

Polymerization Initiated by Inherent Free Radicals on Nanoparticle Surfaces: A Simple Method of Obtaining Ultrastable (ZnO)Polymer Core–Shell Nanoparticles with Strong Blue Fluorescence**

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Luminescent semiconductor nanoparticles, owing to their unique properties and promising applications, have attracted intensive investigation in the past decade.^[1] Because these nanoparticles are apt to aggregate and grow spontaneously, and some of them are unstable in air, water, or sunlight, their photoluminescence (PL) spectra red-shift, broaden, and weaken continuously during storage.^[2] Many efforts have been made to stabilize these nanoparticles, including employing organic ligands, coating nanoparticles with inorganic shells, and initiating polymerization on nanoparticle surfaces. However, because of coordination equilibria between nanoparticles and ligands, ligand-modified nanoparticles in solution are usually unstable if the temperature or concentration changes.^[3] Coating nanoparticles with inorganic shells to form crystalline core–shell nanocrystals do protect the nanocores effectively, but organic ligands are also needed by the shells and thus there still remains the lability caused by ligand–nanoparticle coordination equilibria.^[4] So far, the third method seems to be the optimal choice to stabilize nanoparticles for a long period of time. Under isolation of the polymer shell, particle growth^[5] and the decomposition induced by air or water are thoroughly suppressed, because the solid polymer matrix is so dense that ions and molecules cannot penetrate. Unfortunately, since most of the polymerization products are prepared by either dissolving initiators in monomers or grafting initiators on nanoparticle surfaces, the products are bulk materials^[6] or films^[7] but no longer nanometer-scale materials. As a result, further processing or assembly for application in photonic or optoelectronic devices is severely restricted. Therefore, a method of producing luminescent nanoparticles with long-term stability for practical use, especially in solution, remains a challenge for researchers in this field.

As far as ZnO quantum dots are concerned, the traditional synthetic route through hydrolyzing zinc acetate by LiOH in ethanol produces green-light-emitting colloids, but the colloids become yellow-light-emitting within days at room temperature.^[8] Only recently were blue-light-emitting ZnO nanoparticles prepared in highly dilute solutions^[9] at 0 °C or in polymer matrixes,^[10] but the former were not stable at room temperature while the latter were bulk materials. We also reported blue-light-emitting polyether-grafted ZnO colloids with 30 % quantum yield that are stable for weeks at room temperature,^[11] but the colloids became green-light-emitting when heated at 60 °C for several days. To the best of our knowledge, a quantum yield above 30 % for ZnO nanoparticles has not been reported yet. Since the ZnO visible fluorescence^[12] originates from electrons being trapped in random surface holes, not from electron transitions from the conduction band to valence band, the luminescent properties of CdSe or CdTe are definitely better than those of ZnO quantum dots. Nevertheless, ZnO is a stable, non-poisonous, and cheap luminescent material for practical uses, which makes it more attractive than its rivals. Hence, to obtain luminescent ZnO nanoparticles with high quantum yield and stability for practical application, their surface structures must be adjusted and additional luminescent mechanisms should be included.

In this communication, we present a simple method to initiate polymerization by virtue of the inherent free radicals pre-existing on ZnO nanoparticle surfaces, without any added initiators. Such surface-initiated radical polymerization is precisely controlled to form a thin polymer shell around each ZnO nanoparticle. Even after refluxing in ethanol at 80 °C for a month, the (ZnO)polymer core–shell nanoparticles were stable and their PL spectra showed almost no change except for a slight decrease in intensity. Furthermore, the as-prepared (ZnO)polymer nanoparticles have strong blue-light emission at about 420 nm, and their quantum yield exceeds 80 %, which is remarkable at present.

Figure 1 is a high-resolution transmission electron microscopy (HRTEM) image of the as-prepared (ZnO)PMAA–PMMA core–shell nanoparticles, where PMAA is poly(methacrylic acid) and PMMA is poly(methyl methacrylate), with an average ZnO core diameter of 2.1 nm. These nanoparticles are uniform and monodisperse, even after refluxing in ethanol. Furthermore, the present nanoparticles are steady under the intense electron beams used for HRTEM measurements,^[11] indicating a firm

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[**] This work was supported by the National Natural Science Foundation of China and the Natural Science Foundation of Shanghai. The authors thank Prof. Chen Jie-Sheng of Jilin University for his kind help with HRTEM measurements. Supporting Information is available online from Wiley InterScience or from the author.

