

CrossMark
click for updatesCite this: *RSC Adv.*, 2014, 4, 40748

Lifetime-ultra-prolonged luminescent multilayer thin films with electronic microenvironment†

Tianlei Wang, Meitang Liu,* Hongwen Ma, Xiaojuan Liu, Yu Fu and Kunran Hu

In this report, luminescent multilayer thin films (MTFs) based on functional molecules intercalated into layered double hydroxides (LDHs) and montmorillonite (MMT) nanosheets were fabricated by layer-by-layer assembly method (LBL method). Exfoliated LDHs and MMT nanosheets with opposite charges can be expected to provide an electronic microenvironment (EME) for chromophores, which are not found in previous literatures, and to offer the inorganic rigid building blocks at the same time. Surprisingly, the lifetimes of MTFs with EME's architecture are significantly prolonged, compared with that of the pristine powder, even considerably longer than those of the MTFs without EME's architecture. Therefore, it is highly expected that the EME formed by oppositely-charged inorganic nanosheets has remarkable influence on enhancing the lifetimes of chromophores, which suggests a new potential method to develop novel light-emitting materials and optical devices.

Received 29th June 2014
Accepted 12th August 2014

DOI: 10.1039/c4ra05884d

www.rsc.org/advances

1. Introduction

Organic luminescent materials, because of their chemical stability and excellent luminescence properties, give rise to many possible applications in chemical sensors,^{1,2} optical devices,^{3–7} photovoltaic cells^{8,9} etc. Compared with their solution counterparts, the luminescence performances of solid-state organic materials are still greatly limited by their poor optical stabilities and relatively short service lifetime.¹⁰ For example, the phenomena of fluorescence red or blue shift, broadening, or even quenching, can still occur in the solid state because of the formation of aggregates of such species.^{10–12} Accordingly, the group of Tolbert used the oriented mesoporous silica composites to control the flow of energy transfer, which provide insights to optimize nano-structured materials used in optoelectronic devices,^{13,14} and then other scientists tried changing the external factors, such as thermal and mechanical stimuli, to modify the chemical structure of the molecules for luminescent materials.^{15–18}

Nowadays, layered materials, such as layered double hydroxides,^{19,20} montmorillonite,^{21,22} perovskite oxides,^{23,24} and graphene^{25,26} are attractive targets for both fundamental research and practical application. As a successful liquid exfoliation of layered materials^{27–29} and a productive assembly of inorganic nanosheets,^{30–32} LBL method has been used to build

layered and ordered functional films. Recently, several groups have performed many profound researches by using nanosheets with two-dimensional arrays, which can provide a rigid and stable environment.^{33–38} Especially, Duan *et al.* used LDHs nanosheets to suppress the chromophores' π - π stacking, and assembled well-oriented photoemissive structures with a macroscopic polarized optical effect.^{39–42} Various different inorganic nanosheets possibly contain a number of charges, such as MMT's negative charge and LDHs' positive charge. Oppositely-charged nanosheets are expected to form a nano-scaled capacitor providing an EME, which is not reported in any previous literatures (Fig. 1). Herein, our interest is in knowing whether functional molecules can be designed for intercalating

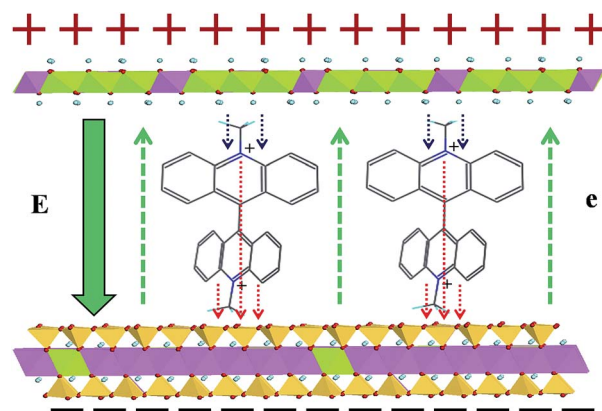


Fig. 1 Schematic of BNMA in EME between the MMT and LDHs monolayers. The green arrows indicate the EME's direction, the red show the repulsion of MMT nanosheets, and the dark blue show the attraction of LDHs nanosheets.

