

CdTe@Co(OH)₂ (core-shell) nanoparticles: aqueous synthesis and characterization†

Liang Li, Huifeng Qian and Jicun Ren*

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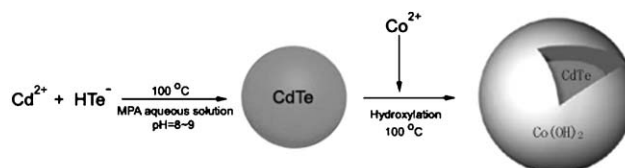
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A seed-mediated growth approach for preparation of multi-functional CdTe@Co(OH)₂ (core-shell) nanoparticles in the aqueous phase is reported.

With the rapid extending of the applications of nanomaterials, the great importance has been recognized to develop functional nanomaterials integrated with multiple functions in a single particle,^{1–6} and core-shell structures are a conventional protocol to realize this aim. The isolation of the core from the surroundings can be used to create objects with fundamentally different properties to those of the bare nanocrystal. For example, the coating may be used to passivate the core chemically to modify its optical properties, or to create nanoscale objects with specific electrical functionality.¹ More recently, coating a semiconductor layer on magnetic nanocrystals was used to create luminescent/magnetic composite nanomaterials.⁶ As is known, quantum dots (QDs) show unique optical properties, and cobalt hydroxide possesses some important properties (electrochemical activity, magnetism, catalysis). In this paper, we consider the idea that a cobalt hydroxide shell around a small quantum dot can lead to composite particles which is expected to lead to some new properties and applications. Recently, we synthesized high photoluminescence quantum yield (QY) CdTe nanocrystals in aqueous solution.^{7,8} Here, the aqueous synthesized CdTe nanocrystals served as cores, and Co(OH)₂ was deposited on them to form core-shell nanoparticles in aqueous solution. Our results demonstrate that the as prepared nanomaterials were water-soluble, and possessed magnetism and high QY up to 30%. This provides some potential applications, such as simultaneous magnetic resonance imaging and fluorescence imaging, use as catalysts and magnetic-optical materials.

The preparation of CdTe@Co(OH)₂ composite nanoparticles was performed using the procedure shown in Scheme 1.† First, highly luminescent CdTe nanocrystals were prepared by adding NaHTe to a CdCl₂ aqueous solution containing mercaptopropionic acid (MPA).⁷ When the CdTe nanocrystals grew to desired sizes, Co(NO₃)₂ aqueous solution (10⁻² M) was injected by multiple-steps to the colloid solution for formation of the Co(OH)₂ shells on the CdTe nanocrystals. Under the alkaline conditions



Scheme 1 Aqueous synthesis route for CdTe@Co(OH)₂ core-shell nanoparticles.

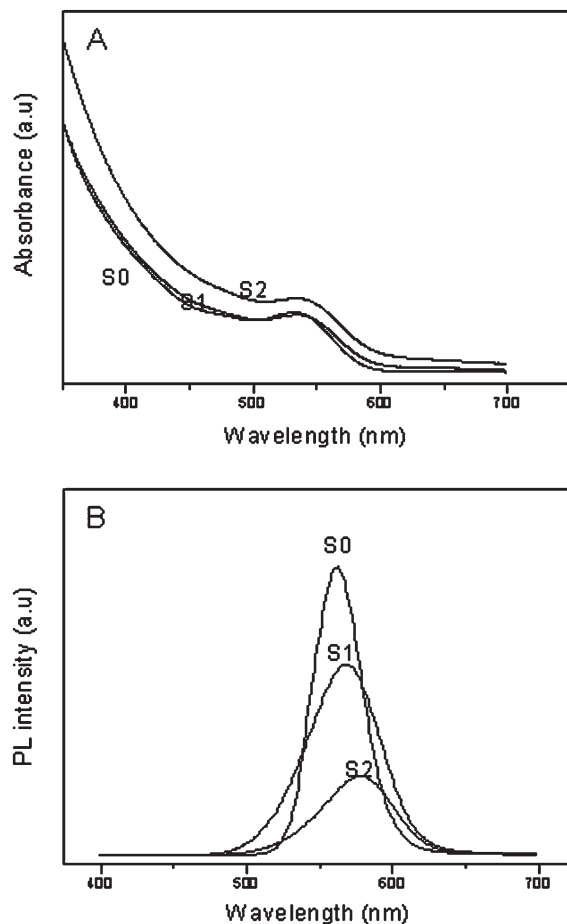
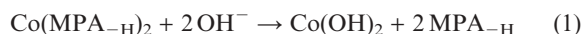


