



NJC

C-dots Sensitized Eu³⁺ Luminescence from Eu³⁺-Doped LaF₃/C dots Nanocomposites

Journal:	<i>New Journal of Chemistry</i>
Manuscript ID:	NJ-ART-09-2014-001647.R1
Article Type:	Letter
Date Submitted by the Author:	30-Oct-2014
Complete List of Authors:	Mahalingam, Venkataramanan; Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur Campus Samanta, Tuhin; Indian Institute of Science Education and Research (IISER)-Kolkata, Chemical Sciences Hazra, Chanchal; Indian Institute of Science Education and Research (IISER)-Kolkata, Chemical Sciences

SCHOLARONE™
Manuscripts

COMMUNICATION

C-dots Sensitized Eu^{3+} Luminescence from Eu^{3+} -Doped LaF_3/C dots Nanocomposites

Cite this: DOI: 10.1039/x0xx00000x

Tuhin Samanta, Chanchal Hazra and Venkataramanan Mahalingam*

Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Very strong Eu^{3+} luminescence is achieved via sensitization by carbon dots (C-dots) in Eu^{3+} -doped LaF_3/C dots nanocomposites for the first time. This energy transfer via C-dots leads to the broad band excitation of Eu^{3+} ions which can have potential use in phosphor based LEDs.

The Lanthanide (La^{3+})-doped nanoparticles have been widely studied because of their sharp electronic transitions occurring within the $4f$ orbitals. These $4f-4f$ transitions are forbidden in nature and possess long luminescence lifetimes and narrow emission peaks. These parity forbidden electronic transitions are partly allowed due to mixing of $4f$ energy states with $5s$ and $5p$ orbitals.¹⁻³ The sharp transitions from Ln^{3+} -doped materials have potential applications as phosphors, luminescence displays, light emitting diodes (LEDs), scintillators, bioimaging etc.⁴⁻⁶ For example, Eu^{3+} -doped Y_2O_3 is a red phosphor, find application in the cathode-ray tubes (CRT).⁷ Similarly, Ce^{3+} -doped YAG is used in phosphor based LEDs.⁸ However, Ln^{3+} -doped materials suffer from low luminescence quantum efficiency due to their low molar absorptivity ($\epsilon = 1-10 \text{ M}^{-1}\text{cm}^{-1}$) and narrow absorption band.⁹⁻¹⁰ To increase the absorption cross section of Ln^{3+} ions some strategies have been developed. One of these strategies is the sensitization of the Ln^{3+} emission via organic ligands (antenna effect).¹¹⁻¹³ In this approach, the organic ligands possessing high absorption co-efficient is first excited and followed by transfer of the excited energy to the Ln^{3+} ions via the triplet state of the organic molecules.¹⁴⁻¹⁵ Another approach is sensitization of Eu^{3+} emissions through energy transfer from Bi^{3+} ions which have broad UV excitation. However, energy transfer from Bi^{3+} doping is generally observed in solid state and mostly restricted up to 3 or 4% doping.¹⁶⁻¹⁷ Thus it is an important challenge to find a strategy to enhance the luminescence efficiency of the Ln^{3+} ions particularly in water dispersible colloidal materials as they find interesting use in bio-imaging.¹⁸ In this work we have developed an approach where carbon dots (C-dots) have been used as a broad band sensitizer for the lanthanide ions such as Eu^{3+} as well as Tb^{3+} ions.

C-dots are a new class of carbon-based nanomaterial which has unique photoluminescence (PL) properties. They are first

obtained during purification of single-walled carbon nanotubes through preparative electrophoresis in 2004.¹⁹ Several strategies have been reported for the preparation of C-dots.²⁰⁻²⁷ The optical properties of the C dots are quite interesting. They show strong excitation dependent PL in the visible region. Though exact reason for this is in debate, it is generally believed to happen due to difference in size as well as presence of several surface related energy states.²⁸⁻³¹ Our idea is to explore this broad excitation to enhance the luminescence quantum efficiency of Eu^{3+} ions in Eu^{3+} -doped LaF_3/C dot nanocomposites.

