged from 5 to 4.4 nm.

The ionic radius of the Mn^{2+} ion is 91 pm, that of Mn^{3+} is 90 pm, and that of Mn^{4+} is 52 pm, whereas that of Sn^{4+} is 74 pm [21]. The small shifting of the diffraction angles and decreased reduction of the crystallite size arise from the smaller ionic radius of Mn^{3+}/Mn^{4+} ions than Sn^{4+} ions. The probability of Mn^{2+} is ruled out because of its higher ionic radii than Sn^{4+} [21]. The lattice strain and dislocation densities were calculated from the diffraction data using the equations $\varepsilon = \beta \cos\theta / 4$ and $\delta = 1/D^2$, respectively [22]. The crystallite size (D), lattice strain (ε), dislocation density (δ), and lattice cell parameters are presented in Table 1. The shifting in diffraction positions leads to decreased crystallite size and lattice cell parameters, which result from micro-strain in the host lattice. The micro-strain and dislocation density were found to be higher in the doped samples than the undoped sample and increased with the concentration of Mn, which caused the decrease in crystallite size [22]. Negative strain values indicate the substitution of Mn^{4+} ions in the sites of Sn^{4+} ions due to the difference in ionic radii

Table 1
Crystallite size, lattice strain, dislocation density, and lattice parameters of pristine undoped and Mn-doped SnO_2 QDs.

Sample	Crystallite size (D nm)	Lattice strain (ε) × 10^{-3}	Dislocation density (δ) × 10^{-17}	Lattice cell parameters	
				a (nm)	c (nm)
SnO_2	5.0	6.95	0.40	0.4651	0.4357
Mn-1	4.8	7.29	0.43	0.4646	0.4351
Mn-2	4.6	7.53	0.46	0.4642	0.4344
Mn-3	4.4	7.82	0.51	0.4633	0.4329

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