Fig. 1 Absorption and photoluminescence spectra of MPA-stabilized CdTe QDs and CdTe@Co(OH)₂ nanoparticles (S0: crude CdTe solution taken at a reflux time of 7 h; S1: sample after adding 8 ml 0.01 M Co(NO₃)₂ solution to 250 ml S0 and further refluxing for 1 h; S2: sample after further addition of 8 ml Co(NO₃)₂ solution to S1 and further refluxing for 1 h).

College of Chemistry & Chemical Engineering, Shanghai Jiaotong University, 800 Dongchuan Road, Shanghai, 200240, P. R. China. E-mail: jicunren@sjtu.edu.cn; Fax: +86-21-54741297; Tel: +86-21-54746001

† Electronic supplementary information (ESI) available: experimental details, EDX spectrum of sample S2; absorption and photoluminescence spectra of the sample in Fig. 2(b); enlarged Fig. 2(b); the thermogravimetric patterns of CdTe seeds and CdTe@Co(OH)₂ composite nanomaterials. See <http://dx.doi.org/10.1039/b505791d>

with the stabilizer (MPA), Co^{2+} hydrolyzed and formed $\text{Co}(\text{OH})_2$ which slowly deposited on the surface of CdTe nanocrystals. This process can be expressed in terms of eqn. (1).



The resulting composite nanomaterials were characterized by UV-visible absorption and fluorescence. The QY of CdTe nanocrystals and CdTe@Co(OH)₂ nanoparticles were measured (Rhodamine 6G was chosen as the reference standard, QY = 95%) according to the method described in ref. 9. Fig. 1(A) and (B) show the absorption and PL spectra of CdTe nanocrystals before and after coating the Co(OH)₂ shell. Before addition of Co(NO₃)₂ solution, CdTe QDs (sample S0) had 50% QY (emission at 562 nm), and served as the seeds in the next step. With the injection of Co(NO₃)₂ solution to the reaction solution and further refluxing, the absorbance of the reaction solution increased, and the QY of CdTe@Co(OH)₂ nanoparticles (sample S1) slightly decreased to about 45% and the PL emission red-shifted slightly. After the second injection of Co(NO₃)₂ solution (Co:Cd mole ratio = 0.64:1.25) and continued refluxing for 1 h, the QY of the as-prepared colloid solution (sample S2) further decreased to 20%, while the peak of the PL spectrum slightly red-shifted to 578 nm. It should be noted that when the as prepared colloid solution was transformed to a solid powder¹⁰ and re-dissolved again, the resulting solution showed a higher QY of 30%. This was due to the elimination of unreacted species by precipitation, which partly led to the increase of QY in the measurement.

Fig. 2(a) shows the TEM image of the CdTe@Co(OH)₂ sample S2. The particles were separately dispersed on a Cu grid and their sizes averaged 4.7 nm. The SAED image of a selected area displays

