Polyether-Grafted ZnO Nanoparticles with Tunable and Stable Photoluminescence at Room Temperature

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Received March 11, 2005
Revised Manuscript Received April 30, 2005

Nanoparticles with size-dependent photoluminescence (PL) have attracted intensive interest during the past decade.[1] This class of materials is potentially applicable for the manufacture of light-emitting thin films,[2] nonlinear optical devices,[3] and biological fluorescent labels.[4] Relevant studies have been focused on CdSe and CdTe nanoparticles which have high quantum yields and controllable emissions from the conduction band to the valence band,[5] while ZnO nanospecies, although nontoxic and much more stable toward air, have rarely been reported as size-dependent PL material.[6] One reason is that ZnO nanocrystals synthesized from sol−gel methods are apt to aggregate and to grow to larger sizes so that their fluorescence red-shifts gradually at room temperature.[7] Another is that ZnO visible emission spectra are wide and weak due to the oxygen vacancy luminescence mechanism.[8] Hence, stable ZnO nanoparticles produced from conventional sol−gel routes are always green or yellow under UV irradiation. Only recently were blue-emitting SiO_2-shelled ZnO colloids prepared[9] in highly diluted solutions at around 0 °C, but the colloids underwent Ostwald ripening[9,10] at room temperature. Several polymer-capped ZnO nanoparticles have also been synthesized.[11] However, these polymer ZnO nanocomposites were usually insoluble solids[12] or simple polymer−nanoparticle mixtures that could not be purified and re-dispersed into solvents,[13] and really stable blue-emitting ZnO colloids at room temperature have not been reported yet. Furthermore, quantum yields (QY) of ZnO nanoparticles were very scarcely addressed in the literature, and the reported experimental QY values, if any, were very low.[14] In the present work, we modified the conventional sol−gel technique and prepared a new type of polymer-grafted ZnO nanoparticles. Poly(ethylene glycol) methyl ether (PEGME) species was used as the grafting polymer, and the size of the as-prepared ZnO particles (designated ZnO(PEGME)) could be easily controlled from 1 to 4 nm, and PL from blue (wavelength ∼ 450 nm) to yellow (wavelength ∼ 570 nm) was realized. The quantum yields of the polyether-grafted ZnO sols are about 30%, much higher than those of the conventional acetate-modified ZnO colloids,[14,15] and their luminescent wavelengths are stable for weeks at least.

Experimentally, $[CH_3O(CH_2CH_2O)_nCH_2COO]_2Zn$ salts, which were synthesized from poly(ethylene glycol) methyl ether (PEGME, M.W. = 350, 750, 2000, 5000, Aldrich) as described in the Supporting Information, were used to react with LiOH at different molar ratios[7,13,15] in ethanol solution to produce ZnO(PEGME) colloids. The colloid concentration (marked as [Zn]) was determined through titration using EDTA and EBT (eriochrome black T) at pH = 10. Such ZnO(PEGME) colloid was concentrated by rotating evaporation and precipitated with anhydrous ether, and then dissolved in absolute ethanol again for testing. The HRTEM images and the electron diffraction patterns were taken on a JEM-3010 transmission electron microscope operated at 300 kV. A Perkin-Elmer LS 55 fluorescence spectrophotometer was used to obtain the photoluminescent spectra for the ZnO colloids. To evaluate the quantum yields of the ZnO(PEGME) nanoparticles, quinine sulfate in 0.5 M sulfuric acid was used as a reference for samples emitting blue light while rhodamine 6G in ethanol was employed as a reference for samples with green and yellow emission.[5,14] Other characterizations are described in the Supporting Information.

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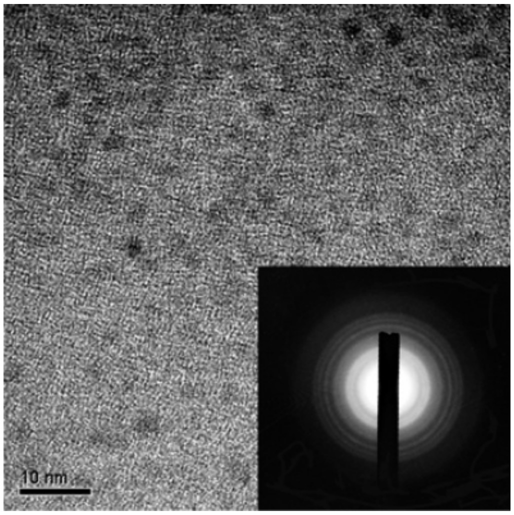

Figure 1. TEM image with the electron diffraction pattern in the inset for ZnO(PEGME350) nanorystals prepared using the molar ratio [LiOH]/[Zn] = 1.4.