In this communication we report the preparation of Eu^{3+} -doped LaF_3/C dots nanocomposites through a hydrothermal process (see ESI† for more details). Eu^{3+} -doped LaF_3/C dots nanocomposites have strong luminescence of C-dots. Upon exciting in C-dots band (340 nm), strong Eu^{3+} emission peaks were observed due to energy transfer from C-dots to Eu^{3+} ions present in LaF_3 . The importance of the nanocomposites in achieving the energy transfer is studied.

Before preparing the nanocomposites, C-dots were prepared independently by the hydrothermal method and characterized. The X-ray diffraction (XRD) pattern of the C-dots shows a broad peak centered at $2\theta = 28^\circ$ which is characteristic of C-dots.³² The broad nature of the peak implies the amorphous nature of the C-dots. The transmission electron microscopy (TEM) indicates that the average size of the C-dots is about 3-4 nm using triethylene glycol as carbon source. The TEM image and the XRD pattern of the C-dots are shown Fig 1.

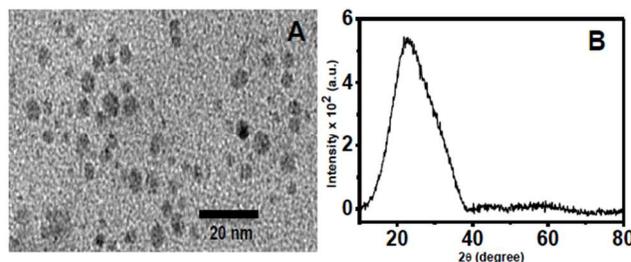


Fig.1 TEM image (A) and XRD pattern (B) of C-dots prepared using triethylene glycol as carbon source.

The photoluminescence (PL) results of the C-dots are shown in Fig. S1. The C-dots show broad emissions in the region when excited characteristic broad absorption between 400 nm to 560 nm when excited between 280 nm and 360 nm. There is gradual shift towards longer wavelength is noted with the increase in the excitation wavelength. This excitation dependent emission maxima is characteristics of C-dots and is moatly related to surface bound energy states.^{30, 31} The lifetime of the C-dots is about 4.7 ns by mneasuring the emission at 420 nm. The decay curve is shown in Fig. S2.

Fig.2 shows the XRD pattern of Eu^{3+} -doped LaF_3/C dots nanocomposites. The pattern clearly indicates the formation of hexagonal LaF_3 . The peak positions and intensities match well with the standard pattern for pure hexagonal LaF_3 crystals (ICSD PDF Card No.; 01-082-0690). The large width of the

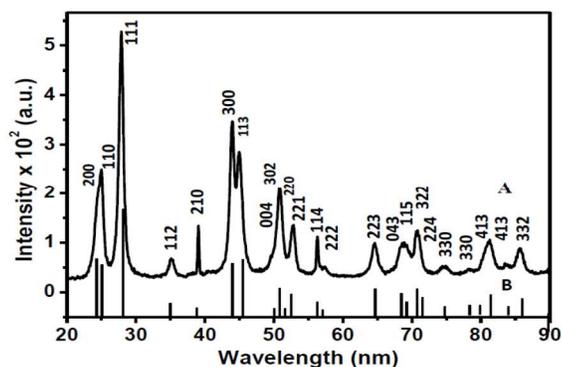


Fig.2 XRD pattern of (A) Eu^{3+} doped LaF_3/C dots nanocomposites and (B) standard pattern for LaF_3 .

diffraction peaks indicates the small size of particles. The lattice parameters are $a = 7.16$ and $c = 7.34$ Å. Average crystalline size calculated from the (111) diffraction peak of the XRD data based on the Debye-Scherrer formula is 11.5 nm. We emphasize that no characteristic peak of C dots near $2\theta = 25^\circ$ is noticed which most likely obscured by the LaF_3 peaks.