School of Materials Science and Technology, China University of Geosciences, Beijing 100083, P. R. China. E-mail: mtliu@cugb.edu.cn; Fax: +86-10-8232-2759; Tel: +86-10-8232-2759

† Electronic supplementary information (ESI) available: Fluorescence lifetimes, parameters of multi-exponential fit to the fluorescence decay, and polarized fluorescence spectra of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n and (MMT/BNMA@PVA)_n MTFs. See DOI: 10.1039/c4ra05884d

into the oppositely-charged LDHs and MMT nanosheets, and how the EME affects the properties of functional molecules.

In this work, a photoactive divalent cation bis(*N*-methyl-acridinium)(BNMA) was intercalated into the LDHs nanosheets and MMT nanosheets, using an optically-inert polyvinyl alcohol (PVA) as bonders for the purpose of fabricating MTFs (Fig. 2). As the assembled nano-scaled capacitor can provide EME to the chromophores in the nano-system, the MTFs exhibit remarkable optical properties with reasonably longer luminescent lifetimes. Herein, this work successfully developed a general and facile method to fabricate novel inorganic–organic luminescent MTFs containing oppositely-charged nanosheets with a suitable and optically-inert polymer as the bonder and puts forward a new concept about the nano-scale capacitor's effects on the chromophores.

2. Results and discussion

The UV-visible absorption spectra of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_{*n*} MTFs with varying numbers of assembly steps are shown in Fig. 3. The intensities of the absorption peaks at 432 nm exhibit linear correlation with the layer number *n* (Fig. 3, inset), which demonstrates a stepwise and regular growth procedure. Furthermore, the fluorescence emission intensity at 510 nm also displays a consistent increase with *n*, as shown in Fig. 4. The photoluminescence spectra of the as-prepared MTFs with different layer number have no obvious red

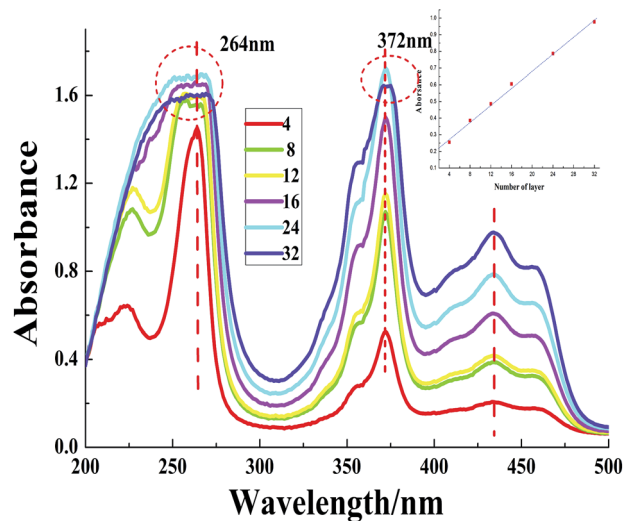


Fig. 3 UV-visible absorption spectra of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_{*n*} MTFs. The inset shows the absorbance increasing linear relationship in 432 nm.

or blue shift, which implies the absence of BNMA aggregates throughout the whole assembly process.