Figure 1 shows the transmission electron microscope (TEM) image and electron diffraction pattern of the ZnO(PEGME) particles prepared by using the PEGME350 as the grafting polymer and the molar ratio of [LiOH]/[Zn] = 1.4. It is seen that the nanoparticles are uniform, monodispersed, and about 2.5 nm in diameter (the average diameter of the ZnO particles prepared through the $ZnAc_2$ route using the same molar ratio is about 3.5 nm). Images with higher resolutions are difficult to take because the intense electron beams decompose the samples to release liquid PEGME molecules so that the ZnO dots move very fast in the visual field. The electron diffraction patterns, however, prove the existence of ZnO cores in the nanoparticles, although XRD patterns indicate that the samples are amorphous because of the presence of thick polymer shell around the ZnO core. For the ZnO(PEGME) samples prepared by using larger [LiOH]/[Zn] ratios, the TEM images are more difficult to distinguish because the ZnO nanoparticles are even smaller. Infrared (IR) spectra suggest that the PEGME groups are bonded covalently on the surface of the ZnO core in the ZnO(PEGME) nanoparticles, while thermogravimetric (TG) data show that the ZnO(PEGME) particles do not decompose up to 400 °C (see Supporting Information), indicating that the nanoparticles have a rather high thermal stability.

Figure 2a presents a photograph of four ZnO(PEGME) ethanol colloid samples under UV irradiation while Figure 2b compares the photoluminescent spectra of the samples with different colors. The emission wavelength of ZnO(PEGME) is easy to control by varying the preparative conditions, and the emission intensity follows the order A > B > C > D with the same ZnO concentration. These samples are diluted to [Zn] = 0.001 M for quantum yield evaluation and the results are 29%, 31%, 27%, and 18% respectively, in comparison with the reported data 1−16% for the conventional ZnO nanoparticles.[14] According to the “anion vacancy” mechanism for ZnO fluorescence,[8] the photoluminescence red-shifts as the particle size increases, and its intensity depends on the number of the adsorbed Zn^{2+} luminescence centers on the ZnO surface. From Figure 2b, it is clear that the larger the ZnO nanoparticles, the longer their fluorescence wavelength. As the particle diameter increases from about 1 nm to around 4 nm, the excitation peak red-shifts from 320 to 365 nm and the emission peak red-shifts from 450 to 570 nm. The emission intensity is determined by the nanoparticle size and aggregation degree, and as a result, the smaller monodispersed ZnO particles which have larger luminescence surface areas emit more intense light than the larger particles. Hence, the present ZnO(PEGME) nanoparticles we prepared have higher quantum yields than the conventional ZnO nanocrystals because the former have much larger luminescent surface areas due to the polymer protection. However, the PEGME molecular weight also influences the luminescence intensity. Provided that the [LiOH]/[Zn] ratio and the [Zn] concentration remain constant, the higher the PEGME molecular weight, the weaker the ZnO(PEGME) fluorescence. This phenomenon can be ascribed to light absorption of PEO chains which are attached on the ZnO nanoparticle surface.[16]