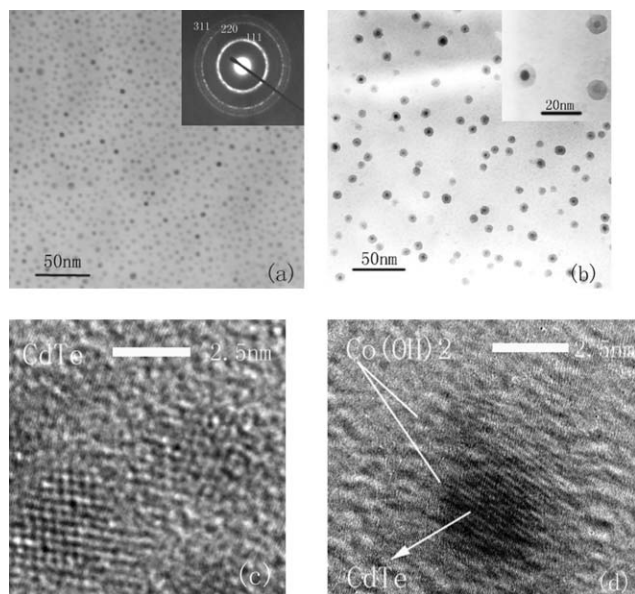


Fig. 2 TEM images of the as-prepared CdTe@Co(OH)₂ nanoparticles and HRTEM images of a typical sample before and after coating of Co(OH)₂. (a) Sample S2 obtained for a Co:Cd mole ratio in the reaction solution of 0.64:1.25; inset: its SAED pattern. (b) Sample obtained for a Co:Cd mole ratio in the reaction solution of 1:1.25; (c) HRTEM image of CdTe nanocrystals; (d) HRTEM image of CdTe@Co(OH)₂ core-shell nanoparticles.

rings which identify the crystalline structure of the CdTe core. The EDX (energy-dispersive X-ray spectrometry) results indicated the presence of Cd, Te, Co, O and S in the CdTe with Co(OH)₂ shell. The S peak was attributed to the stabilizer (MPA). The Cu peaks result from the sample grid (see ESI†). Varying the reflux time can readily control the size of the CdTe core. The thickness of the shell can be tuned by the added amount of Co solution (Co:Cd ratio). Fig. 2(b) shows the TEM image of the sample prepared using the same CdTe seeds as sample S2 but adding further Co²⁺ solution (Co:Cd ratio = 1:1.25) leading to thicker Co(OH)₂ shells. The TEM image clearly shows that the as-prepared nanoparticles have a core-shell structure; the diameters of the spherical particles are about 8.5 ± 0.83 nm and the size of the core is about 3 nm. The HRTEM images of a typical sample before and after coating with Co(OH)₂ also confirmed the formation of core-shell structures.

Fig. 3(A) shows XRD patterns obtained from the CdTe seeds and the core-shell samples with Co(OH)₂ shell. There is no recognizable difference on the positions of XRD reflections between the two samples. However, the main peaks on the XRD pattern of the core-shell samples were lower than that of “bare” CdTe nanocrystals. This is likely attributed to the coating of an amorphous Co(OH)₂ shell on the CdTe core. In order to further reveal the morphology of Co on CdTe, the composite