To understand the shape and size of the Eu^{3+} -doped LaF_3/C dot nanocomposites, TEM image was taken (shown in Fig.3). The image indicates the formation of slightly distorted nanocomposites with an average diameter of 13-14 nm. This value is in agreement with that calculated from Debye-Scherrer formula. We emphasize that some agglomeration of particles leading to bigger particles was also observed. We emphasized that the presence of C-dots in the nanocrystals is not clear. This might be due to the very small size of the C-dots (3-4 nm) as shown in Fig.1A However, energy dispersive X- Ray (EDX) Spectroscopy of the nanocomposites shows the presence of C dots. EDX EDX measurements indicate the presence of C, La, F and Eu^{3+} in the nanocomposites. To verify that the observed carbon peak is indeed due to C dots, we heated the Eu^{3+} -doped LaF_3/C dots nanocomposites at 400°C to remove the C dots. The resulting sample shows very less intense carbon peak, mostly arising from the carbon present in the glass slide (see Fig S3). Further support for the presence of C-dots in the nanocomposites comes from Zeta Potential measurement. Zeta

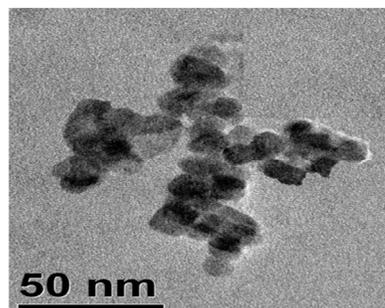


Fig. 3 TEM image of Eu^{3+} -doped LaF_3/C dot nanocomposites

potential values of Eu^{3+} -doped LaF_3/C dots nanocomposites, Eu^{3+} -doped LaF_3 and free C dots are -18.7 mV, 5 mV and -13 mV at pH 7, respectively. These results indicate the presence of C-dots in the nanocomposites and also suggest the stability of nanocomposites in water. In addition, UV absorbance peaks of the nanocomposites show a characteristic peak which is similar to the C dots absorbance spectra reported in the literature (see Fig S4).³³

The PL studies confirm the presence of C-dots in the nanocomposites. **Fig 4** shows the PL spectrum of the water dispersed Eu^{3+} -doped LaF_3/C dot nanocomposites at different excitation wavelength from 280 to 360 nm. Strong C-dots emission peaks are observed from 360 to 550 nm when excited between 280 and 360 nm. It shows maximum emission intensity at 420 nm when excited at 340 nm. The corresponding excitation spectrum (see inset of Fig. 4) indicates excitation maxima at 340 nm. In addition, strong Eu^{3+} emission peaks are observed near 590 and 612 nm upon C-dots excitation (i.e. at 340 nm). These transitions are assigned to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions, respectively. The PL spectrum of the nanocomposites is shown in Fig. 5 along with the PL spectrum of Eu^{3+} -doped LaF_3 nanoparticles. The strong Eu^{3+} emissions from the nanocomposites are believed to occur via energy transfer from C-dots. This is verified from the excitation spectrum of the nanocomposites which shows broad band characteristic of C-dots along with sharp peaks from Eu^{3+} due to ${}^5\text{L}_0 \leftarrow {}^7\text{F}_0$ (see inset of Fig.5). In addition, under identical condition the PL analysis of Eu^{3+} -doped LaF_3 nanoparticles shows only very weak Eu^{3+} emission intensity (see Fig.5). This strongly suggests that the strong Eu^{3+} emissions at 340 nm excitation are due to C-dots sensitization.

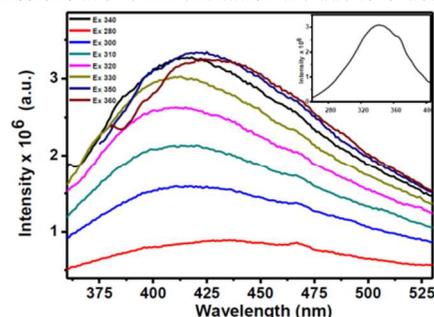


Fig. 4 PL spectra of Eu^{3+} -doped LaF_3/C dots nanocomposites with different excitation. Inset shows excitation spectrum of Eu^{3+} -doped LaF_3/C dots nanocomposites obtained by measuring at 420 nm emission.

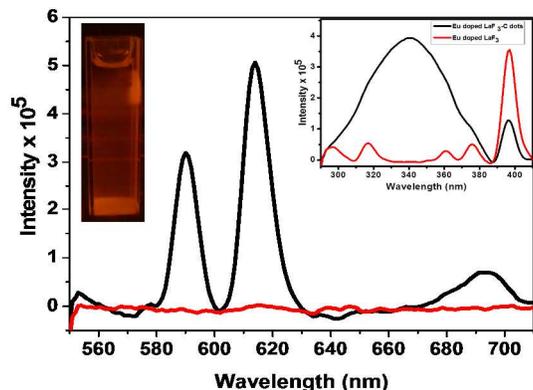


Fig.5 PL spectra of Eu^{3+} -doped LaF_3/C dots nanocomposites (black trace) and Eu^{3+} -doped LaF_3 (red trace). Inset show the corresponding excitation spectra (right) and the digital image (left) of the nanocomposites under UV light using 550 nm filter.