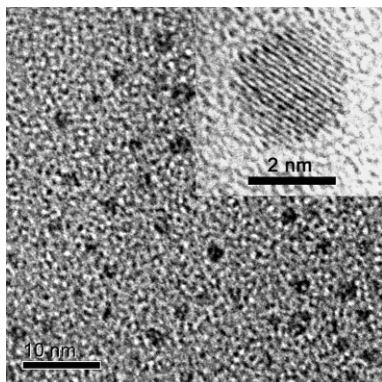


Figure 1. HRTEM image of the as-prepared (ZnO)PMAA-PMMA nanoparticles. Inset: Image of a single nanocrystal.

bonding between the ZnO core and polymer shell. IR measurements prove covalent bonds form bridges^[13] between ZnO and carboxyl groups from the polymer shells, and suggest a closed net structure of the PMAA-PMMA copolymer shells. Because the organic shells cannot be observed directly by HRTEM, the core-shell nanoparticles were detected by tapping-mode atomic force microscopy (AFM) to evaluate the particle sizes.^[14] The dominant feature height of the (ZnO)polymer nanoparticles on silicon surface is 4 nm, so the thickness of the polymer shell for each (ZnO)polymer nanoparticle is about 1 nm.

To understand the reaction mechanism between the monomers and ZnO-MAA (ZnO nanoparticles modified by methacrylic groups), three ZnO-MAA samples were prepared by controlling the synthesis conditions.^[11] Their average diameters were 2.1 nm (blue-light-emitting, sample A), 2.9 nm (green-light-emitting, sample B), and 4.2 nm (yellow-light-emitting, sample C). When the clear solutions resulting from centrifuging the (ZnO-MAA + monomer) mixtures were heated at 60 °C, only the solution containing sample A and the monomer remained transparent; the other two solutions produced precipitates. After centrifugation to remove precipitates, the obtained clear solution containing sample B showed weak emission at 420 nm, but the solution for sample C had almost no luminescence. HRTEM measurements on the obtained solutions showed that only ZnO-MAA nanoparticles smaller than about 2.5 nm could survive when heated with monomers; the larger particles had aggregated and precipitated. Near-IR data proved that the ZnO-MAA nanoparticles had free radicals on their surfaces,^[15] and their free radical concentrations followed the order $A > B > C$, while no free radicals were detected for the (ZnO)polymer sample after polymerization. Gel permeation chromatography (GPC) results revealed that after decomposition of the (ZnO)polymer sample by HCl the remaining shell molecules had higher molecular weights than the monomers (Fig. 2), while the pure monomers without ZnO-MAA nanoparticles did not polymerize after being heated at 60 °C for 2 h. On the basis of these results, we believe that polymerization was initiated by the inherent free radicals pre-existing on ZnO-MAA nanoparticle surfaces.

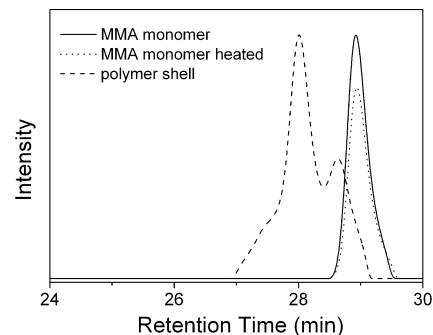


Figure 2. Gel permeation chromatography data for the pure MMA monomer, the MMA monomer heated at 60 °C for 2 h, and the polymer shell resulting from decomposition of (ZnO)polymer nanoparticles by HCl.

Figure 3 shows photographs of one (ZnO)PMAA-PMMA colloid in sunlight and one under a UV lamp, although the colloid appears colorless indoors. The as-prepared (ZnO)polymer nanoparticles dissolved in many solvents, such as ethanol, chloroform, and tetrahydrofuran (THF), to form stable colloids. These colloids exhibited extremely high quantum yields (QYs) over 80 % using quinine sulfate in 0.5 M sulfuric acid as a reference (QY = 55 %),^[16] indicating some special luminescence mechanisms for this type of core-shell nanoparticles. Furthermore, after the (ZnO)polymer nanoparticles had been refluxed in ethanol at 80 °C for ten days, their QY remained above 60 %. To ensure such intensive fluorescence is not from the monomers, oligomers, by-products, or impurities, if any, these possible substances were isolated and tested. All experiments confirmed that the blue emission arises from nothing but the (ZnO)polymer core-shell nanoparticles themselves. Vollath et al.^[17] also observed such blue emission from PMMA-coated ZrO₂ and HfO₂ nanoparticles prepared by a microwave plasma process, but in their ZnO-PMMA samples the luminescence at 420 nm was so weak that it was hidden by the ZnO characteristic yellow emission, whose QY is actually below 10 %. Furthermore, they reported their ceramic-polymer core-shell particles to be insoluble in THF,^[17] while our (ZnO)polymer nanoparticles can be dissolved by THF readily.

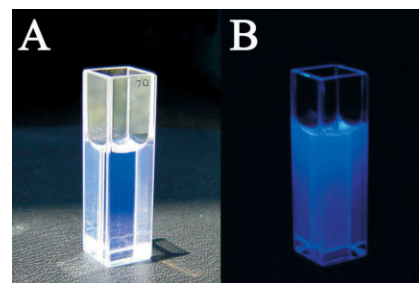


Figure 3. Photographs of the (ZnO)PMAA-PMMA colloids A) in sunlight and B) under a 254 nm UV lamp.

