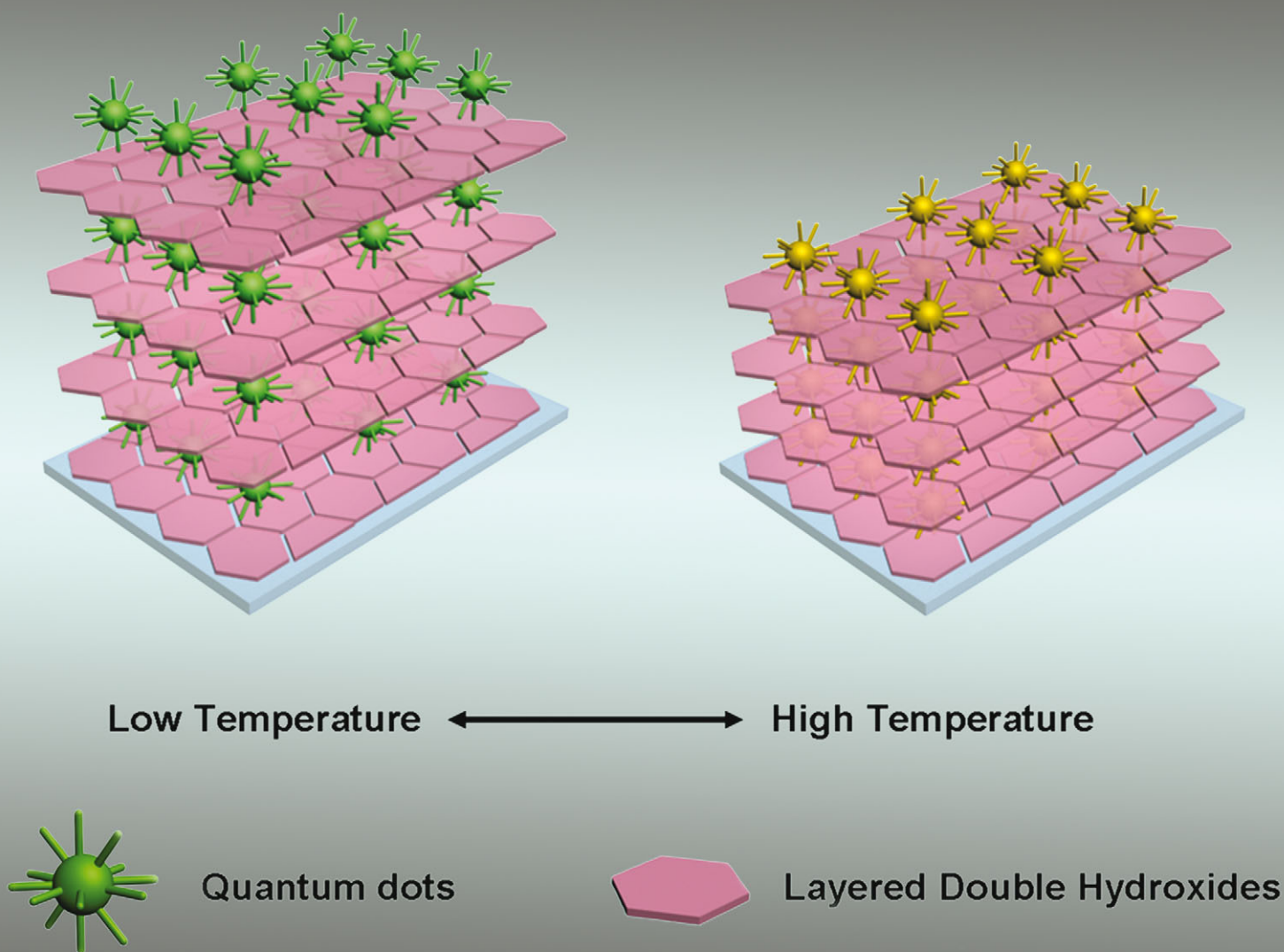


ChemComm

Chemical Communications

www.rsc.org/chemcomm

Volume 49 | Number 10 | 1 February 2013 | Pages 933–1024



ISSN 1359-7345

RSC Publishing

COMMUNICATION

Min Wei *et al.*

A temperature sensor based on CdTe quantum dots-layered double hydroxide ultrathin films *via* layer-by-layer assembly

