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Formation of stable and strong green luminescent ZnO/Cd(OH)$_2$ core-shell nanostructure by sol–gel method

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Highly stable and strong green luminescent ZnO/Cd(OH)$_2$ core-shell nanoparticles have been synthesised by simple sol–gel route. X-ray diffraction (XRD) and energy dispersive analysis of X-rays confirm the formation of ZnO/Cd(OH)$_2$ core-shell nanoparticles. The XRD and UV–visible spectroscopy shows that ZnO core size can be efficiently engineered by varying initial precursor ratio. The photoluminescence emission spectra showed the remarkably stable and enhanced visible (green) emission from suspended ZnO/Cd(OH)$_2$ nanoparticles in comparison with bare ZnO nanoparticles. It was postulated that Cd(OH)$_2$ layer at the surface of ZnO nanoparticles prevent the agglomeration of nanoparticles and efficiently assist the trapping of hole at the surface site, a first step necessary for visible emission.

Keywords: core-shell nanoparticles; green luminescence; surface state

1. Introduction

ZnO has a wide band gap of 3.37 eV at room temperature and a large exciton binding energy of 60 meV. The luminescent properties of ZnO have received considerable attention due to its potential application in diverse areas, such as ultraviolet (UV) light emitters, lasers, varistors, transparent high power electronics, chemical sensors and phosphors for flat panel display devices [1–4].

The discovery of quantum size effect in nanometre sized particles has led to more interest in ZnO material. To date, the most successful approach to obtain quantum-sized ZnO has been the sol–gel route [5]. The ZnO nanocrystals prepared by this method exhibits remarkably high green luminescence as compared with that of UV luminescence. These properties are considered to provide a major advantage in the development of full colour displays and biological fluorescence labelling applications. However, ZnO nanocrystals tend to aggregate or undergo Ostwald ripening owing to their high surface energy [6]. As a result, such nanocrystals are unstable in dispersions or in powder form

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during storage [7]. Dijken et al. [8] reported in their studies of ZnO nanoparticle that as the size increases intensity of UV emission increases while that of green emission intensity decreases. The strategies to control the particle sizes include encapsulating an organic capping agent on the nanoparticle surfaces such as alkylthiols, polymers micelles [9,10] or inorganic SiO_2 shells [11]. Generally any attempt to stabilise ZnO nanocrystals by using capping agents diminishes green emission and enhances UV emission due to surface passivation [10,12,13]. Thus it seems experimental challenge to synthesise stable and strong green luminescent ZnO nanocrystals.

Dijken et al. [14] have also proposed a model to explain the luminescence property of ZnO nanoparticle on the basis of steady and time resolved luminescence measurements on the suspensions of ZnO nanoparticles synthesised by solution precipitation route. With the help of the model we can outline the necessary conditions to obtain stable and strong green emission from ZnO nanocrystals as

(1) Quenching the growth of ZnO nanocrystals at the smaller particle size to increase the probability of tunnelling process.
(2) Efficient trapping of hole at the surface site.

In this work we have proposed the synthesis of $ZnO/Cd(OH)_2$ core-shell nanoparticles for stable and strong green emission and also explained how $ZnO/Cd(OH)_2$ nanostructure satisfies the above outlined conditions for green emission.

2. Experimental details

2.1. *Chemicals*

Zinc acetate dihydrate $[Zn(CH_3COO)_2 \cdot 2H_2O]$, cadmium acetate dihydtrate $[Cd(CH_3COO)_2 \cdot 2H_2O]$ from Merck (Mumbai, India) and lithium hydroxide monohydrate $(LiOH \cdot H_2O)$ from Thomas Baker (Mumbai, India) were used as precursors, and absolute ethanol and *n*-Heptane (Merck, India) were used as solvents directly without any further purification.