We believe the energy transfer from the C-dots to the Eu^{3+} -doped LaF_3 is likely of FRET type. This is supported by the overlap between the emission spectrum of the C-dots with the excitation spectrum of the Eu^{3+} -doped LaF_3 (shown in Fig. S5). We emphasize that the emission intensity of Eu^{3+} ions in the nanocomposites upon 340 nm excitation is more intense compared to 394 nm excitation (see Fig.S6). The C-dot sensitization of the Eu^{3+} ions is further verified using lifetime measurements. The lifetimes were measured by exciting the sample at 340 nm and monitoring the emission at 612 nm. This value is 0.32 ms for the Eu^{3+} -doped LaF_3/C dots nanocomposites, whereas it is about 0.27 ms for the Eu^{3+} -doped LaF_3 nanoparticles at 394 nm excitation. The results are shown in Fig.S7. To evaluate the energy transfer efficiency, we measured the donor (C-dots) lifetime with and without the acceptor (nanocomposites) using the equation $1-\tau_0/\tau$ where τ is the lifetime of the C-dots emission in Eu^{3+} -doped LaF_3/C dots nanocomposites and τ_0 is the lifetime of the C-dots. The values of τ and τ_0 are 3.6 ns and 4.02 ns respectively. The calculated energy transfer efficiency is about 11%. The lifetime decay curves of both C-dots emission and same from nanocomposites are shown in Fig.8. Though this efficiency seems low, this is good as lanthanide ions generally possess low absorption efficiency.

To understand the importance of the nanocomposite formation in the energy transfer, we performed the following control experiment. A physical mixture of Eu^{3+} -doped LaF_3 nanoparticles and C-dots was prepared by simple mixing of the corresponding dispersions. This physical mixture shows strong C-dots emission and only very weak Eu^{3+} emission upon excitation at 340 nm. This suggests that formation of nanocomposites is important to observe C-dots sensitized Eu^{3+} emission (see Fig. S9). Furthermore, simple mixture containing the C-dots and $\text{Eu}(\text{NO}_3)_3$ in water shows only an intense C-dots emission (see Fig. S10). All these imply the importance of doping Eu^{3+} ions in a suitable matrix and the formation of nanocomposites.

We have extended similar study to Tb^{3+} ions by preparing Tb^{3+} -doped LaF_3/C dots nanocomposites under similar experimental condition. The PL study shows strong Tb^{3+} emission at C-dots excitation with a background emission from C-dots. The PL spectrum of Tb^{3+} -doped LaF_3/C dots nanocomposites is shown Fig. S11 along with Tb^{3+} -doped LaF_3 nanoparticles. Here again the C-dots sensitization leads to higher Tb^{3+} emission intensity compared to Tb^{3+} -doped LaF_3 nanocrystals alone. Extending the study to other Ln^{3+} ions such as Dy^{3+} and Tm^{3+} is obscured by strong C-dots emission in their emission region.

In conclusion we report the hydrothermal synthesis of Eu^{3+} -doped LaF_3/C dots nanocomposites and observed very strong Eu^{3+} luminescence via sensitization by carbon dots (C-dots) for the first time. This energy transfer via C-dots leads to the broad band excitation. The maxima of this broad band excitation is toward far UV (340 nm) compared to direct excitation of Eu^{3+} (394 nm) which can have potential use in phosphor based LEDs.

Experimental

In a typical procedure, 15 mL triethylene glycol (TREG) was added to $\text{La}(\text{NO}_3)_3$ (0.95 mmol) and $\text{Eu}(\text{NO}_3)_3$ (0.05 mmol) and heated at 40° C with vigorous stirring to make a homogeneous dispersion. After 1 h stirring solution was transferred to the Teflon-lined stainless-steel autoclave with total volume 100 mL. The autoclave was sealed and maintained at 200°C for 10 h. After the autoclave was cooled to room temperature naturally, the products were collected by centrifugation, washed several times with absolute ethanol, and then dried at vacuum desiccator. Supernatant Carbon dots (C dots) was also collected after centrifugation and stored at 4° C.