The PL and UV-vis spectra of (ZnO)polymer, ZnO-MAA, and polymer-shell samples are compared in Figure 4. The UV absorption spectra and PL excitation data illustrate that the (ZnO)polymer colloid (sample a) has a broad absorption in the range 280–400 nm, which involves two absorption bands,

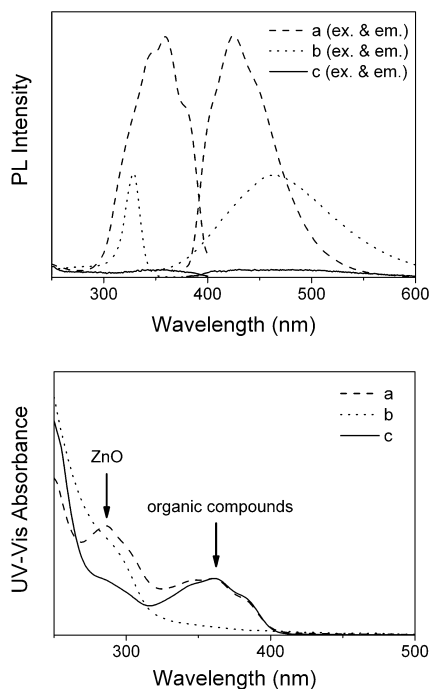


Figure 4. PL and UV-vis absorption spectra of the samples a) (ZnO)PMAA-PMMA, b) ZnO-MAA, and c) the polymer shell resulting from decomposition of (ZnO)PMAA-PMMA by HCl. For the PL spectra, samples a and b were excited by 360 and 320 nm light, respectively, while their excitation spectra were recorded at 425 and 465 nm.

marked by arrows. One is generated by a highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) transition, like the absorption of the typical ZnO quantum dots (sample b); the other is ascribed to organic species on ZnO nanoparticle surfaces. These organic compounds may include PMMA, PMAA, and their copolymers. However, these organic compounds (sample c) had almost no fluorescence after they were removed from the ZnO nanoparticle surfaces. Therefore, we consider that the strong blue emission of (ZnO)polymer nanoparticles probably arises from both the ZnO nanoparticles and the organic species on the ZnO surfaces. The former is the typical ZnO visible fluorescence, which may be enhanced by their special surface state, while the latter is organic luminescence, which is sensitized by ZnO cores, i.e., there is some energy transfer from ZnO cores to the organic species. Since the mechanism for ZnO visible fluorescence remains unclear^[12] and the special luminescence phenomena for our ZnO(polymer) core-shell nanoparticles appear much more complicated, further re-

search to disclose the influence of polymer shells on ZnO PL and the interactions between ZnO cores and polymer shells is under way.

In conclusion, our work reveals a very effective method to stabilize colloidal nanoparticles that handily utilizes the inherent free radicals on ZnO nanoparticle surfaces to initiate polymerization to form a protective thin polymer shell around each quantum dot. Because of such a special structure, (ZnO)polymer nanoparticles exhibit remarkably high quantum yield and stability. These nanoparticles with intense blue fluorescence can be redissolved by many solvents to form stable colloids that are convenient for further processing, assembly, or application.

Experimental

All chemicals and solvents were reagent grade and used as received, except that the commercially available monomers such as methyl methacrylate (MMA, 99 %) and styrene (99 %) were distilled under vacuum before use. Methacrylic-group-modified ZnO nanoparticles (designated ZnO-MAA) were synthesized through a sol-gel reaction between zinc methacrylate and LiOH with the molar ratio [LiOH]/[Zn] = 3.5 in absolute ethanol [11]. The obtained ZnO-MAA ethanol colloids had a blue emission at about 460 nm and quantum yield of about 20 % using quinine sulfate in 0.5 M sulfuric acid as a reference. The colloids were concentrated in a rotating evaporator at 40 °C until some ZnO-MAA solid emerged. The ZnO-MAA solid was purified by centrifugation, and further dried under vacuum at 60 °C in a vacuum oven. The freshly dried solid was immediately dispersed into a liquid monomer such as MMA or styrene by sonication. Then the mixture was centrifuged to remove undissolved solid and the resulting clear solution was heated at 60 °C for some minutes in a flowing water bath. (ZnO)polymer core-shell nanoparticles with strong blue emission were prepared under the above conditions, purified from the reaction systems using a nonsolvent method [11,13], and dissolved in absolute ethanol for measurement. A JEM-3010 transmission electron microscope operated at 300 kV was employed to obtain HRTEM images. To determine the (ZnO)polymer composition, (ZnO)polymer nanoparticles were decomposed by a small amount of HCl and then dissolved in THF for GPC measurement on an Agilent 1100 gel permeation chromatograph. The PL spectra and UV-vis absorption data were recorded on a Varian Cary Eclipse fluorescence spectrophotometer and a Perkin Elmer Lambda 40 UV-vis spectrometer, respectively. The optical density at the excitation wavelength of a colloid and a quinine sulfate solution was set to a similar value, and then the integrated PL intensities of the colloid were divided by that of the quinine sulfate to calculate the quantum yield of the colloid [16]. Other characterizations are found in the Supporting Information.

Received: September 9, 2005
Final version: January 25, 2006

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