To gain insight into the photophysical properties, the MTFs were studied by detecting the luminescence lifetimes. Surprisingly, it is interesting that the lifetimes of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_{*n*} MTFs were prolonged nearly 40-fold

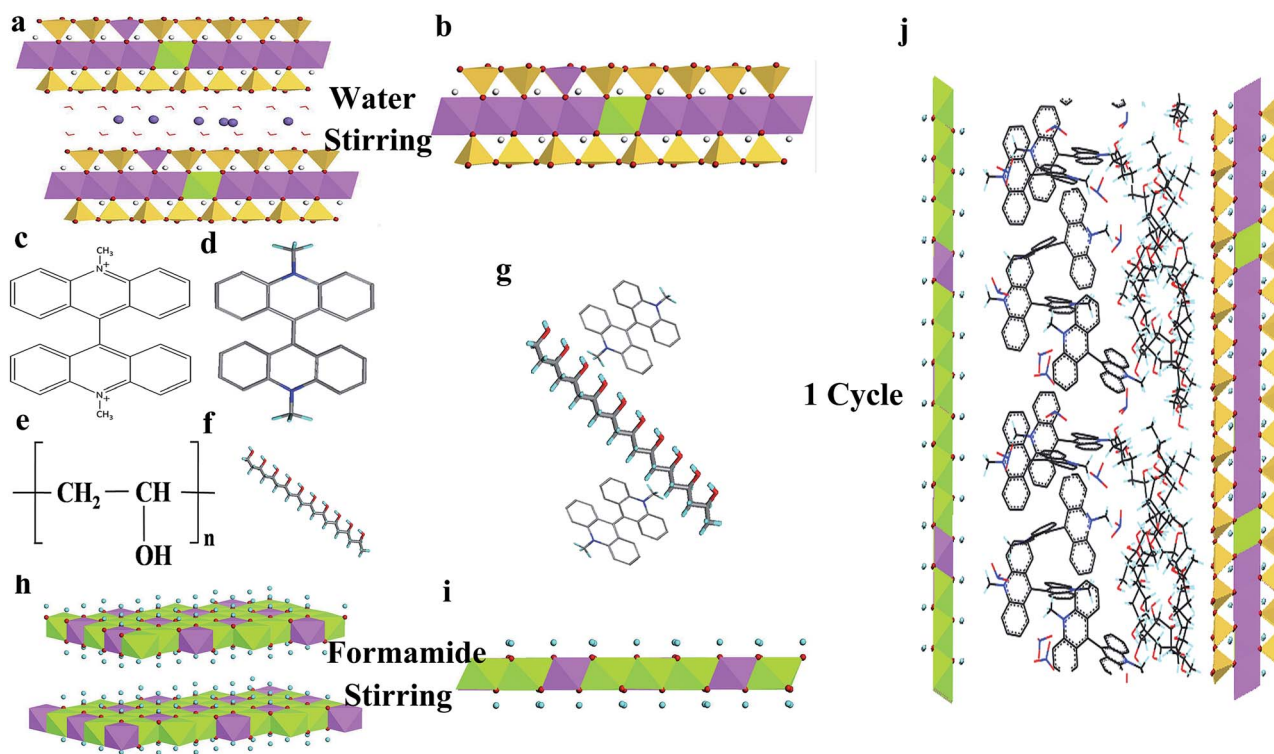


Fig. 2 Assembly process of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_{*n*} MTFs, (a) a representation of MMT, pink: aluminium–oxygen octahedron, green: silicon–oxygen tetrahedron, yellow: magnesium–oxygen octahedron, (b) the nanosheet of MMT, (c) chemical formula of BNMA, (d) structure of BNMA, (e) chemical formula of PVA, (f) structure of PVA, (g) a representation of BNMA@PVA solution, (h) a representation of LDHs, pink: Al(OH)₆ octahedra, green: Mg(OH)₆ octahedra, (i) the nanosheet of LDHs, (j) the MTFs in 1 cycle.