VM thanks the Department of Science and Technology (DST), India, Council for Scientific and Industrial Research (CSIR) and IISER-Kolkata for the funding. TS and CH thank UGC and IISER-K, respectively for the scholarship.

Notes and references

^a Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER), Kolkata, Mohanpur, West Bengal 741252, India. Fax: 91-33-25873020; Tel: +91(0)9007603474; E-mail: mvenkataramanan@yahoo.com

†Electronic Supplementary Information (ESI) available Synthesis of Eu^{3+} -doped LaF_3/C dots nanocomposites, Eu^{3+} -doped LaF_3/C dots nanocomposites, Tb^{3+} -doped LaF_3/C dots nanocomposites, Dy^{3+} -doped LaF_3/C dots nanocomposites & Tm^{3+} -doped LaF_3 , TEM, EDAX, Life time of nanocomposites, UV-Vis spectra, PL of physical mixture of Eu^{3+} -doped LaF_3 & C dots and PL of Tb^{3+} -doped LaF_3/C -dots nanocomposites and Tb^{3+} -doped LaF_3 . See DOI: 10.1039/b000000x/

- (a) R. X. Yan, Y. D. Li *Adv. Funct. Mater.*, 2005, **15**, 763; (b) F. Wang, Y. Han, C. S. Lim, Y. Lu, J. Wang, J. Xu, H. Chen, C. Zhang and X. Liu, *Nature*, 2010, **463**, 1061; (c) H. A. Hoppe, *Angew. Chem., Int. Ed.* 2009, **48**, 3572; (d) F. Wang, R. Deng, J. Wang, Q. Wang, Y. Han, H. Zhu, X. Chen, X. Liu, *Nat. Mater.* 2011, **10**, 968.
- (a) S. Cotton, *Lanthanide and Actinide Chemistry*, John Wiley & Sons, West Sussex, 2006; (b) J. C. G. Bünzli, *Chem. Rev.*, 2010, **110**, 2729, (c) V. Sudarsan, F. C. J. M. van Veggel, R. A. Herring and M. Raudsepp, *J. Mater. Chem.*, 2005, **15**, 1332. (d) M. Haase, H. Schafer, *Angew. Chem. Int. Ed.* 2011, **50**, 5808; (e) P. Rahman and M. Green, *Nanoscale*, 2009, **1**, 214.
- (a) P. Y. Jia, J. Lin, M. Yu, *J. Luminescence*, 2007, **122-123**, 134 (b) C. Feldmann, M. Roming, K. Trampert, *Small* 2006, **2**, 1248 (c) H. Goesmann, C. Feldmann, *Angew. Chem. Int. Ed.* 2010, **49**, 1362; (d) T. Montini, A. Speghini, L. DeRogatis, B. Lorenzut, M. Bettinelli, M. Graziani and P. Fornasiero, *J. Am. Chem. Soc.*, 2009, **131**, 13155.
- (a) Z. L. Wang, Z. W. Quan, P. Y. Jia, C. K. Lin, Y. Luo, Y. Chen, J. Fang, W. Zhou, C. J. O'Connor, J. Lin, *Chem. Mater.*, 2006, **18**, 2030; (b) F. Meiser, C. Cortez, F. Caruso, *Angew. Chem., Int. Ed.* 2004, **43**, 5954; (c) D. B. Barber, C. R. Pollock, L. L. Beecroft, C.K. Ober, *Opt. Lett.* 1997, **22**, 1247.
- (a) J.C.G. Bünzli, C. Piguat, *Chem. Soc. Rev.* 2005, **34**, 1048; (b) J. S. Wang, Y. X. Li, Q. Q. Ge, H. C. Yao and Z. J. Li, *Appl. Surf. Sci.* 2011, **257**, 4100; (c) A. Kar, A. Datta and A. Patra, *J. Mater. Chem.*, 2010, **20**, 916.
- (a) J. Pichaandi, J. C. Boyer, K. R. Delaney, F. C. J. M. van Veggel, *J. Phys. Chem. C* 2011, **115**, 19054; (b) J. W. Stouwdam, F. C. J. M. van Veggel, *Nano Lett.* 2002, **2**, 733. (c) A. Patra, C. S. Friend, R. Kapoor, P. N. Prasad, *Appl. Phys. Lett.* 2003, **83**, 284; (d) H. Sami, A. Maparu, A. Kumar