COMMUNICATION

A temperature sensor based on CdTe quantum dots–layered double hydroxide ultrathin films *via* layer-by-layer assembly†

Cite this: *Chem. Commun.*, 2013, **49**, 969

Received 17th October 2012,
Accepted 26th November 2012

DOI: 10.1039/c2cc37553b

www.rsc.org/chemcomm

Ruizheng Liang, Rui Tian, Wenying Shi, Zhihui Liu, Dongpeng Yan, Min Wei,*
David G. Evans and Xue Duan

Ordered ultrathin films based on alternate assembly of CdTe QDs and layered double hydroxide monolayers have been fabricated, which can be used as a photoluminescence temperature sensor with dual-parameter signals and high response sensitivity.

Recently, colloidal semiconductor quantum dots (QDs) have attracted considerable attention for their excellent behavior in light-emitting diodes (LEDs),^{1a} optically pumped lasers,^{1b} photovoltaic cells,^{1c} and biomedicine.^{1d} Compared with traditional organic fluorophores, they offer several advantages including flexible photoexcitation, tailored wavelength, sharp photoemission as well as superb resistance to photobleaching.² However, the use of colloidal QDs results in undesirable leaching and pollution, high cost and inconvenient manipulation. From the viewpoint of practical application, incorporation of QDs into solid matrices for the fabrication of macroscopic arrays has been demonstrated to be an efficient resolution to obtain optoelectronic devices with high stability, recyclability and long-term service.³

Luminescence thermometry, which exploits temperature-dependent changes in the luminescence properties (*e.g.*, excited state lifetime or emission intensity) of an indicator or probe, is a versatile optical technique for the measurement of local temperature.⁴ To date, a variety of luminescent compounds have been employed as optical temperature probes, including inorganic phosphors,⁴ organic dyes,^{5a} and luminescent coordination complexes.^{5b} Compared with these luminescent materials, QDs possess the advantages of strong PL intensity, narrow half peak width and multi-parameter detectable signals. However, several problems in the application of QDs-based optical temperature probes are not well resolved. For instance, previously solid-state CdSe QDs-polymer films only have an alternative detectable signal

(PL intensity^{6a} or emission energy^{6b,c,7}), and the response sensitivity is not very satisfactory. In addition, these QDs-polymer films generally suffer from poor thermal stability and limited temperature response range,^{6,7} since the geometrical or electronic structure of polymers changes easily under thermal agitation.⁸ Therefore, how to fabricate new types of QDs-based optical temperature sensors with high sensitivity, stability as well as reproducibility remains a challenging goal.

Layered Double Hydroxides (LDHs) are a class of layered anionic clays which have been widely used in the fields of catalysis, biology, and optical materials.⁹ LDHs can be exfoliated into positively charged nanosheets as building blocks for the fabrication of functional ultrathin films (UTFs).¹⁰ Herein we present a UTF system as a temperature sensor based on the layer-by-layer (LBL) assembly of mercaptosuccinic acid modified CdTe QDs and positively charged LDH nanosheets (Scheme S1, ESI†), which shows dual-parameter detectable signals and superior temperature response sensitivity. XRD and SEM indicate that the CdTe QDs-LDH UTF has long-range order structure, with a periodic repeating distance of 12.33 nm. The UTF exhibits a linear response in luminescence intensity as well as peak position in the temperature range 23–80 °C, with a fast response, high sensitivity, good repeatability and photostability. This work provides a successful paradigm for the design and fabrication of highly-oriented luminescence film *via* incorporation of QDs into a 2D inorganic matrix, and demonstrates its prospective application as an optical temperature sensor.

Mercaptosuccinic acid modified CdTe QDs with a particle size of ~2.7 nm show strong yellow-green emission at 550 nm with a quantum yield of 53% (see Fig. S1, ESI†). Scheme S1 (ESI†) shows the multilayer assembly process of the CdTe QDs-LDH UTFs, in which CdTe QDs and LDH nanosheets were alternately deposited on the surface of quartz substrates *via* the LBL method. UV-vis absorption spectra (Fig. S2-A, ESI†) of these UTFs show that the intensity of the absorption band at 519 nm increases gradually with the bilayer number *n*, indicative of a stepwise and regular deposition procedure with an approximately equal amount of CdTe QDs incorporated in each cycle. The UTFs are nearly colorless and highly transparent (Fig. S2-B, ESI†), as shown by the lack of visible absorption between 400 and 800 nm (Fig. S2-A, ESI†). The (CdTe QDs-LDH)_{*n*}

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China.