2.2. *Sample preparation*

The synthesis of bare and core-shell ZnO nanocrystals were carried out by the sol–gel method of Bahnemann et al. and Spanhel et al. with few modifications under room temperature conditions [5,15]. The preparation procedure was as follows: 0.14 M lithium hydroxide was dissolved in 50 mL ethanol in an ultrasonic bath to obtain a clear solution. Then 0.1 M zinc acetate was dissolved in 75 mL boiling ethanol (75°C) at atmospheric pressure under refluxing, and the solution was allowed to cool at room temperature. The hydroxide-containing solution was then added drop wise, under vigorous stirring, to the zinc acetate solution, resulting in a transparent sol, which when exposed to UV radiation, exhibits green luminescence. Following the same procedure, core-shell nanostructures were synthesised by taking 0.1 M (cadmium acetate + zinc acetate) solution in place of zinc acetate solution. In this case also we get a transparent sol of core-shell nanoparticles. Both bare and core-shell nanoparticle solutions were precipitated by addition of excess *n*-Heptane. The final ZnO nanoparticle and core-shell nanoparticle powdered samples were obtained by centrifugation of the precipitate and heated at 100°C for 12 h.

The core-shell nanoparticles were synthesised for 5, 10, 15, 20, 25 and 30% concentrations of cadmium in an initial precursor solution. The bare ZnO and core-shell nanoparticles were named as ZnO_0, ZnO_5, ZnO_10, ZnO_15, ZnO_20, ZnO_25 and ZnO_30.

2.3. *Characterisation*

All the measurements for characterisation were performed at room temperature. The X-ray diffractometry (XRD) for the crystal structure of the dried powder samples was carried out with Rigaku D/MAX-2200 H/PC diffractometer. The optical absorption and photoluminescence spectra of nanoparticles were examined with a Perkin-Elmer Lambda 35 UV–Visible spectrometer and Perkin-Elmer LS 55 spectrophotometer, respectively. For photoluminescence study we have taken a fixed amount sol (10 µl) in a cuvette filled with ethanol.

3. Results and discussions

It is known from the basic chemistry that CdO is formed only at temperature above 200°C, and below 200°C synthesis by the acetate route leads to only $CdCO_3$ or $Cd(OH)_2$. Thus, incorporation of Cd in ZnO is possible only when the reaction temperature is above 200°C; however, we have performed all the reactions at the room temperature and precipitates are dried at temperatures below 100°C. Therefore, this reaction condition rules out the possibility of $Zn_{1-x}Cd_xO$ alloy formation.

As shown in Figure 1, the X-ray diffraction (XRD) patterns of all the powdered nanoparticles show peaks corresponding to ZnO hexagonal phase without any shift and no appearance of any peaks corresponding to any other compound. This shows the possibility of formation of ZnO core-shell nanoparticle as the XRD pattern of core-shell nanoparticle shows peaks corresponding to core only. Also the energy dispersive analysis of X-rays (EDAX) spectrum of samples shows that zinc, cadmium and oxygen are the main elemental components. Thus by the combined XRD and EDAX analyses and also with the help of basic chemistry we can say that $ZnO/Cd(OH)_2$ core-shell nanostructure is formed in this case. By analysing the expected reaction procedure step-by-step, it is clear that initially only $Cd(OH)_2$ and basic zinc acetate complex is formed, when the cadmium acetate and zinc acetate is refluxed in the ethanolic medium. When LiOH is added in the reaction medium at room temperature, nucleation of ZnO starts in the presence of $Cd(OH)_2$, an ideal condition for capping of ZnO with $Cd(OH)_2$. In this way $ZnO/Cd(OH)_2$ core-shell nanoparticle is formed as a final product.

As the concentration of cadmium increases the XRD peak broadening also increases, this indicates that ZnO core size decreases as Cd to Zn ratio increases. By applying Debye–Scherrer formula, we can calculate the sizes of ZnO core in different core-shell nanoparticles as it is known that II–VI semiconductor core/shell nanocrystals such as CdS:Mn/ZnS [16] or CdSe/CdS [17] exhibited no XRD peak broadening upon the deposition of the shell layer. The size of ZnO core are 13.8 nm, 11.8 nm, 9.5 nm, 8.6 nm, 6.4 nm for ZnO_0, ZnO_5, ZnO_10, ZnO_15, ZnO_30 core-shell nanoparticle, respectively.