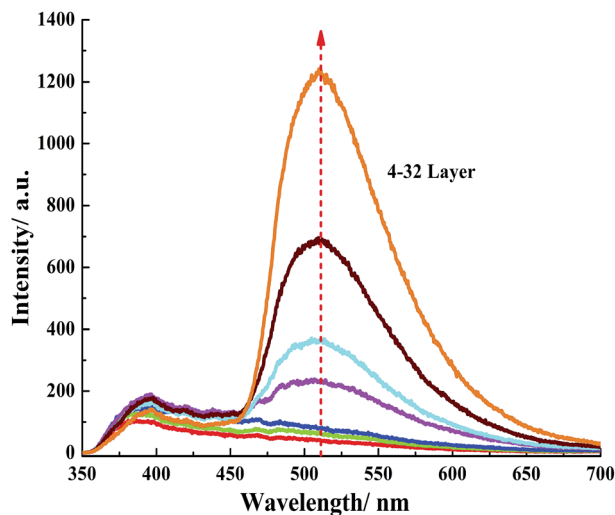


Fig. 4 Photoluminescence spectra of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs.

(13.81–17.02 ns) (Table 1, ESI Fig. S1†) compared with the pristine powder BNMA (0.37 ns), and were also prolonged 3-fold compared with the LDHs/BNMA@PVS MTFs (4.61–4.88 ns).⁴⁰ This remarkable increase was partially because of the isolation effect (IE) caused by the rigid LDHs and MMT monolayer, preventing the aggregation of chromophores. Most importantly, positively charged LDHs and negatively charged MMT nano-sheets formed a nano-scaled capacitor, thus providing BNMA with an EME that could apparently affect the vibration of the valence electron of the chromophores, which will definitely prolong their lifetimes. In order to verify this phenomenon, (MMT/BNMA@PVA)_n MTFs were fabricated using LBL method, and their lifetimes are shown in ESI Table S2 and Fig. S2.† Combined with the results of these MTFs' lifetimes, it is obvious that the lifetimes of MTFs are nearly in a stable growth, but the (MMT/BNMA@PVA)_n MTFs' lifetimes increase was linear and more steep. Furthermore, the (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs' lifetimes were obviously longer than (MMT/BNMA@PVA)_n MTFs' in the same cycles. According to this remarkable increase, as mentioned in the above theory, it can be reasonably concluded that EME can definitely prolong chromophores' lifetimes. Fig. 5 illustrates the comparison of chromophores' lifetimes at different states under different

Table 1 The summary of MTFs' lifetimes containing BNMA. τ_1 represents (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs' lifetimes, τ_2 represents (LDHs/BNMA@PVS)_n MTFs' lifetimes⁴⁰

Layer number	8	16	24
Lifetime τ_1 (ns)	13.81	14.50	17.02
Lifetime τ_2 (ns)	4.61	4.83	4.88
τ_1/τ_{01} ^a	37.34	39.21	46.00
τ_1/τ_2	3.00	3.00	3.49

^a τ_{01} represents the lifetime of the pristine powder BNMA, equaling to 0.37 ns.

environments, and it is obvious that the chromophores under EME have amazing ultra-prolonged lifetimes. Moreover, these results support that the EME has remarkably effective influence on enhancing the lifetime of the chromophores.

3. Experimental section

3.1 Reagents and materials

All the chemicals were of analytical grade and used as received without further purification. Bis(*N*-methylacridinium) (BNMA) was purchased from Sigma Chemical. Co. Ltd, and polyvinyl alcohol (PVA, MW = 1750) was purchased from Tianjin Fuchen Chemical Reagent Plant. Na-montmorillonite (MMT) was purchased from Zhejiang Sanding Co. Ltd. Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O were all supplied by the Xilong Chemical Plant. NaOH, H₂O₂ (30%), H₂SO₄ (95–98%) were supplied by the Beijing Chemical Reagent Company.

3.2 Characterization

UV-visible absorption spectra were obtained in the range from 200 to 500 nm on a TU-1901 Double beam UV-vis spectrophotometer with a slit width of 2.0 nm. Fluorescence spectra was recorded on F-4600 Fluorospectrophotometer. The fluorescence emission spectra were in the range from 350 to 700 nm, and both the excitation and emission slit were set to 2.0 nm. The fluorescence decay and polarized photoluminescence measurements of MTFs were recorded by using an Edinburgh Instruments' Steady and transient time-resolved fluorescence spectrometer.

