SDBS@BaSO$_4$: an efficient wastewater-sorbing material†

Jing Lin and Hong-Wen Gao*

Received 2nd March 2009, Accepted 27th April 2009
First published as an Advance Article on the web 6th May 2009
DOI: 10.1039/b904303a

A new type of porous material as a highly-effective adsorbent was synthesized by a template-free hybridisation of sodium dodecyl benzenesulfonate (SDBS) with barium sulfate; it simultaneously adsorbed cationic dye and persistent organic pollutants *via* charge attraction and hydrophobic stacking.

A great deal of concentrated industrial wastewater containing toxic chemicals, *e.g.* aromatic amines, persistent organic pollutants (POPs) produced from the dye, pesticide and fine chemical industries, is not treated effectively and is discharged into aquatic environments, especially in developing countries. Dye pollutants are an important source of environmental contamination. Over 7×10^5 tonnes of dyes are produced annually and over 5% are discharged into wastewaters from textile industries.[1] In recent years, a number of dye/drug/electronic plants located in the Yangtze Delta Area valley have seriously influenced the water quality of Taihu Lake, which is an important drinking water source for the most developed region of China.[2] Organic wastewaters, especially those with dyes and POPs, offer considerable resistance to biodegradation because synthetic aromatic compounds containing a variety of functional groups are resistant to light, heat and oxidizing agents. Many may cause allergy, dermatitis, skin irritation, cancer and mutations in humans.[3] Adsorption, a typical physical treatment, is simple and effective for removing organic contaminants from wastewater. However, low adsorption capacities, long equilibration times and difficulties in replication have restricted the use of conventional adsorbents.[4] Recently, attention has focused on synthetic adsorbents with higher adsorption capacities.[5]

Inorganic/organic hybridization is employed to synthesize functional materials for use in *e.g.* sensors, catalysts, thin films and solar cells[6] but is seldom considered for pollution control, *e.g.* treating industrial wastewater. The precipitation of sodium dodecyl benzenesulfonate (SDBS; R) by Ba^{2+} and SO_4^{2-} may be expressed as the reaction: $N\,R^- + SO_4^{2-} + Ba^{2+} \rightarrow [(BaSO_4)R_N]^{N-}\downarrow$, where N is the saturating number of SDBS molecules associated with BaSO$_4$. When the molarity of Ba^{2+} (SO_4^{2-}) is over twice that of SO_4^{2-} (Ba^{2+}), SO_4^{2-} (Ba^{2+}) may react completely (refer to ESI,† Fig. S1). Very little SDBS hybrid is formed if the SO_4^{2-} concentration is excessive (refer to ESI, † Fig. S2). In contrast, correspondingly more is formed if the molar amount of Ba^{2+} is 1.5–3.5 times that of SO_4^{2-} (refer to ESI, † Fig. S2–3). The least amount of SDBS is formed when the addition sequence is SO_4^{2-}–Ba^{2+}–SDBS but the greatest amount is formed when the sequence is SO_4^{2-}–SDBS–Ba^{2+} (Fig. 1A). This is because SDBS is adsorbed only on the BaSO$_4$ particle surfaces in the former case. Ba^{2+} reacts first with SDBS if SO_4^{2-} is added last. By varying the addition of SDBS (Fig. 1B), N of SDBS remains at a maximal constant value, 0.082, when the initial SDBS:SO_4^{2-} molar ratio is over 0.15:1 (Fig. 1C), *i.e.* approximately 12 BaSO$_4$ molecules are loaded per SDBS. The BaSO$_4$-SDBS hybrid material was synthesized using the addition sequence SO_4^{2-}–SDBS–Ba^{2+} and the initial molar Ba^{2+}:SO_4^{2-}:SDBS ratio was 1.5:1:0.2. Liquid and powder forms of the BaSO$_4$-SDBS hybrid material were prepared and the composition was determined by XRF, C and S elemental analysis and spectrophotometry (refer to ESI, † text and Fig. S4). The Ba^{2+}:SO_4^{2-}:SDBS molar ratio in the product was 1:(0.95 ± 0.05):(0.10 ± 0.02). Thus, the addition of SDBS did not affect the formation of BaSO$_4$, *i.e.* SDBS was bound by electrostatic interaction.[7] Approximately 10 BaSO$_4$ were associated with one SDBS. The TGA results show marked thermal decomposition of SDBS between 400 and 500 °C, incurring 45% weight loss (Fig. 1D). This is attributed to volatilization of the alkyl chain. The weight loss of the hybrid material over the same temperature range was 6%. Thus, 13% of the SDBS is included in the hybrid material, which is identical with the above result.