The UV–Visible absorption spectra (Figure 2) of the ZnO bare and core-shell nanoparticles show the blue shift in absorption edge. It means increase in band gap as

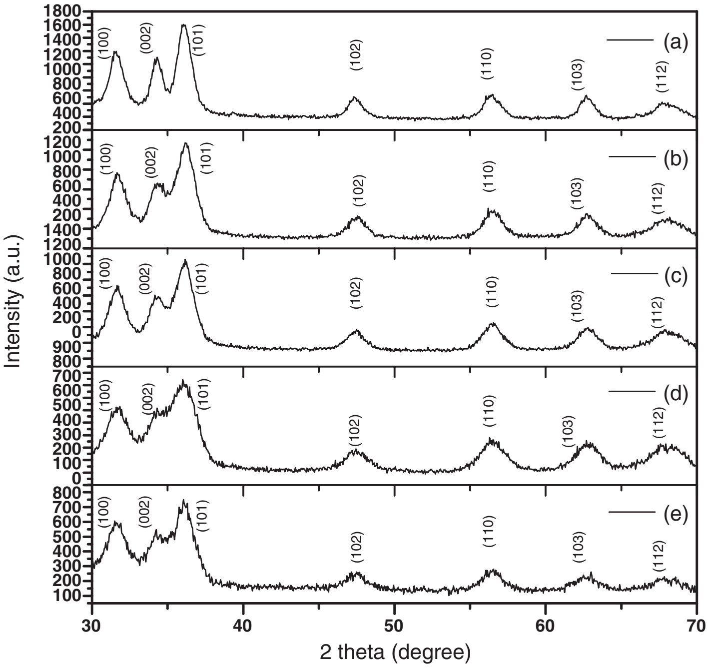

Figure 1. XRD patterns from powdered nanoparticles: (a) ZnO_0, (b) ZnO_5, (c) ZnO_10, (d) ZnO_15, (e) ZnO_30.

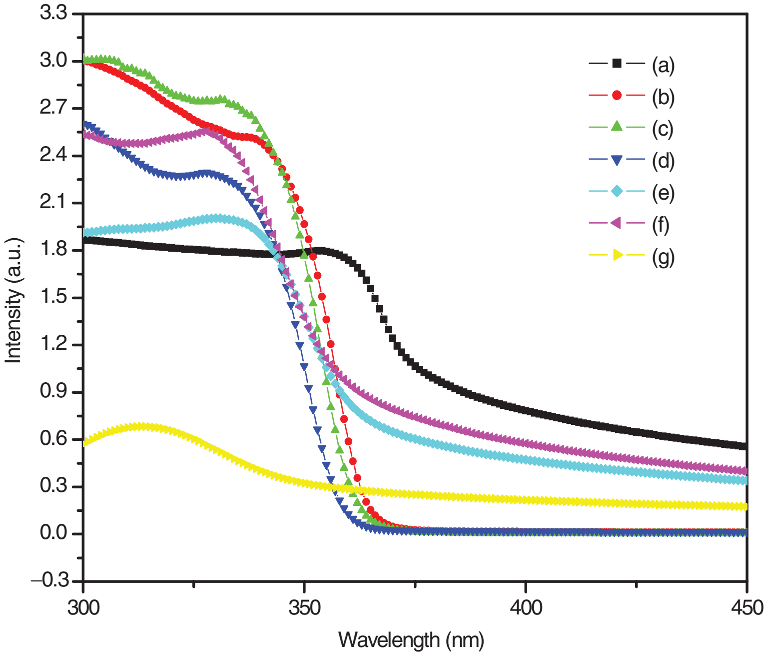

Figure 2. UV–visible absorption spectra of ZnO bare and core-shell nanoparticle suspensions: (a) ZnO_0, (b) ZnO_5, (c) ZnO_10, (d) ZnO_15, (e) ZnO_20, (f) ZnO_25, (g) ZnO_30.

Table 1. Evaluated band gap and core size from absorption spectra.