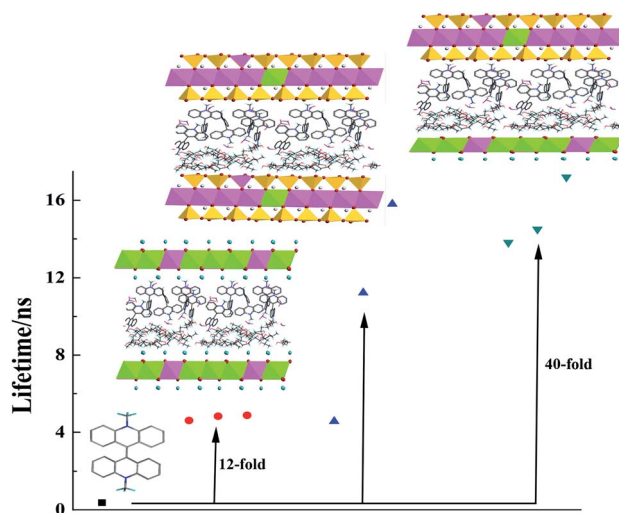


Fig. 5 The comparison of chromophores' lifetimes at different states under different environments. Black dot represents the BNMA's lifetime, the red stand for the lifetimes of (LDHs/BNMA@PVS)_n MTFs, the blue represent the lifetimes of (MMT/BNMA@PVA)_n MTFs, and the dark green show the lifetimes of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs. IE is stands for isolation effect, and EME is stands for electronic microenvironment.

3.3 Fabrication of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs

A mixed aqueous nitrate solution (Mg/Al molar ratio equals 2.0) was prepared, and the concentration of Mg²⁺ was 0.8 mol L⁻¹. The solution of sodium hydroxide (2.4 mol L⁻¹) was mixed with the salt solution at the same rate with vigorous stirring. Then the suspension was stirred at 80 °C for 24 h under nitrogen gas flow. The precipitate was centrifuged, washed with hot distilled water and dried under vacuum at 60 °C.

The product (0.1 g) LDHs was mixed with 100 mL formamide in a flask, which was tightly sealed after purging with nitrogen gas. The mixture was vigorously shaken by a mechanical shaker at a speed of 160 rpm for 2 days. The upper suspension with exfoliated LDHs nanosheets were obtained after centrifugation at 10 000 rpm for 10 min. The MMT powder (1 g) was dissolved in 1000 mL distilled water. After vigorous stirring for 4 weeks, the insoluble fraction was allowed to deposit for 24 h and the suspension with exfoliated MMT nanosheets was collected for subsequent use. Quartz slides (1.5 × 1.5 cm²) were cleaned in a "piranha" solution (H₂SO₄ : H₂O₂ = 3 : 1 in volume), and then thoroughly rinsed with distilled water and dried under nitrogen flow. PVA was dissolved in distilled water to obtain 1 wt% aqueous solution, the BNMA (1 g) was dissolved in 100 mL of distilled water, then the solution of BNMA and PVA were mixed (1 : 1 in volume) to form BNMA@PVA solution, which had 0.5 g L⁻¹ of BNMA. The heterogeneous thin films were fabricated by applying a cyclic repetition of the following steps: (a) immersed the quartz slide into exfoliated MMT solution for 5 min, then thoroughly rinsed it with distilled water and dried it at room temperature; (b) dipped it into an aqueous solution of BNMA@PVA for 5 min, then thoroughly rinsed it with distilled water and dried it at room temperature; (c) dipped it into exfoliated LDHs suspension for 5 min, then rinsed it with distilled water and dried it as mentioned above; (d) dipped it into an aqueous solution of BNMA@PVA for 5 min, then washed with distilled water and dried it. All these procedures were repeated as necessary to obtain the desired number of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n.

3.4 Fabrication of (MMT/BNMA@PVA)_n MTFs

The processes of fabrication of (MMT/BNMA@PVA)_n is similar to (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n, except for the aqueous nanosheets solution of LDHs.