From the SEM images, the individual BaSO$_4$ particles are 80–120 nm in size (Fig. 2A) but they aggregate into huge particles mostly exceeding 10 μm (refer to ESI, † Fig. S5A and Fig. S6A). The BaSO$_4$-SDBS hybrid particles form loose aggregates, in which many small hybrid particles are cemented together (Fig. 2B). Most of the aggregates are larger than 0.5 μm (refer to ESI, † Fig. S5B). It is clear that the addition of SDBS in the solution plays an important role in controlling size and morphology of BaSO$_4$ particles formed. The presence of SDBS results in a remarkable decrease in the sizes of BaSO$_4$ particles. Also, BaSO$_4$-SDBS particles are highly dispersed in their solid form (refer to ESI, † Fig. S6B), and aggregation of these particles results in a porous material (Fig. 2B). In contrast, aggregation of BaSO$_4$ particles in the absence of SDBS leads to a solid material (Fig. 2A). This may be because when the long alkyl chain ($-C_{12}H_{25}$) of SDBS became bound to the BaSO$_4$ nanoparticles, further growth was inhibited. From the TEM images of a material fragment (refer to ESI, † Fig. S6C–E), irregular regions were always attached to regular crystalline regions. Since the molar ratio of Ba to S was 0.6:1 in region a of the EDX and 1:1 in region b (Fig. 2C), region a contained much SDBS and little BaSO$_4$ while region b was filled with BaSO$_4$. In addition, many irregular lines with rings were seen in region a (Fig. 2C), in contrast to TEM of BaSO$_4$-only fragments (refer to ESI, † Fig. S6F–H), so they indicate SDBS sites.[8] This confirmed that the SDBS was hybridized to the BaSO$_4$ particles to form a loose porous material. Furthermore, the BET specific surface areas (SSA) of these three kinds of materials were determined to be 8.06 m^2/g for BaSO$_4$-only, 25.1 m^2/g for BaSO$_4$-SDBS hybrid material and only 1.22 m^2/g for BaSO$_4$ surface modifying SDBS. The SDBS-loading into BaSO$_4$ obviously increased the SSA of the hybrid

---

State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai, 200092, China. E-mail: hwgao@tongji.edu.cn; Fax: (+) 86-21-65988598

† Electronic supplementary information (ESI) available: Experimental detail including the apparatus and instrumentation and Fig. S1–S13. See DOI: 10.1039/b904303a