E-mail: weimin@mail.buct.edu.cn; Fax: +86-10-64425385; Tel: +86-10-64412131

† Electronic supplementary information (ESI) available: The details of CdTe QDs; the characterization of (CdTe QDs/LDH)_{*n*} UTFs; the luminescence behavior of pristine CdTe QDs solution, film and (CdTe QDs/LDH)₃₀ UTF at various temperatures; photo-, thermal- and storage stability of CdTe QDs/LDH UTF. See DOI: 10.1039/c2cc37553b

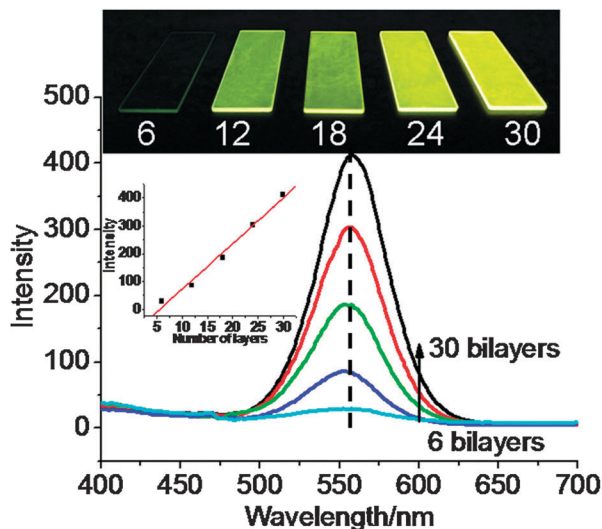


Fig. 1 Fluorescence spectra of $(\text{CdTe QDs-LDH})_n$ UTFs ($n = 6-30$); the insets show a linear correlation between intensity at ~ 558 nm and bilayer number as well as photographs of these UTFs under UV irradiation.

UTFs display strong yellow-green emission under UV-light irradiation, and the intensity at ~ 558 nm also exhibits a monotonic increase along with n (Fig. 1). This was further confirmed visually by the gradual increase in the UTF brightness under UV irradiation (Fig. 1, inset). Photoluminescence quantum yield (PLQY) of the $(\text{CdTe QDs-LDH})_{30}$ UTF is 16.5%, which was measured using a fluorescence spectrometer equipped with an integrating sphere. The luminescence emission of the CdTe QDs-LDH UTFs shows a little red-shift compared with the pristine solution of CdTe QDs (Fig. S1-C, ESI[†]), which can be ascribed to the electrostatic interaction between LDH nanosheets and CdTe QDs .

The surface morphology and thickness of $(\text{CdTe QDs-LDH})_n$ UTFs were investigated by scanning electron microscopy (SEM). The top-view images (Fig. S3, ESI[†]) display the homogeneity of the UTFs upon increasing bilayer number n , and a typical SEM image of the $(\text{CdTe QDs-LDH})_{30}$ UTF is shown in Fig. 2A. The UTFs' thickness with various n can be estimated from their side-view SEM images (Fig. 2B; Fig. S4, ESI[†]). The approximately linear increase in thickness as a function of n was observed, with an average thickness increment of ~ 11.96 nm per bilayer cycle (Table S1, ESI[†]). The AFM topographical images ($2 \mu\text{m} \times 2 \mu\text{m}$) of the CdTe QDs-LDH UTFs are illustrated in Fig. 2C and Fig. S5 (ESI[†]). The value of root-mean-square (rms) roughness for the $(\text{CdTe QDs-LDH})_n$ UTFs increases gradually from 5.40 to 12.75 nm as the bilayer number varies from 6 to 30 (Table S1, ESI[†]), indicating a relatively smooth surface of these UTFs. Furthermore, the $(\text{CdTe QDs-LDH})_{30}$ UTF shows a homogeneous yellow-green color with strong brightness under a fluorescence microscope (Fig. 2D), indicating that the CdTe QDs are distributed uniformly throughout the UTF.