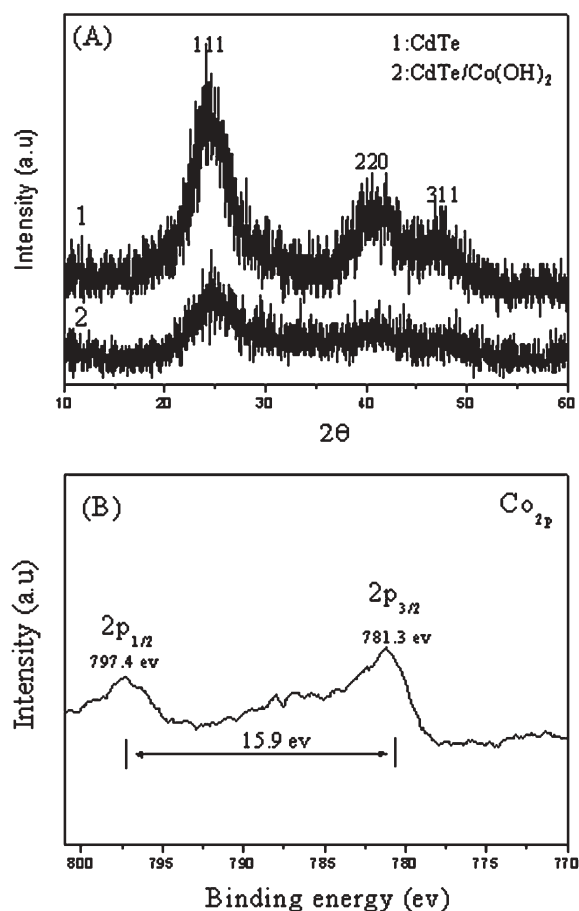


Fig. 3 (A) XRD patterns obtained from CdTe seeds and CdTe@Co(OH)₂ powders (shown in Fig. 2(a)) precipitated from colloid solution. (B) XPS of Co 2p from the CdTe@Co(OH)₂ nanoparticles (~5 nm) recorded at an excitation energy of 1253.6 eV.

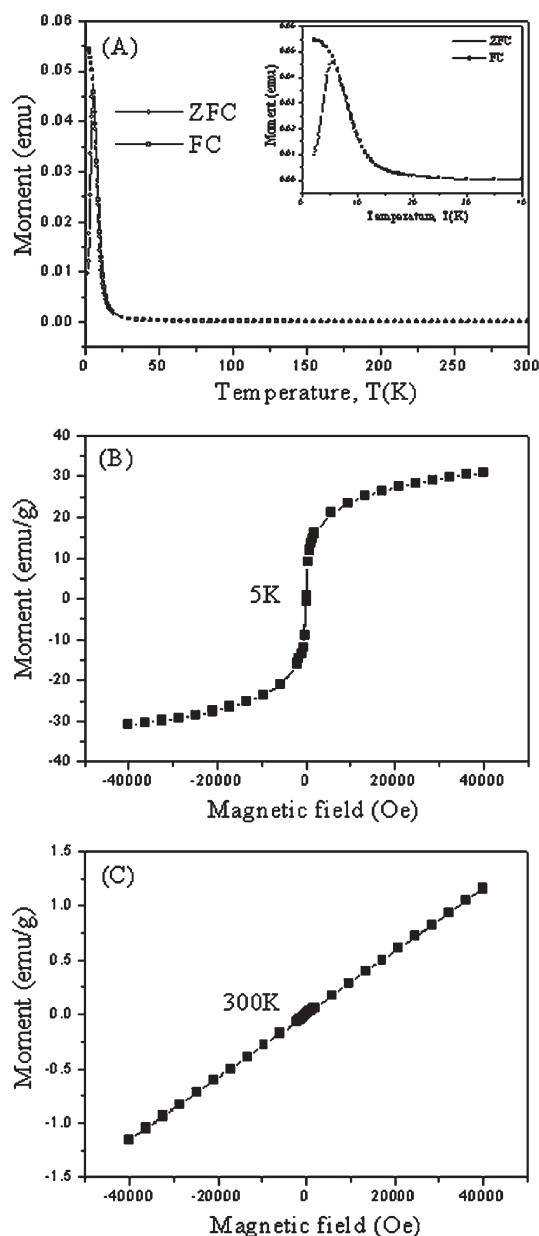


Fig. 4 (A) Temperature dependence of the magnetization for CdTe@Co(OH)₂, measured under conditions of zero-field-cooled (ZFC) and field-cooled (FC) conditions in a magnetic field of 100 Oe. Inset: magnified regions of the ZFC and FC curves. (B, C) Field dependence of the magnetization for CdTe@Co(OH)₂ composite nanoparticles.