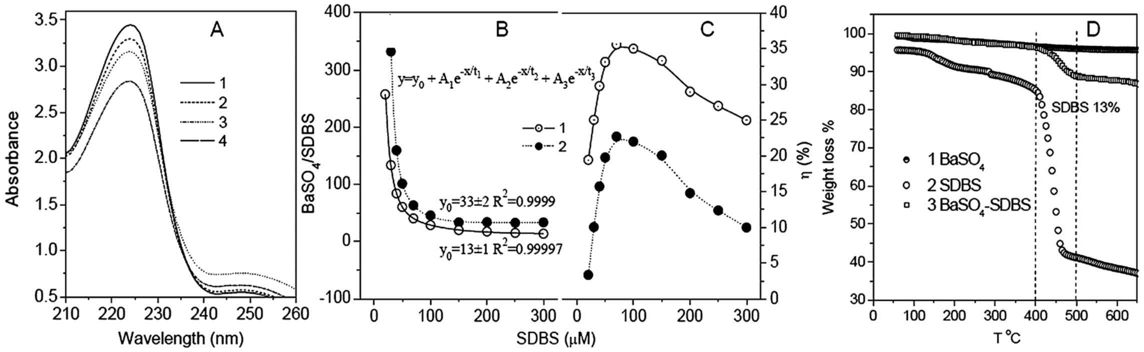

Fig. 1 A: Effect of the sequence of addition of the reactants on the SDBS hybrid. 1: SDBS only; 2: Ba^{2+}–SO_4^{2-}–SDBS, 3: Ba^{2+}–SDBS–SO_4^{2-}, 4: SO_4^{2-}–SDBS–Ba^{2+}, where 1.0 mM Ba^{2+}, 1.5 mM SO_4^{2-} and 0.30 mM SDBS were added. The third reactant was added after the others had been mixed and allowed to react for 10 min. All the liquids were centrifuged at 8000 rpm for 10 min and the supernatants were examined. B, C: Effect of SDBS concentration on the hybridization of SDBS in $BaSO_4$ particles. B: Molar $BaSO_4$:SDBS ratio. C: The hybridization rate (η) of SDBS. 1: total inclusion in the Ba-SDBS particles and 2: inclusion in $BaSO_4$-only particles. When the particles were washed repeatedly with deionized water, Ba^{2+} was released from the Ba-SDBS particles into the solution but SDBS remained in the $BaSO_4$ particles. This was confirmed by determining the composition of the adsorbent. D: TGA of $BaSO_4$-only (1), SDBS (2) and $BaSO_4$-SDBS hybrid material (3).

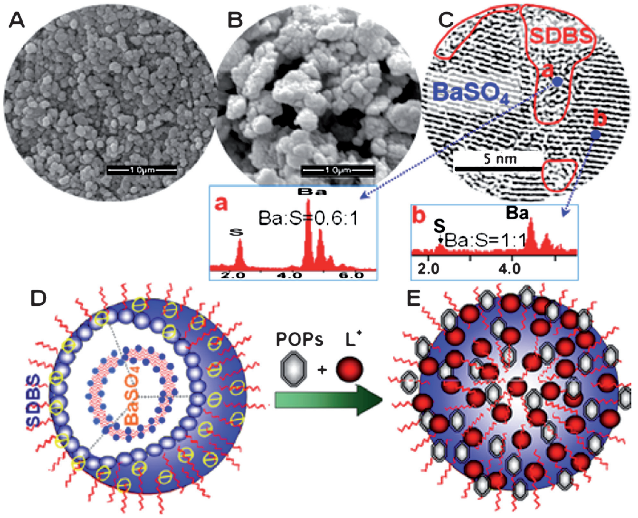

Fig. 2 SEM of $BaSO_4$-only (A) and $BaSO_4$-SDBS hybrid material (B) and TEM of the material with both a and b measurement points for the EDX analysis of S and Ba elements (C), where both brightness and contrast were adjusted to remove the interference of substrate from the original photograph. Cartoon illustration of the formed particle structure (D) and simultaneous captures of the cationic dye (L^+)-POPs mixture (E).

material while the SDBS-modified $BaSO_4$ surface caused the blocking of holes. This confirmed that the $BaSO_4$-SDBS hybrid formed a porous material. XRD of the material confirmed that the only inorganic substance in the hybrid material was $BaSO_4$ in the form of crystals with small particle size (refer to ESI, † Fig. S7).