The CdTe QDs-LDH UTF undergoes a significant change in both luminescence intensity and peak position upon heat treatment for a short period of time. Upon heating the $(\text{CdTe QDs-LDH})_{30}$ UTF from 23 to 80°C , the luminescence intensity gradually decreases with a rather high response sensitivity ($\sim 1.47\%$ per $^\circ\text{C}$); concomitantly, its peak position exhibits a red-shift with a temperature sensitivity of $0.193 \text{ nm } ^\circ\text{C}^{-1}$ (Fig. 3A). The response sensitivity is much higher

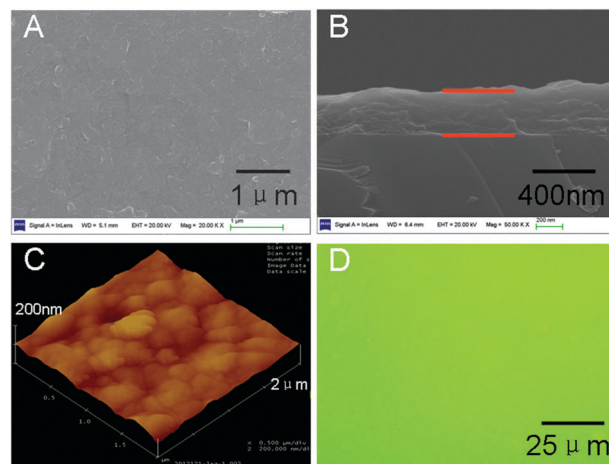


Fig. 2 Morphology of the $(\text{CdTe QDs-LDH})_{30}$ UTF: (A) top-view SEM image; (B) side-view SEM image; (C) tapping-mode AFM image; (D) fluorescence microscope image.

than previously reported work ($\sim 1\%$ per $^\circ\text{C}$ (ref. 6a) and $0.1 \text{ nm } ^\circ\text{C}^{-1}$ (ref. 7)). Visually, a color change from yellow-green to yellow along with a decrease in brightness can be clearly observed upon heating the $(\text{CdTe QDs-LDH})_{30}$ UTF from 23 to 80°C ; as the film is cooled to room temperature, it recovers its original color completely with reverse fluorescence spectrum changes (Fig. 3B; inset; Fig. S6, ESI[†]). The reversible process in the temperature range $23-80^\circ\text{C}$ can be readily repeated up to 8 cycles (Fig. 3B), and a relatively obvious decrease in the PL intensity was observed in the following cycles. Small angle XRD was performed to illuminate the structural variation in this heating-cooling cycle. As shown in Fig. 3C, the basal spacing (d_{003}) decreases from 12.33 to 10.50 nm as the temperature rises from 23 to 80°C . The contraction of basal spacing is possibly attributed to the aggregation of CdTe QDs in the LDH nanosheets gallery, which leads to a red-shift in emission and fluorescence quenching. After cooling to 23°C ,

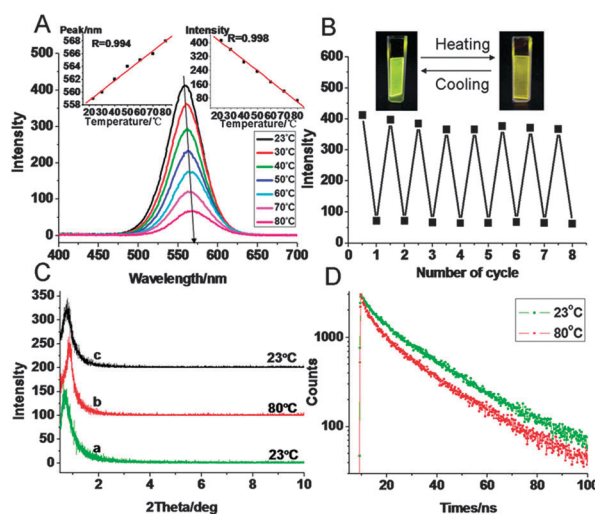


Fig. 3 (A) The luminescence spectra of the $(\text{CdTe QDs-LDH})_{30}$ UTF in the temperature range $23-80^\circ\text{C}$ (inset: the emission position or intensity as a function of temperature, respectively); (B) the reversible fluorescence response of eight consecutive cycles (the inset shows the UTF photographs at 23 and 80°C , respectively); (C) the small angle XRD patterns in a heating-cooling cycle: (a) 23°C , (b) 80°C and (c) 23°C ; (D) typical fluorescence decay curves (green: 23°C ; red: 80°C).

the basal spacing recovers to 12.06 nm, indicating a reversible aggregation state of CdTe QDs. This was further verified by fluorescence lifetime measurements. The fluorescence lifetime of the UTF was determined to be 17.12 ns at 23 °C and 14.25 ns at 80 °C, and the fluorescence decay at high temperature is faster than that at low temperature (Fig. 3D). The results indicate that nonradiative decay enhances significantly at high temperature, resulting in the reduced luminescence intensity.¹¹ Therefore, the dual parameters and high sensitivity of the (CdTe QDs-LDH)₃₀ UTF will guarantee its practical application in temperature sensing.

