



Tunable synthesis and multifunctionalities of Fe₃O₄–ZnO hybrid core-shell nanocrystals

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ABSTRACT

We report the tunable synthesis and multifunctionalities of Fe₃O₄–ZnO hybrid core-shell nanocrystals as prepared through controlled sequential nanoemulsion processes. The characterization shows the orderly variations of the structural, magnetic, photoluminescent and absorption properties of the nanocrystals versus the nanoshell thickness. The nanocrystals reveal structural features unique to the core-shell design and exhibit well-defined superparamagnetic behavior at room temperature. In opposite to the decreasing magnetization, both bandgap and induced surface emissions depend strongly on the increasing nanoshell thickness. Moreover, the FTIR analysis provides the fingerprints of the polymer surfactant, ZnO and Fe₃O₄ in the same nano-entity and the core-shell nanocrystals could be directly dispersed in both aqueous and organic media for application readiness. Aptly tunable in nanostructures and thus optimized properties, this kind of monosized, high quality, and multifunctional core-shell nanocrystals could be of interest for fundamental studies and potential applications.

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1. Introduction

Multifunctional nanoparticles properly assembled from different compositions, owing to their unique spatial configuration, multiple functionalities, better properties and induced phenomena, proffer exciting opportunities in fundamental studies and top-notch applications, in contrast to that of their single-component counterparts [1–7]. The compositions are versatile and in abundance, ranging from magnetic, semiconductor, inorganic, organic, and metallic to dielectric materials. Among considerable researches concentrated on magnetic and semiconductor substances, magnetite (Fe₃O₄) and zinc oxide (ZnO) are two typical materials of great importance [8–11]. Fe₃O₄ has an assortment of exceptional physicochemical properties in magnetic materials and is especially interesting to the biomedical community. It exhibits many fascinating phenomena such as charge ordering, mixed valence, and metal-insulator transition known as the Verwey transition [12]. For its outstanding biocompatibility and bio-safety, Fe₃O₄ together with other forms of iron oxide nanoparticles has been comprehensively investigated for various biomedical purposes, for instance, to manipulate or convey carriers to a precise site by applying an external magnetic

field [8,9,13–19]. Alternatively, ZnO is a transparent, wide bandgap oxide semiconductor showing many attractive properties including piezoelectricity, photoluminescence and biocompatibility [10,11,20–27]. The material has great potentiality in smart nanolasers [20,21], solar cells [22–24], spintronics [28], optoelectronic gadgets [10,26], nanocatalysts [27,29], field emission devices [30], nanobiomedical reagents [31,32] and labeling [33,34]. The combination of these two materials into a single nano-entity has been attempted with encouraging outcomes, as represented in the nano-architecture of core-shell nanoparticles of different quality [35–41] or nanorods [42].

As often nanoparticles as synthesized are of necessity to be transferred to and processed in an aqueous medium in applications of nanobiotechnology and nanomedicine, moreover, a biocompatible, hydrophilic and reactive surface is keenly pursued, which is generally attained through a second stage of surface tailoring [43]. In our researches, high-quality nanoparticles could be acquired by nanoemulsion methodologies, especially using biocompatible polymer surfactants such as poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEO-PPO-PEO) and poly(vinylpyrrolidone) (PVP) [17,44,45]. Resembling PVP, the PEO-PPO-PEO triblock copolymer and related polymer families possess many distinctive qualities such as aqueous solubility, non-charging, non-toxicity, and are frequently used in diverse fields [18,46–48]. In a previous investigation, we reported the successful application of Fe₃O₄–ZnO hybrid core-shell nanocrystals to dendritic cell-based cancer immunotherapy, which were directly

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synthesized by means of a one-pot nanoemulsion process assisted by PEO-PPO-PEO [17,35]. In the present work, we conduct the tunable synthesis of such monodisperse, multifunctional Fe_3O_4 -ZnO hybrid core-shell nanocrystals, as prepared in the nano-micelles formed by the polymer molecules. Coupling the magnetic properties of Fe_3O_4 and the optical characteristics of ZnO, the highly crystalline nanocrystals with various nanoshell thicknesses manifest structural features unique to the core-shell design and exhibit well-defined superparamagnetic behavior at room temperature. The photoluminescence outcomes evidence two kinds of emissions relevant to bandgap excitons and surface/interface effects. It is observed that in opposite to the decreasing magnetization, both bandgap and induced surface emissions depend strongly on the increasing nanoshell thickness. Furthermore, the FTIR analysis provides the fingerprints of the polymer surfactant on the nanocrystal surface and the nanomaterials themselves. In addition, the Fe_3O_4 -ZnO nanocrystals could be directly dispersed in both aqueous and organic media, bestowing the interesting amphiphilicity. Overall, the approach reported here offers an easy, effective route to produce high quality, monosized, multifunctional Fe_3O_4 -ZnO hybrid nanocrystals with tuneability and optimization in the properties for basic studies and potential applications in various areas.

2. Material and methods

2.1. Materials

The two precursors used are zinc acetylacetonate ($\text{Zn}(\text{acac})_2$, 99.9%) and iron (III) acetylacetonate ($\text{Fe}(\text{acac})_3$, 99.9%). Other chemicals include 1,2-hexadecanediol ($\text{C}_{14}\text{H}_{29}\text{CH}(\text{OH})\text{CH}_2(\text{OH})$, 90%), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) or PEO-PPO-PEO, octyl ether ($\text{C}_8\text{H}_{17}\text{OC}_8\text{H}_{17}$, 99%), hexane and ethanol. All materials were purchased from Aldrich and used as received without further processing.