Speculatively, the SDBS-hybridizing mechanism may be as follows. During growth of the hybrid $BaSO_4$-SDBS particles, SDBS enters the colloidal electric bilayer and its $-SO_3^-$ group is electrostatically attracted to the $BaSO_4$;[7] SDBS then forms a micelle aggregate shell (Fig. 2D). The $-SO_3^-$ groups on the SDBS outer surface again attract Ba^{2+} and then SO_4^{2-} captures the Ba^{2+} to form a $BaSO_4$ outer shell. Thus, $BaSO_4$ particle growth forms an inorganic encircling shell and then SDBS binds to this shell to form an organic encircling shell (Fig. 2E). Thus, the organic SDBS layer is sandwiched between $BaSO_4$ layers. In comparison to other (templated) hybridization methods,[9] such a simple chemical co-precipitation is more practical for producing a functional material. The hybrid material carries many negative charges when dispersed in water, so it may certainly be used to adsorb organic cations. The material still has a hydrophobic shell formed by the adsorption of SDBS on to the particle surface (Fig. 2E) and may therefore capture hydrophobic organic chemicals *e.g.* carcinogenic POPs.

The $BaSO_4$-SDBS hybrid material was used to treat four dye solutions: reactive brilliant red X-3B, weak acid green GS, methylene blue (MB) and basic violet 16 (BV). $BaSO_4$-only and $BaSO_4$-SDBS surface-modified materials were compared (refer to ESI, † Fig. S8). Neither anionic dye was significantly captured. MB and BV (L) were most effectively removed by the hybrid adsorbent while the surface-modified material showed low efficacy and the $BaSO_4$-only material had no effect at all. This selectivity shows that the adsorption of cations results from electrostatic attraction. From plots of γ *vs.* c_{L0} (Fig. 3A) (γ = binding number of L and c_{L0} = initial molarity of L),

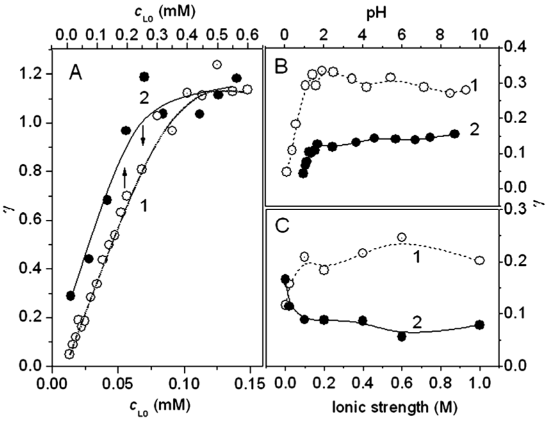

Fig. 3 A: Adsorption of MB and BV on the $BaSO_4$-SDBS hybrid adsorbent (0.2%). 1: MB and 2: BV. B: Effect of pH. 1: 0.040 mM MB and 0.020% adsorbent and 2: 0.040 mM BV and 0.030% hybrid adsorbent were added. C: Effect of ionic strength. 1: 0.010 mM MB and 0.01% adsorbent and 2: 0.030 mM BV and 0.030% hybrid adsorbent were added.

the γ values of MB and BV to SDBS achieve a constant maximum, 1. The saturating amounts of BV or MB adsorbed were just sufficient to neutralize all the negative charges on the particles, a relationship expressed as: $[(BaSO_4)_{10}(SDBS)]^- + L^+ = L[(BaSO_4)_{10}(SDBS)]\downarrow$ This again demonstrates charge pairing. Even if the SDBS is located inside the $BaSO_4$ particle, the adsorption capacity of the material is not affected, *i.e.* it depends on the number of SDBS molecules hybridized. The adsorption of MB and BV decreased when the pH was below 2 (Fig. 3B). The reason is that the protonation of SDBS reduced the charge attraction of the material. Variation of ionic strength affected the adsorption of BV and MB on the material (Fig. 3C) and increase of temperature led to decrease of adsorption of BV and MB (refer to ESI, † Fig. S9). These facts indicated that the electrostatic attraction occurred between BV or MB and the material.[10] The adsorption time indicated that equilibration was rapid (refer to ESI, † Fig. S10); activated carbon may be effective but its equilibration time is over 2 h.