- and Sri Sivakumar., *PLoS one* 2012, 7, 1; (e) B. S. Naidu, B. Vishwanadh, V. Sudarsan, and R. K. Vatsa, *Dalton Trans.*, 2012, **41**, 3194.
- 7 (a) J. Li, X. Li, X. Sun and T. Ishigaki, *J. Phys. Chem. C*, 2008, **112**, 11707. (b) J. Yang, Z. Quan, D. Kong, X. Liu, and J. Lin, *Crystal Growth & Design*, 2007, **7**, 730.
- 8 A. Lakshmanan, R. S. Kumar, V. Sivakumar, P. C. Thomas and M. T. Jose, *Indian Journal of Pure and Applied Physics*, 2010, **49**, 303.
- 9 (a) S. Li, X. Zhang, Z. Hou, Z. Cheng, P. Maa and J. Lin, *Nanoscale*, 2012, **4**, 5619; (b) A. K. Parchur, A. I. Prasad, A. A. Ansari, S. B. Rai and R. S. ingthoujam, *Dalton Trans.*, 2012, 41, 11032.
- 10 F. Vetrone, J. C. Boyer, J. A. Capobianco in *The Handbook of Luminescence, Display Materials and Devices* (Eds.: L. S. Rohwer, H. S. Nalwa), American Scientific Publishers, Los Angeles, 2003
- 11 (a) S. I. Weissman, *J. Chem. Phys.*, 1942, **10**, 214; (b) A. Beeby, R. S. Dickins, S. Faulkner, D. Parker and J. A. G. Williams, *Chem. Commun.*, 1997, 1401.
- 12 R. van Deun, P. Fias, P. Nockemann, K. van Hecke, L. Van Meervelt and K. Binnemans, *Inorg. Chem.*, 2006, **45**, 10416.
- 13 J. Zhang, C. M. Shade, D. A. Chengelis and S. Petoud, *J. Am. Chem. Soc.*, 2007, **129**, 14834.
- 14 (a) A. M. Cross, P. S. May, F. C. J. M. van Veggel and M. T. Berry, *J. Phys. Chem. C*, 2010, **114**, 14740; (b) J. Zhang, C. M. Shade, D. A. Chengelis and S. Petoud, *J. Am. Chem. Soc.*, 2007, **129**, 14834; (c) Y. Chen, Y. M. Chi, H. M. Wen and Z. H. Lu, *Anal. Chem.*, 2007, **79**, 960.
- 15 L. J. Charbonniere, J. L. Rehspringer, R. Ziessel and Y. Zimmermann, *New J. Chem.*, 2008, **32**, 1055.
- 16(a) G. F. Ju, Y. H. Hu, L. Chen, X. J. Wang, Z. F. Mu, H. Y. Wu and F. W. Kang, *J. Electrochem. Soc.*, 2011, **158**, J294; (b) M. N. Luwang, R. S. Ningthoujam, S. K. Srivastava and R. K. Vatsa, *J. Am. Chem. Soc.*, 2011, **133**, 2998; (c) F. Xiao, Y. N. Xue and Q. Y. Zhang, *Spectrochim. Acta, Part A*, 2009, **74**, 498; (c) Y. Tian, B. J. Chen, R. N. Hua, L. H. Cheng, H. Y. Zhong, J. S. Sun, B. Wang, J. Wan, W. L. Lu and K. W. Jang, *J. Nanosci. Nanotechnol.*, 2010, **10**, 1943.
- 17(a) C. C. Lin, K. M. Lin, Y. Y. Li, *J. Lumin.* 2007, **126**, 795; (b) Y. C. Kang, S. B. Park, I. W. Lenggoro, K. Okuyama, *J. Phys. Chem. Solids* 1997, **60**, 379; (c) H. S. Roh, Y. C. Kang, S. B. Park, *J. Colloid Interface Sci.* 2000, **228**, 195.
- 18 C. Sun, G. Pratz, C. M. Carpenter, H. Liu, Z. Cheng, S. S. Gambhir, and L. Xing, *Adv. Mater.* 2011, **23**, H195.