Nanoparticles	Band gap (eV)	Core size (nm)
ZnO_0	3.39	13.2
ZnO_5	3.41	10.8
ZnO_10	3.43	9.3
ZnO_15	3.46	7.9
ZnO_20	3.48	7.3
ZnO_25	3.50	6.8
ZnO_30	3.52	6.4

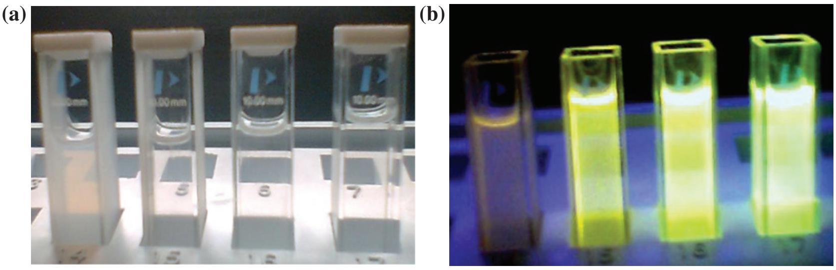

Figure 3. Direct photographs of ZnO_0, ZnO_5, ZnO_15, ZnO_25 core-shell nanoparticle suspensions from left to right under visible light (a) and under UV irradiation (b), taken after 1 week of synthesis.

the amount of Cd to Zn salt increases because of continuous decrease in ZnO core size. The increase in band gap by decreasing ZnO core size is observed due to well-known quantum confinement effect [18,19]. ZnO is a direct band gap semiconductor, and therefore its absorption coefficient is related to the excitation energy ($E_{exc} = h\nu$) by $(\alpha h\nu)^2 = \text{constant}\ (h\nu = E_g)$, where E_g is the band gap energy [20]. Thus we can calculate the band gap by $(\alpha h\nu)^2$ *versus* energy $h\nu$ plot (tauplot). After calculating band gap, we can determine the sizes of ZnO core by using a relation between band gap and radius of nanocrystal [21].

The ZnO core sizes calculated using absorption spectra are consistent with size calculated with XRD spectra using the Debye–Scherrer formula (Table 1). These results show that by varying the initial precursor ratio we can efficiently stop the growth of nanoparticles at the smaller particle size desired for green emission.

The photographs shown in Figure 3 clearly show the remarkable enhanced stability and luminescence intensity of ZnO core-shell nanoparticles in comparison with bare ZnO nanoparticles. It is clear from the photograph that the suspension of bare ZnO nanoparticle becomes turbid after 1 week of synthesis and also luminescence intensity is much decreased while ZnO core-shell nanoparticle suspension remains transparent and luminescence intensity is maintained without any change in the colour (wavelength) of emission. The luminescence intensity of ZnO core-shell nanoparticles continuously increases as the size of ZnO core decreases.

The room temperature photoluminescence spectra (excitation wavelength: 325 nm) of the bare and core-shell ZnO nanoparticles are shown in Figure 4. It is observed that bare

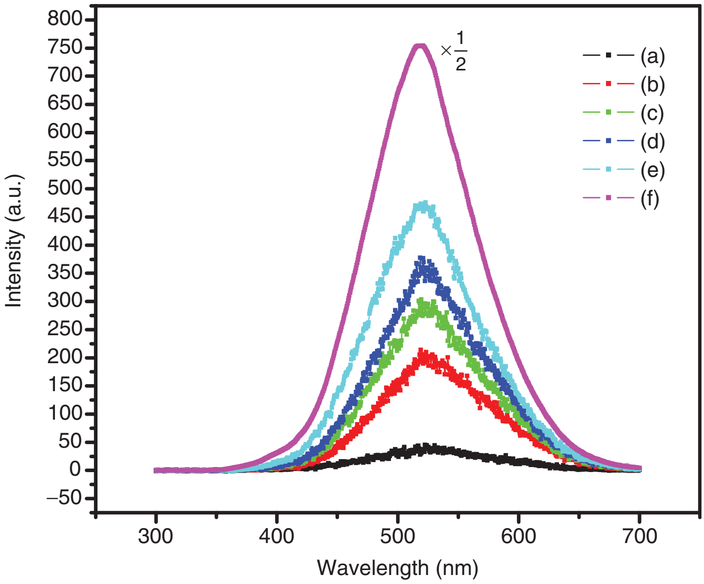

Figure 4. Photoluminescence spectra from suspended bare and core-shell ZnO nanoparticles: (a) ZnO_0, (b) ZnO_5, (c) ZnO_15, (d) ZnO_20, (e) ZnO_25, (f) ZnO_30.