Four POPs—phenanthrene (Phe), fluorene (Flu), biphenyl (Bip) and naphthalene (Nap)—were used to evaluate the performance of the hybrid adsorbent. In contrast to the cationic dyes, POP adsorption does not flatten out gradually (Fig. 4A). From the plots of $c_{L/p}$ *vs.* c_L ($c_{L/p}$ = mass concentration of POP in adsorbent and c_L = concentration in aqueous phase), POPs obeyed the lipid-water partition law. Hydrophobic stacking may occur between the alkyl chain of SDBS and the POP. The partition coefficients (K_{pw}) in the hybrid adsorbent are in direct proportion to their K_{ow}[11] values (Fig. 4B). As with other hydrophobic adsorbents, *e.g.* membranes, the amount of POPs captured depends on the lipophilicity. From the slope, approximately 5 g of the hybrid adsorbent is equivalent to 1 g of octanol.

A BV solution mixed with Phe was treated with the hybrid adsorbent. The γ value of BV approached 1 and the gradient of Phe (5924 L/kg) approached its K_{pw} (Fig. 5). Concomitant application of cationic and hydrophobic organic substances does not affect the adsorption of either (Fig. 2E). The material is also adaptable to chemical wastewater treatment.

Two kinds of organic wastewaters were treated. The color of the dye-containing wastewater obviously decreased with increasing amounts of adsorbent (Fig. 6A); decolorization was over 99% when 2% adsorbent was added. The chemical oxygen demand (COD) decreased from 3800 mg/L to only 350 mg/L with 2% adsorbent and then increased to 810 mg/L at 6% adsorbent (refer to ESI, † Fig. S11A). This may be attributed to the leaching of SDBS from the hybrid material (refer to ESI, † Fig. S12). The hybrid material is more suitable for treating concentrated dye wastewater. Other wastewaters were treated with the adsorbent. Four chlorobenzene compounds—*o*-, *p*- and *m*-dichlorobenzenes and 1,2,4-trichlorobenzene—were examined (refer to ESI, † Fig. S13). Their removal increased from 60 to 80% with increasing amounts of adsorbent (refer to ESI, † Fig. S11B), but less dichlorobenzene than trichlorobenzene was captured (Fig. 6B). This may be attributed to the stronger lipophilicity of trichlorobenzene.

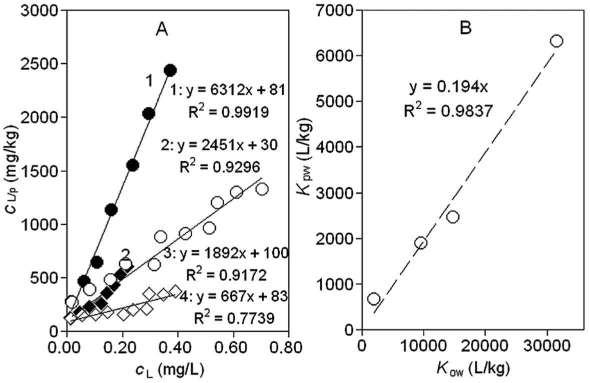

Fig. 4 A: Adsorptions of POPs. From 1 to 4: Phe, Flu, Bip and Nap. $BaSO_4$-SDBS hybrid adsorbent (0.2%) was added. B: Correlation between K_{ow} and K_{pw} of POPs.

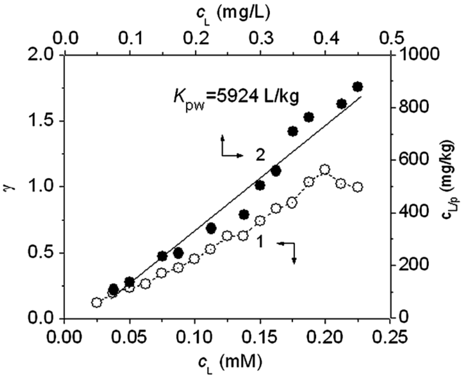

Fig. 5 Adsorption of the BV-Phe mixture when the $BaSO_4$-SDBS hybrid adsorbent (0.2%) was added. 1: BV; 2: Phe.