- 19 X. Y. Xu, R. Ray, Y. L. Gu, H. J. Ploehn, L. Gearheart, K. Raker, W. A. Scrivens, *J. Am. Chem. Soc.* 2004, **126**, 12736.
- 20 Y. P. Sun, B. Zhou, Y. Lin, W. Wang, K. A. S. Fernando, P. Pathak, M. J. Mezziani, B. A. Harruff, X. Wang, H. Wang, P. G. Luo, H. Yang, M. E. Kose, B. Chen, L. M. Veca and S. Y. Xie, *J. Am. Chem. Soc.*, 2006, **128**, 7756.
- 21 (a) S. C. Ray, A. Saha, N. R. Jana and R. Sarkar, *J. Phys. Chem. C*, 2009, **113**, 18546; (b) H. Liu, T. Ye and C. Mao, *Angew. Chem., Int. Ed.*, 2007, **46**, 6473.
- 22(a) S. T. Yang, L. Cao, P. G. Luo, F. Lu, X. Wang, H. Wang, M. J. Mezziani, Y. Liu, G. Qi and Y. P. Sun, *J. Am. Chem. Soc.*, 2009, **131**, 11308; (b) W. Kwon and S. Rhee, *Chem. Commun.*, 2012, **48**, 5256.
- 23 (a) S. L. Hu, K. Y. Niu, J. Sun, J. Yang, N. Q. Zhao and X. W. Du, *J. Mater. Chem.*, 2009, **19**, 484; (b) Y. Zhang, H. Goncalves, J. C. G. Esteves da Silva and C. D. Geddes, *Chem. Commun.*, 2011, **47**, 5313; (c) L. Y. Zheng, Y. W. Chi, Y. Q. Dong, J. P. Lin and B. B. Wang, *J. Am. Chem. Soc.*, 2009, **131**, 4564.
- 24 J. Lu, J. X. Yang, J. Wang, A. Lim, S. Wang, K. P. Loh, *ACS Nano* 2009, **3**, 2367.
- 25 A. B. Bourlinos, A. Stassinopoulos, D. Anglos, R. Zboril, V. Georgakilas, E. P. Giannelis, *Chem. Mater.* 2008, **20**, 4539.
- 26 A. B. Bourlinos, A. Stassinopoulos, D. Anglos, R. Zboril, M. Karakassides, E. P. Giannelis, *Small* 2008, **4**, 455.
- 27(a) H. Zhu, X. Wang, Y. Li, Z. Wang, F. Yang and X. Yang, *Chem. Commun.*, 2009, 5118. (b) W. Xiaohui, Q. Konggang, X. Bailu, R. Jinsong, Q. Xiaogang, *J. Mater. Chem.*, 2011, **21**, 2445 (c) H. Yan M. Tan, D. Zhang, F. Cheng, H. Wu, M. Fan, X. Mab, J. Wang, *Talanta*, 2013, 108, 59.
- 28 H. Li, X. He, Y. Liu, H. Huang, S. Lian, S. T. Lee and Z. Kang, *Carbon*, 2011, **49**, 605.
- 29 P. C. Hsu, H. T. Chang, *Chem. Commun.*, 2012, **48**, 3984.
- 30 X. Xu, R. Ray, Y. Gu, H. J. Ploehn, L. Gearheart, K. Raker and W. A. Scrivens, *J. Am. Chem. Soc.*, 2004, **126**, 12736.
- 31 F. Wang, Z. Xie, H. Zhang, C. Y. Liu and Y. G. Zhang, *Adv. Funct. Mater.*, 2011, **21**, 1027.
- 32 N. Puvvada, B. N. P. Kumar, S. Konar, H. Kalita, M. Mandal and A. Pathak, *Sci. Technol. Adv. Mater.*, 2012, **13**, 045008.
- 33 Y. Sun, B. Zhou, Y. Lin, W. Wang, K. A. S. Fernando, P. Pathak, M. J. Mezziani, B. A. Harruff, X. Wang, H. Wang, P. G. Luo, H. Yang, M. E. Kose, B. Chen, L. Monica Veca, and S. Xie, *J. Am. Chem. Soc.*, 2006, **128**, 7756.