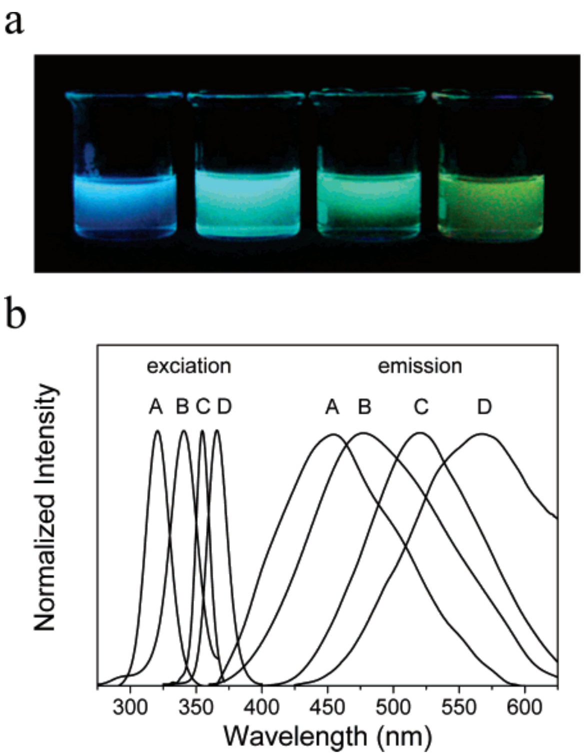

Figure 2. A photograph under 254 nm UV light (a) and photoluminescent spectra (b) of ZnO(PEGME350) ethanol colloid samples. The different samples were obtained by varying the [LiOH]/[Zn] ratio in the reaction system or by thermal treatment of a particular sample. Sample A: [LiOH]/[Zn] = 3.5; Sample B: [LiOH]/[Zn] = 1.4; Sample C: [LiOH]/[Zn] = 1.0; and Sample D is Sample C after heating at 60 °C for 24 h. The excitation spectra were recorded by monitoring the peak wavelengths of the corresponding emission spectra (454, 477, 520, and 568 nm, respectively).

The properties of the ZnO(PEGME) nanoparticles show great advantages over those of the ZnO(Ac) nanoparticles prepared through the conventional $ZnAc_2$ route. To compare the stabilities of ZnO(PEGME) and ZnO(Ac) colloids, $[CH_3O(CH_2CH_2O)_nCH_2COO]_2Zn$ and $ZnAc_2$ ethanol solutions (precursors) were mixed with appropriate amounts of LiOH solutions, respectively, and diluted to form ZnO

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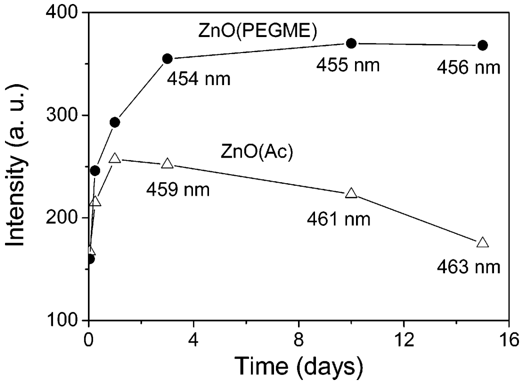

Figure 3. Emission peak intensity and position versus storage time for ZnO(PEGME350) and ZnO(Ac) ethanol colloid solutions prepared with the same molar ratio [LiOH]/[Zn] = 3.5 and zinc concentration [Zn] = 0.01 M.

colloids containing 0.01 M zinc. Storage time was recorded for each sample upon mixing. The PL spectra of these ZnO colloid samples were monitored from the first hour to the 15th day, and the data for the two typical samples are compared in Figure 3. For the ZnO(PEGME) colloid, the PL emission intensity increases gradually in the first 3 days and remains almost unchanged in the following 12 days, indicating that the ZnO(PEGME) nanoparticles nucleate and grow, their surface atoms self-organize in the first period (within 3 days), and the whole system becomes stable in the second period (after 3 days). In contrast, without polymer protection, the ZnO(Ac) nanoparticles nucleate and grow quickly so that the PL emission intensity reaches the maximum after 1 day reaction. After that, the ZnO(Ac) nanoparticles continue to grow and aggregate, and precipitate appears on the third day. Therefore, the ZnO(Ac) colloid is not stable even under the protection of excess LiOH, while our ZnO(PEGME350) nanoparticles are stable due to the presence of the polyether molecules surrounding the ZnO core. Furthermore, the ZnO(PEGME) nanoparticles isolated from the colloid solution formed through the reaction of $[CH_3O(CH_2CH_2O)_nCH_2COO]_2Zn$ and LiOH are re-dispersible in ethanol and many other solvents such as chloroform, acetonitrile, and toluene to form stable colloids with photoluminescence tunable from blue to yellow. The re-dispersed ethanol colloids have almost the same PL and UV−vis absorption spectra as the original colloids, with only a little red-shift because of nanoparticle aggregation in the purifying process (see Supporting Information). Such re-dispersability of PEGME-grafted ZnO nanoparticles cannot be achieved for the ZnO(Ac) powder that is precipitated from the colloid by nonsolvents and only has yellow emission.[7,14,15]

Since many other polymers with carboxyl groups can also be used in the present sol−gel route, our approach opens a new vista to stabilize oxide nanoparticles and to tune their size-dependent properties.

Acknowledgment. This work was financially supported by the National Natural Science Foundation of China.

Supporting Information Available: Experimental details, TEM, IR, TG, UV−vis absorption, and PL data, along with discussion on stabilization effects of polymer groups. This material is free of charge via the Internet at http://pubs.acs.org.

CM050556R