In conclusion, template-free preparation of the $BaSO_4$-SDBS hybrid material is simple with readily available reactants, ease of application and low cost. Comparison with conventional adsorbents and flocculants shows notable features *e.g.* high sorption capacity, rapid equilibration, no return of color and less leaching. Unlike other inorganic skeletons,[12] barium sulfate has seldom been selected in

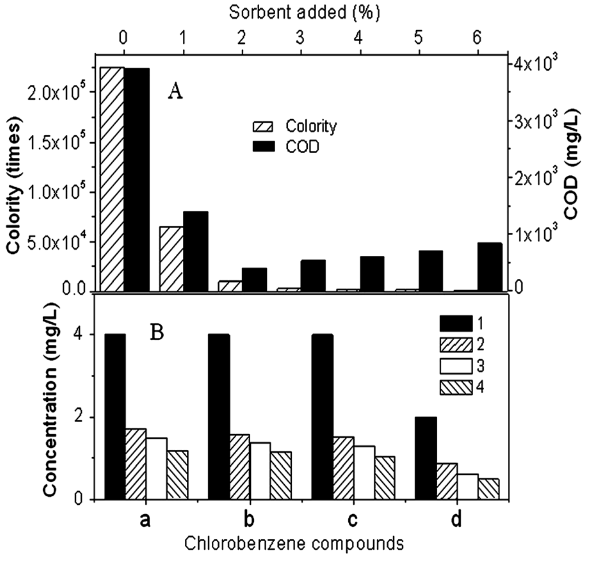

Fig. 6 A: Treatment of a dye wastewater with 230 000 times the color density and 3800 mg/L COD. the hybrid adsorbent was added from 1 to 6%. B: Treatment of a chlorobenzene chemical wastewater. a: *o*-dichlorobenzene, b: *p*-dichlorobenzene, c: *m*-dichlorobenzene and d: 1,2,4-trichlorobenzene. The hybrid adsorbent was added from 0 (column 1), 0.01 (2) and 0.05 (3) to 0.10% (4).

mineralization reactions.[13] However, it is better suited to wastewater treatment owing to its insolubility in water and acid resistance. Thus, not only was the SDBS loaded on to the barium sulfate not released, but also the hybrid adsorbent may readily be replicated in acidic media from dye-contaminated sludge.

Acknowledgements

We thank the State Key Laboratory Foundation of Science and Technology Ministry of China (Grant No. PCRRK08003) and the National Key Technology R&D Program of China (No. 2008BAJ08B13) for financially supporting this work.

Notes and references

1 G. McMullan, C. Meehan, A. Conneely, N. Kirby, T. Robinson, P. Nigam, I. M. Banat, R. Marchant and W. F. Smyth, *Appl. Microbiol.Biotechnol.*, 2001, **56**, 81; L. Laasri, M. K. Elamrani and O. Cherkaoui, *Env. Sci. Pollut. Res.*, 2007, **14**, 237; R. Gong, M. Li, C. Yang, Y. Suna and J. Chen, *J. Hazard. Mater.*, 2005, **121B**, 247.

2 M. Yang, J. W. Yu, Z. L. Li, Z. H. Guo, M. Burch and T. F. Lin, *Science*, 2008, **319**, 158a.

3 C. Sudipta, C. Sandipan, P. C. Bishnu, R. D. Akhil and K. G. Arun, *J. Colloid Interf. Sci.*, 2005, **288**, 30; J. P. Maloney, A. C. Halbower, B. F. Fouty, K. A. Fagan, V. Balasubramaniam, A. W. Pike, P. V. Fennessey and M. N. Moss, *New Engl. J. Med.*, 2000, **343**, 1047.