nanomaterial was characterized by X-ray photoelectron spectra (XPS) and thermogravimetry (TG). As shown in Fig. 3(B), the appearance of characteristic Co 2p peaks at 797.4 and 781.3 eV and the separation of 15.9 eV between Co 2p_{1/2} and Co 2p_{3/2} (ΔE_b) confirmed that the Co mainly existed as Co(OH)₂, because these values were very similar to previous data for Co(OH)₂.^{11,12} TGA experiments in the temperature range 20–800 °C under an N₂ atmosphere showed a characteristic weight-loss peak between

206 and 301 °C, which further proved the existence of Co(OH)₂ in the composite nanomaterials. (see ESI†)

The temperature-dependent magnetization of CdTe@Co(OH)₂ (core-shell) nanoparticles was studied using a PPMS system (Quantum design, USA) between 2 and 300 K using zero-field-cooling (ZFC) and field-cooling (FC) procedures in an applied field of 100 Oe. A characteristic peak (5.5 K, blocking temperature) due to superparamagnetic behavior indicates the nanoscale nature of the CdTe@Co(OH)₂ (core-shell) particles. The blocking temperature is the threshold point of thermal activation, at which magnetocrystalline anisotropy is overcome by thermal activation and the nanoparticles become superparamagnetic.¹³ The isothermal magnetization at 5 and 300 K is shown in Fig. 4. The “S” shape hysteresis loop at 5 K indicated very weak hysteresis (coercive field: ~40 Oe) consistent with the result of the blocking temperature. The hysteresis loop obtained at 300 K did not show hysteresis behavior, and was field dependent and linear.

In summary, this communication describes a new method to prepare luminescent/magnetic core-shell CdTe@Co(OH)₂ nanoparticles based on a seed-mediated growth approach. The as-prepared nanomaterials were water-soluble, and possessed a degree of magnetism and a high QY of 30%. The synthetic procedure is very simple, mild and easily scaled up, which would be a good choice for synthesis of multifunctional nanomaterials of core-shell structure. We have already successfully extended this process to prepare other core-shell nanomaterials such as CdTe@Fe(OH)₃ nanoparticles. In the functional nanomaterials, CdTe nanocrystals present unique optical and electronic properties, and cobalt (iron) hydroxide possesses some important characteristics (electrochemical activity, magnetism, catalysis). We predict that these multifunctional nanomaterials may have some important applications in bio-labelling, catalytic reactions, fabrication of sensors, and energy storage.

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Notes and references

- G. Oldfield, T. Ung and P. Mulvaney, *Adv. Mater.*, 2000, **12**, 1519.
- A. G. Tkachenko, H. Xie, D. Coleman, W. Glomm, J. Ryan, M. F. Anderson, S. Franzen and D. L. Feldheim, *J. Am. Chem. Soc.*, 2003, **125**, 4700.
- N. Gaponik, I. L. Radtchenko, G. B. Sukhorukov and A. L. Rogach, *Langmuir*, 2004, **20**, 1449.
- D. Wang, J. He, N. Rosenzweig and Z. Rosenzweig, *Nano Lett.*, 2004, **4**, 409.
- H. Gu, R. Zheng, X. Zhang and B. Xu, *J. Am. Chem. Soc.*, 2004, **126**, 5664.
- H. Kim, M. Achermann, P. L. Balet, J. A. Hollingsworth and V. I. Klimov, *J. Am. Chem. Soc.*, 2005, **127**, 544.
- L. Li, H. Qian and J. C. Ren, *J. Luminesc.*, DOI: 10.1016/j.jlumin.2005.03.001.
- L. Li, H. Qian and J. C. Ren, *Chem. Commun.*, 2005, 528.
- G. A. Crosby and J. N. Demas, *J. Phys. Chem.*, 1971, **75**, 991.
- Z. Tang, N. A. Kotov and M. Giersig, *Science*, 2002, **297**, 237.
- R. Xu and H. C. Zeng, *Chem. Mater.*, 2003, **15**, 2040.
- NIST Standard Reference Database 20, Version 3.4.
- C. Liu and Z. J. Zhang, *Chem. Mater.*, 2001, **13**, 2092.