4. Conclusions

In brief, this work proposes a new method to assemble a novel luminescent MTFs with ultra-prolonged lifetime, as the chromophores were confined in the oppositely-charged inorganic layer hosts. It successfully demonstrates that the EME is sufficiently beneficial to enhancing the lifetimes of MTFs. Therefore, the as-fabricated MTFs are expected to have considerable flexibility and be potential for designing, constructing and investigating novel optoelectrical devices. Further work is going on with the research on lifetime of various luminescent

guests imbedded in a series of different LDHs/MMT nanosheets with EME.

Acknowledgements

This work was supported partially by the National Natural Science Foundation of China (Grant no. 40802013), Key Projects in the National Science & Technology Pillar Program (Grant no. 2006BAD10B04), the Fundamental Research Funds for the Central Universities (Grant no. 2011YXL058).

Notes and references

- W. Samuel Thomas III, D. J. Guy and M. S. Timothy, *Chem. Rev.*, 2007, **107**, 1339.
- L. Jukka, S. Mikko, V. Antti, A. Timo, P. Janika, K. Natalia and K. Jouko, *J. Am. Chem. Soc.*, 2001, **123**, 6083.
- C. A. Strassert, C. H. Chien, M. D. G. Lopez, D. Kourkoulos, D. Hertel, K. Meerholz and D. C. Luisa, *Angew. Chem., Int. Ed.*, 2011, **50**, 946.
- Q. S. Zhang, T. Komino, S. P. Huang, S. Matsunami, K. Goushi and C. Adachi, *Adv. Funct. Mater.*, 2012, **22**, 2327.
- M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, *Chem. Soc. Rev.*, 2009, **38**, 1330.
- J. Schmidtke, W. Stille, H. Finkelmann and S. T. Kim, *Adv. Mater.*, 2002, **14**, 746.
- Q. L. Niu, Y. Zhou, L. Wang, J. B. Peng, J. Wang, J. Pei and Y. Cao, *Adv. Mater.*, 2008, **20**, 964.
- J. Piris, N. Kopidakis, D. C. Olson, S. E. Shaheen, D. S. Ginley and G. Rumbles, *Adv. Funct. Mater.*, 2007, **17**, 3849.
- K. M. Jeremiah, R. P. Mauricio, W. David, A. Nisha, S. S. Kirk and R. R. John, *Langmuir*, 2005, **21**, 10123.
- A. L. Igor, K. Jinsang and M. S. Timothy, *J. Am. Chem. Soc.*, 1999, **121**, 1466.
- S. R. Amrutha and M. Jayakannan, *J. Phys. Chem. B*, 2008, **112**, 1119.
- C. Xia and R. C. Advincula, *Macromolecules*, 2001, **34**, 5854.
- T. Q. Nguyen, J. J. Wu, V. Doan, B. J. Schwartz and S. H. Tolbert, *Science*, 2000, **288**, 652.
- A. P. Clark, K. F. Shen, Y. F. Rubin and S. H. Tolbert, *Nano Lett.*, 2005, **5**, 1647.
- M. Toshiki, S. Hiroyuki and A. Koji, *Nat. Mater.*, 2005, **4**, 685.
- Y. Sagara and T. Kato, *Nat. Chem.*, 2009, **1**, 605.
- X. L. Luo, J. N. Li, C. H. Li, L. Q. Heng, Y. Q. Dong, Z. P. Liu, Z. S. Bo and B. Z. Tang, *Adv. Mater.*, 2011, **23**, 3261.
- T. Mutai, H. Satou and K. Araki, *Nat. Mater.*, 2005, **4**, 685.
- P. J. Sideris, U. G. Nielsen, Z. H. Gan and C. P. Grey, *Science*, 2008, **321**, 113.
- D. H. Park, S. J. Hwang, J. M. Oh, J. H. Yang and J. H. Choy, *Prog. Polym. Sci.*, 2013, **38**, 1442.
- M. Ikeda, T. Yoshii, T. Matsui, T. Tanida, H. Komatsu and I. Hamachi, *J. Am. Chem. Soc.*, 2011, **133**, 1670.
- M. T. Liu, M. F. Pu, H. W. Ma, Y. F. Hu, X. J. Liu and X. Pang, *Polym. Compos.*, 2011, **32**, 1002.
- Y. Tokunaga, N. Furukawa, H. Sakai, Y. Taguchi, T. H. Arima and Y. Tokura, *Nat. Mater.*, 2009, **8**, 558.