and core-shell nanoparticles exhibit a broad emission band in the green region only; however, a very small peak in the UV region is also observed from bare ZnO nanoparticles (not clearly shown in the figure because of high luminescence intensity in visible region from other core-shell nanoparticles). The intensity of green emission increases continuously from ZnO_0 to ZnO_25 nanoparticles. For ZnO_30 core-shell nanoparticle, a drastic increase in luminescence intensity is observed due to much controlled core size and nearly complete passivation by $Cd(OH)_2$ shell. The shift in the green emission peak from 528 nm for ZnO_0 to 517 nm for ZnO_30 core-shell nanoparticle is also observed due to decreased particle size leading to increased band gap E_g [8]. This explanation assumes that the energy of shallow surface defect level will shift with changes in the valence band edges, but that deep defect levels associated with oxygen vacancies will not shift [14].

As Cd and Zn belonging to the same group have very much similar property, so Cd^{II} can easily sit at the position of Zn^{II} at the surface of ZnO nanoparticle, by increasing cadmium salt concentration, more and more $Cd(OH)_2$ molecules are absorbed at the surface of ZnO nanoparticle. Zn^{II} and Cd^{II}, being in the same group element, can be treated similar to the surface of ZnO nanoparticle from the luminescence point of view; that means, it does not introduce any new luminescence characteristic in ZnO nanoparticle.

Now, how $Cd(OH)_2$ at the surface of ZnO nanoparticle supports the visible emission. It has been shown by several authors [22,23] that if a molecule or functional group is absorbed at the surface of a ZnO nanoparticle it dominantly controls the emission property of the ZnO nanoparticle. Sakohara et al. [22] have reported in their studies that the ZnO nanoparticle synthesised by sol–gel method are not chemically pure but have acetate groups, which originate from the reagent materials absorbed on the surface of the nanoparticle. The acetate groups consist of a mixture of unidentate, chelate and bridging type structures. In their report, unidendate complex is believed to trap the photo-generated holes formed during UV excitation, and this phenomenon intensifies the visible luminescence, while the bidentate type is capable of capturing the electron, and it quenches the visible luminescence. The coverage of the ZnO quantum dot surface with $Zn(OH)_2$ shell has been reported to decrease the intensity of the excitonic emission and enhance the visible emission [23]. Similarly Norberg and Gamelin [24] showed a direct correlation between green emission intensities with surface hydroxide concentration and they propose the identity of the O^{2-} surface trap to be surface OH^-. They showed that surface-absorbed OH^- ions behave like O^{2-} surface sites and trap the hole at the surface site resulting in visible emission. As mentioned above, there is no difference between Cd^{II} and Zn^{II} at the surface of a ZnO nanoparticle, thus the $ZnO/Cd(OH)_2$ core-shell nanoparticle can be simply treated as the ZnO nanoparticle having a shell of hydroxyl functional group on its surface. Thus in the view of above studies, we can also propose the hydroxyl ion present at the surface of ZnO nanoparticle as the fast trapping centre of the hole at the surface site, a first step necessary for the visible emission according to Dijken's model. The higher the concentration of hydroxyl ions at the surface, the higher the probability of surface trapping of holes at the surface site and the greater the visible luminescence intensity and the lower the excitonic emission intensity.

4. Conclusions

In summary, we have prepared a series of $ZnO/Cd(OH)_2$ core-shell nanoparticles by the sol–gel method having continually decreasing core size and increasing effective passivation by $Cd(OH)_2$ molecules. The $Cd(OH)_2$ shell controls the growth of ZnO nanoparticles and also increases the green emission intensity. This work proposes a method to synthesise highly luminescent and stable green emitting ZnO nanoparticles.

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