To further give insight into the largely enhanced response sensitivity of the CdTe QDs-LDH UTF, another two samples, CdTe QDs solution and a pristine CdTe QDs film prepared by using the solvent evaporation method, were used for comparison. The two samples also show a linear decrease in fluorescence intensity in the temperature range 23–80 °C, with a low response sensitivity of −0.57% per °C and −0.83% per °C, respectively (Fig. S7 and S8, ESI†), in contrast to the sensitivity of −1.47% per °C for the (CdTe QDs-LDH)₃₀ UTF. Only the temperature-dependent nonradiative decay of CdTe QDs is responsible for the decrease in luminescence intensity of the two pristine CdTe QDs samples. In the case of CdTe QDs-LDH UTF however, both the temperature-dependent nonradiative decay and the QDs aggregation lead to its luminescence quenching, accounting for the largely enhanced sensitivity.

Good photo-, thermal- and storage stability are extremely important criteria in practical applications for a temperature sensor. To illustrate the advantages of incorporation of CdTe QDs into a 2D inorganic matrix, a CdTe QDs-polymer film sample was fabricated by LBL assembly of QDs and poly dimethyldiallylammonium chloride (PDDA) with a similar method. The fluorescence intensities of CdTe QDs-LDH UTF and CdTe QDs-PDDA UTF were recorded by illuminating them with UV-light in a comparative study. After a 5 h irradiation, the fluorescence intensity of the CdTe QDs-PDDA UTF decreased 55.6%; while 38.7% loss was found for the CdTe QDs-LDH UTF (Fig. S9 and S10-A, ESI†). The results confirm that the CdTe QDs-LDH system possesses a better UV-resistance stability than the CdTe QDs-PDDA one. Subsequently, as the irradiated CdTe QDs-LDH and CdTe QDs-PDDA UTF are immersed into water for 2 min, the CdTe QDs-LDH UTF recovers its original intensity completely (Fig. S10-B, ESI†), but the CdTe QDs-PDDA UTF only returns to 71.4% of its primary value (Fig. S10-C, ESI†). The CdTe QDs-LDH UTF system exhibits a surprising UV-resistance stability as well as retrievability. Moreover, the response reversibility of the two samples was also studied. For the CdTe QDs-PDDA UTF, the luminescence intensity only recovered to 83.2% in the first heating-cooling cycle, and a continuous decrease in luminescence emission was observed in the following cycles (Fig. S11, ESI†). In contrast, a high reversibility of the CdTe QDs-LDH UTF was obtained (Fig. 3B). Generally, the geometrical or electronic structure of organic polymer changes easily under thermal agitation, giving rise to spontaneous fluorescence quenching of QDs dispersed within the polymer matrix.⁸ In the case of the CdTe QDs-LDH UTF however, the rigid LDH nanosheets are insensitive to thermal relaxation and therefore provide a stable microenvironment for the QDs. Furthermore, the CdTe QDs-LDH UTF did not show any decrease in fluorescence intensity when dipping in water for 5 s, even for 100 repeated cycles (Fig. S12-A, ESI†). No delamination

or peeling occurred on cross-cutting the UTF surface (Fig. S12-B, ESI†), indicating a strong adhesion of the film to the substrate. In addition, the storage stability test of the CdTe QDs-LDH UTF shows that ~97.4% of its original fluorescence intensity remained after one month (Fig. S13, ESI†). The results above demonstrate that the CdTe QDs-LDH UTF possesses strong photostability, thermostability, mechanical and storage stability, which can be used as a promising candidate for temperature sensing.

In summary, we have fabricated CdTe QDs-LDH UTFs as a temperature sensor based on a long-range order architecture comprising CdTe QDs and LDH nanosheets. The UTF exhibits significant and reversible transformations (fluorescence intensity and wavelength) in the temperature range 23–80 °C. Both the temperature-dependent nonradiative decay and the reversible QDs' aggregation in the LDH matrix account for the largely enhanced response sensitivity of the CdTe QDs-LDH UTF. In addition, the photo-, thermal- and storage stability as well as excellent reversibility promise long service lifetime of the UTFs under practical conditions. It is expected that the strategy demonstrated in this work can be extended to the fabrication of other QDs-LDH UTFs with specific functionality.