2.2. Synthesis of Fe_3O_4 -ZnO hybrid core-shell nanocrystals

The Fe_3O_4 -ZnO nanocrystals were prepared by the controlled sequential synthesis of the ZnO capping onto the surface of the Fe_3O_4 seeds. The reactions were completed in a 250 ml flask in a heating mantle, equipped with a cooling condenser and a thermocouple. The heating profile was regulated by a programmable temperature controller (TC, SM-960) which was assembled in this lab from commercial components and calibrated against an Hg-thermometer (within an error of $\pm 5^\circ\text{C}$). In a typical experiment, the Fe_3O_4 seeds (Sample S1) were first produced by the reduction of $\text{Fe}(\text{acac})_3$ (0.5 mmol) by 1,2-hexadecanediol (0.6468 g) at high-temperature in the presence of the polymer surfactant molecules of PEO-PPO-PEO (0.7878 g) dissolved in dioctyl ether (10–15 ml). The mixed solution was gradually heated to 125°C under magnetic stirring, homogenized for 1 h at 125°C , and then rapidly heated to 300°C for the completion of the reaction. After cooling down to room temperature, $\text{Zn}(\text{acac})_2$ with more dioctyl ether and 1,2-hexadecanediol was added to the solution for coating ZnO nanolayers. At this stage, the reaction profile started with heating the solution to 80°C , homogenizing for 2 h at 80°C , then rapidly heated to 300°C and refluxing for 1 h at 300°C . After the completion of the reaction, ethanol was added to the product mixture to precipitate the nanocrystals. The precipitated Fe_3O_4 or Fe_3O_4 -ZnO nanocrystals were purified several times and separated by centrifugation to remove the solvent molecules and other residuals from the nanocrystals. The control of the ZnO nanolayer thickness was accomplished by adding a meted quantity of $\text{Zn}(\text{acac})_2$ and three different thicknesses were prepared after addition of 0.31 mmol $\text{Zn}(\text{acac})_2$ for the thin ZnO nanolayer (Sample S2), 1.09 mmol

$\text{Zn}(\text{acac})_2$ for the intermediate ZnO nanolayer (Sample S3) and 1.74 mmol $\text{Zn}(\text{acac})_2$ for the thick ZnO nanolayer (Sample S4), separately.

2.3. Characterization and analysis of the resultant nanocrystals

The microstructure and grain size of the nanocrystals were acquired by X-ray diffraction (XRD, Bruker M18XCE and a synchrotron beamline at Pohang Accelerator Laboratory, Korea) and transmission electron microscopy (TEM, JEOL 2010F) including the mode of high resolution (HRTEM) and compositional analysis by energy dispersive X-ray analysis (EDX), in addition to elemental mapping. The magnetic properties of the nanocrystals were analyzed by vibrating sample magnetometry (VSM, Lakeshore 7300) and/or a superconducting quantum interference device (SQUID, Quantum Design), whereas using samples in hexane, the UV-vis spectra were measured by an Agilent 8453E spectrophotometer and the fluorescence spectra were obtained with a Shimadzu RF-5301 spectrofluorophotometer. Moreover, the Fe_3O_4 -ZnO nanocrystals and pure PEO-PPO-PEO polymer were examined by Fourier transform infrared spectroscopy (FTIR) using an Avatar 360 FTIR spectrometer (Nicolet Company, USA). The dispersion-magnetic collection processes of the Fe_3O_4 -ZnO nanocrystals in both water and hexane were visually demonstrated for application readiness.

3. Results and discussion

3.1. Synthesis of hybrid core-shell nanocrystals with different nanoshell thicknesses

As illustrated in Fig. 1, the preparation of the multifunctional Fe_3O_4 -ZnO hybrid core-shell nanocrystals was accomplished by the controlled sequential reactions in the one-pot process [17,35,44,45]. In the stage A, the iron precursor and 1,2-hexadecanediol under magnetic stirring and steady heating were homogenized with the polymer surfactant molecules in the solvent of octyl ether to form the nano-micelles. Then, the temperature was rapidly raised to 300°C to generate the Fe_3O_4 seeding nanocrystals via thermal reduction of $\text{Fe}(\text{acac})_3$, as indicated in the stage B. Subsequently, a certain amount of $\text{Zn}(\text{acac})_2$ with more 1,2-hexadecanediol and the solvent was added to the solution for homogenization, allowing diffusion of the $\text{Zn}(\text{acac})_2$ molecules into the nano-micelles, as drawn in the stage C. Thereafter, the temperature was swiftly elevated to 300°C to promote the solid formation of the ZnO crystalline layer on the Fe_3O_4 surface, as shown in the stage D. In the experiment, the ZnO nanolayer thickness is gauged through the total amount of $\text{Zn}(\text{acac})_2$ added and three different thicknesses are acquired here. It is constructive to note that all Fe_3O_4 or Fe_3O_4 -ZnO nanocrystals as prepared could

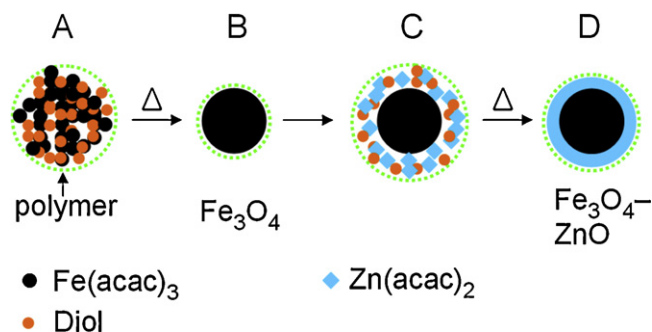


Fig. 1. Illustration of the growth route of the Fe_3O_4 -ZnO core-shell nanocrystals in the nano-micelles formed by the PEO-PPO-PEO macromolecules.

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