4 G. Crini and P. M. Badot, *Prog. Polym. Sci.*, 2008, **33**, 399; M. Gonzalez, M. D. Mingorance, L. Sanchez and A. Pena, *Env. Sci. Pollut. Res.*, 2008, **15**, 8.

5 B. Pan, W. Zhang, H. Qiu, Q. Zhang, Q. Zhang and S. Zheng, *Environ. Sci. Technol.*, 2008, **42**, 7411.

6 Y. Takahashi, H. Kasai, H. Nakanishi and T. M. Suzuki, *Angew. Chem. Int. Ed.*, 2006, **45**, 913; Y. Zhou, M. Kogiso and T. Shimizu, *J. Am. Chem. Soc.*, 2009, **131**, 2456; C. S. Xu, H. Kim, H. Yang and C. C. Hayden, *J. Am. Chem. Soc*, 2007, **129**, 11008.

7 X. Zhao, J. Yu, H. Tang and J. Lin, *J. Colloid Interf. Sci.*, 2007, **311**, 89; W. Ni, Z. Yang, H. Chen, L. Li and J. Wang, *J. Am. Chem. Soc.*, 2008, **130**, 6692; H. P. Cong and S. H. Yu, *Adv. Funct. Mater.*, 2007, **17**, 1814.

8 E. Nakamura, M. Koshino, T. Tanaka, Y. Niimi, K. Harano, Y. Nakamura and H. Isobe, *J. Am. Chem. Soc.*, 2008, **130**, 7808; M. Koshino, T. Tanaka, N. Solin, K. Suenaga, H. Isobe and E. Nakamura, *Science*, 2007, **316**, 853.

9 Q. F. Zhang, T. P. Chou, B. Russo, S. A. Jenekhe and G. Z. Cao, *Angew.Chem. Int. Ed.*, 2008, **47**, 2402; S. Minakata, R. Tsuruoka and M. Komatsu, *J. Am. Chem. Soc.*, 2008, **130**, 1536.

10 F. F. Chen, S. L. Wang, X. H. Liu, R. Xu and H. W. Gao, *Anal. Chim. Acta*, 2007, **596**, 55; H. W. Gao, Q. Xu, L. Chen, S. L. Wang, Y. Wang, L. L. Wu and Y. Yuan, *Biophys. J.*, 2008, **94**, 906.

11 X. L. Qu, X. R. Wang and D. Q. Zhu, *Environ. Sci. Technol.*, 2007, **41**, 8321; B. S. Jeong, M. M. Wander, S. Kleineidamaq, P. Grathwohl, B. Ligouis and C. J. Werth, *Environ. Sci. Technol.*, 2008, **42**, 1458.

12 K. Hou, Q. Song, D. Nie, F. Li, Z. Bian, L. Liu, L. Xu and C. Huang, *Chem. Mater.*, 2008, **20**, 3814; S. F. Chen, S. H. Yu, J. Jiang, F. Q. Li and Y. K. Liu, *Chem. Mater.*, 2006, **18**, 115; R. Karinaga, Y. Jeong, S. Shinkai, K. Kaneko and K. Sakurai, *Langmuir*, 2004, **21**, 9398.

13 S. H. Yu, M. Antonietti, H. Colfen and J. Hartmann, *Nano Lett.*, 2003, **3**, 379; J. H. Li, R. Y. Hong, H. Z. Li, J. Ding, Y. Zheng and D. G. Wei, *Mater. Chem. Phys.*, 2009, **113**, 140; B. M. Nagaraja, K. D. Jung, B. S. Ahn, H. Abimanyu and K. S. Yoo, *Ind. Eng. Chem. Res.*, 2009, **48**, 1451; W. Ni, Z. Yang, H. Chen, L. Li and J. Wang, *J. Am. Chem. Soc.*, 2008, **130**, 6692.