- 24 A. Bera, H. Y. Peng, J. Lourembam, Y. D. Shen, X. W. Sun and T. Wu, *Adv. Funct. Mater.*, 2013, **23**, 4977.
- 25 L. Wang, I. Meric, P. Y. Huang, Q. Gao, Y. Gao, H. Tran, T. Taniguchi, K. Watanabe, L. M. Campos, D. A. Muller, J. Guo, P. Kim, J. Hone, K. L. Shepard and C. R. Dean, *Science*, 2013, **342**, 6158.
- 26 X. Y. Dong, L. Wang, D. Wang, C. Li and J. Jin, *Langmuir*, 2012, **28**, 293.
- 27 V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano and J. N. Coleman, *Science*, 2013, **340**, 1420.
- 28 Z. P. Liu, R. Z. Ma, M. Osada, N. Iyi, Y. Ebina, K. K. Takada and T. Sasaki, *J. Am. Chem. Soc.*, 2006, **128**, 4872.
- 29 L. Li, R. Z. Ma, Y. Ebina, N. Iyi and T. Sasaki, *Chem. Mater.*, 2005, **17**, 4386.
- 30 P. Podsiadlo, A. K. Kaushik, E. M. Arruda, A. M. Waas, B. S. Shim, J. D. Xu, H. Nandivada, B. G. Pumplin, J. Lahann, A. Ramamoorthy and N. A. Kotov, *Science*, 2007, **318**, 80.
- 31 V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano and J. N. Coleman, *Science*, 2013, **340**, 1420.
- 32 S. Huang, X. Cen, H. D. Peng, S. Z. Guo, W. Z. Wang and T. X. Liu, *J. Phys. Chem. B*, 2009, **113**, 15225.
- 33 D. M. Xu, M. Y. Guan, Q. H. Xu and Y. Guo, *J. Hazard. Mater.*, 2013, **262**, 64.
- 34 H. J. Li, G. Zhu, Z. H. Liu, Z. P. Yang and Z. L. Wang, *Carbon*, 2010, **48**, 4391.
- 35 Q. Wang and D. O'Hare, *Chem. Rev.*, 2011, **112**, 4124.
- 36 D. P. Yan, J. Lu, J. Ma, M. Wei, D. G. Evans and X. Duan, *Angew. Chem., Int. Ed.*, 2011, **50**, 720.
- 37 F. Leroux and C. Taviot-Gueho, *J. Mater. Chem.*, 2005, 36258.
- 38 J. L. Gunjekar, T. W. Kim, H. N. Kim, I. Y. Kim and S. J. Hwang, *J. Am. Chem. Soc.*, 2011, **133**, 14998.
- 39 D. P. Yan, J. Lu, J. Ma, S. H. Qin, M. Wei, D. G. Evans and X. Duan, *Angew. Chem., Int. Ed.*, 2011, **50**, 7037.
- 40 D. P. Yan, J. Lu, L. Chen, S. H. Qin, J. Ma, M. Wei, D. G. Evans and X. Duan, *Chem. Commun.*, 2010, 5912.
- 41 D. P. Yan, J. Lu, M. Wei, J. B. Han, J. Ma, F. Li, D. G. Evans and X. Duan, *Angew. Chem., Int. Ed.*, 2009, **48**, 3073.
- 42 D. P. Yan, J. Lu, J. Ma, M. Wei, X. R. Wang, D. G. Evans and X. Duan, *Langmuir*, 2010, **26**, 7007.