This work was supported by the National Natural Science Foundation of China (NSFC) and the 973 Program (Grant No. 2011CBA00504). M. Wei particularly appreciates the financial aid from the China National Funds for Distinguished Young Scientists of the NSFC.

Notes and references

- (a) J. M. Bruchez, M. Moronne, P. Gin, S. Weiss and A. P. Alivisatos, *Science*, 1998, **281**, 1033; (b) V. I. Klimov, A. A. Mikhailovsky, S. Xu, A. Malko, J. A. Hollingsworth, C. A. Leatherdale, H. J. Eisler and M. G. Bawendi, *Science*, 2000, **290**, 314; (c) S. Gunes, H. Neugebauer and N. S. Sariciftci, *Chem. Rev.*, 2007, **107**, 1324; (d) Y. Guo, D. L. Shi, H. Cho, Z. Y. Dong, A. Kulkarni, G. M. Pauletti, W. Wang, J. Lian, W. Liu, L. Ren, Q. Q. Zhang, G. K. Liu, C. Huth, L. M. Wang and R. C. Ewing, *Adv. Funct. Mater.*, 2008, **18**, 2489.
- X. Gao, L. Yang, J. A. Petros, F. F. Marshall, J. W. Simons and S. Nie, *Curr. Opin. Biotechnol.*, 2005, **16**, 63.
- D. V. Talapin, J. S. Lee, M. V. Kovalenko and E. V. Shevchenko, *Chem. Rev.*, 2010, **110**, 389.
- S. W. Allison and G. T. Gillies, *Rev. Sci. Instrum.*, 1997, **68**, 2615.
- (a) D. Yan, J. Lu, J. Ma, M. Wei, D. G. Evans and X. Duan, *Angew. Chem., Int. Ed.*, 2011, **50**, 720; (b) K. Maruszewski, D. Andrzejewski and W. Strek, *J. Lumin.*, 1997, **72–74**, 226.
- (a) G. W. Walker, V. C. Sundar, C. M. Rudzinski, A. W. Wun, M. G. Bawendi and D. G. Nocera, *Appl. Phys. Lett.*, 2003, **83**, 3555; (b) A. Al Salman, A. Tortschanoff, M. B. Mohamed, D. Tonti, F. van Mourik and M. Chergui, *Appl. Phys. Lett.*, 2007, **90**, 093104; (c) A. Joshi, K. Y. Narsingi, M. O. Manasreh, E. A. Davis and B. D. Weaver, *Appl. Phys. Lett.*, 2006, **89**, 131907.
- S. Li, K. Zhang, J. M. Yang, L. Lin and H. Yang, *Nano Lett.*, 2007, **7**, 10.
- B. Qin, H. Y. Chen, H. Liang, L. Fu, X. F. Liu, X. H. Qiu, S. Q. Liu, R. Song and Z. Y. Tang, *J. Am. Chem. Soc.*, 2010, **132**, 2886.
- (a) M. Adachi-Pagano, C. Forano and J. P. Besse, *Chem. Commun.*, 2000, 91; (b) C. A. Antonyraj, P. Koilraj and S. Kannan, *Chem. Commun.*, 2010, **46**, 1902; (c) A. I. Khan, L. X. Lei, A. J. Norquist and D. O'Hare, *Chem. Commun.*, 2001, 2342; (d) A. M. Fogg, A. J. Freij and G. M. Parkinson, *Chem. Mater.*, 2002, **14**, 232; (e) G. M. Lombardo, G. C. Pappalardo, F. Costantino, U. Costantino and M. Sisani, *Chem. Mater.*, 2008, **20**, 5585; (f) F. Leroux and J. P. Besse, *Chem. Mater.*, 2001, **13**, 10.
- (a) D. Yan, J. Lu, M. Wei, J. Ma, D. G. Evans and X. Duan, *Chem. Commun.*, 2009, 6358; (b) X. Guo, F. Zhang, D. G. Evans and X. Duan, *Chem. Commun.*, 2010, **46**, 5197.
- Y. N. Hwang, S. H. Park and D. Kim, *Phys. Rev. B*, 1999, **59**, 7285.