

One-step synthesis of yellow-emitting carbogenic dots toward white light-emitting diodes

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Abstract We report herein the synthesis of carbogenic dots (CDs) by a one-step pyrolysis from *N*-acetylcysteine. The as-prepared CDs show excellent dispersibility with particle sizes in the range of 3–5 nm. Under stimulation with blue light, the CDs emit broad yellow fluorescence, which is still rarely reported by now. The optical properties were thoroughly investigated, and we found the CDs exhibit stable fluorescence, high quantum yield, and pH dependence. Moreover, an economical approach for constructing white light-emitting diodes (LEDs) was developed by combining the yellow-emitting CDs with blue GaN-based LED chips. The white LEDs exhibit warm white light with the color coordinates of (0.34, 0.35), very close to the coordinates of balanced white-light emission (0.33, 0.33). These results suggest that the CDs can be a promising candidate as yellow-emitting phosphor for white LEDs.

Introduction

Solid-state optoelectronic devices in the form of light-emitting diodes (LEDs) have been the subject of intense research for years due to their potential applications in backlighting, general illumination, and liquid-crystal

displays of digital cameras, cellular phones, and notebook computers [1–11]. An efficient and commercial route for constructing white LEDs is to combine blue-LED chips with broadband yellow-emitting phosphors, such as $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG:Ce) [2], Sr_3SiO_5 [3, 4], Sr- α -SiAlON:Eu²⁺ [5], and $\text{Ba}_3\text{SiO}_5:\text{Eu}^{2+}$ [6]. However, these phosphors were synthesized with expensive raw materials and high reaction temperature at least over 1200 °C. More recently, semiconductor quantum dots (QDs) for white LEDs have been reported, like trap-rich CdS [7], silica-coated InP/ZnS nanocrystals [8], and CdSe nanocrystals [9–11]. Nevertheless, the fabrication and isolation process of semiconductor QDs often involve the tremendous energy consumption as well as the occurrence of aggregation, photooxidation, and fluorescence diminishing of QDs, along with the intrinsic toxicity and potential environmental hazards, greatly limiting their practical applications.

Recently, carbogenic dots (also called carbon dots, CDs) have been extensively spotlighted to be a promising alternative to traditional toxic metal-based semiconductor QDs because of their excellent properties such as unique fluorescence, photostability, chemical resistance, low toxicity, and good biocompatibility [12–35]. Up to now, a variety of methods have been developed to prepare CDs, such as laser ablation of graphite [13–16], electrochemical oxidation of multiwalled carbon nanotubes or graphite [17, 18], chemical oxidation of carbohydrates or activated carbon [19, 20], separation of candle soot [21, 22], supported synthesis [23, 24], thermal oxidation of suitable precursors [25, 26] or microwave routes [27–29]. Simultaneously, great efforts have been made to exploit the potential applications of fluorescent CDs in bioimaging [30–32], biological labeling [33] and optoelectronic devices [34]. For instance, despite rare reports, CDs have been explored for the application of LEDs. A LED based on CDs' electroluminescence was

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reported by Liu et al. in 2011 [35]. Our previous work has reported that CDs generated from unzipping of poly(styrene-co-glycidylmethacrylate) photonic crystals could be applied in white LEDs [36]. Much work is still needed in this fledgling area, since either most of reported synthesis methods often require elaborate equipment, multi-step procedure, expensive raw materials, complicated and time-consuming isolation or purification, or the obtained products usually exhibit dull blue fluorescence under single-wavelength ultraviolet (UV) excitation or low quantum yields.

Herein, we developed a simple route to fabricate CDs derived from *N*-acetylcysteine (NAC) precursor by a simple pyrolysis process (Fig. 1a). Interestingly, the obtained CDs exhibit unique yellow-emitting fluorescence with quantum yield of 13 %, overcoming the drawback of the dull blue fluorescence of traditional CDs. The PL properties and stability in different solvents and pH conditions were thoroughly investigated. Also, we applied these CDs as yellow phosphor coated on blue-LED chips to produce white LEDs. In comparison with conventional phosphor (YAG:Ce), this new generation of phosphor presents advantages: easy fabrication with lower reaction temperature, lower cost, and lower toxicity. Also, the white LEDs developed herein are more powerful and less-cost than those constructed from CDs with white emission stimulated by UV-LED chips.

Experimental

Materials

Reagent-grade NAC was purchased from Aldrich and used as-received. Reagent-grade cyclohexane, toluene, ethanol, *N,N*-dimethylformamide (DMF) and cyclohexanone were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as purchased. Epoxy resin A and epoxy resin B were purchased from Shenzhen

Gaohejidian Co., Ltd. (China). The commercial blue GaN-based LED chips (peak at 460 nm) were obtained from Lambert Co., Ltd. (China). High-purity water with the resistivity greater than $18 \text{ M}\Omega \text{ cm}^{-1}$ was used in the experiments.

Preparation of CDs

NAC was chosen as the precursor. In a typical process, 0.3 g NAC was directly calcined in a tube furnace at $300 \text{ }^\circ\text{C}$ for 2 h under N_2 flow with a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$. The as-derived carbogenic solid was grinded in a mortar and dispersed in ethanol. The suspension solution of carbogenic solid was sonicated, followed by high-speed centrifugation (12000 rpm, 20 min) to remove large particles. The resultant homogeneous supernatant contained strongly fluorescent CDs, which was kept for further use. The CDs powder was prepared by volatilizing solvent in air.

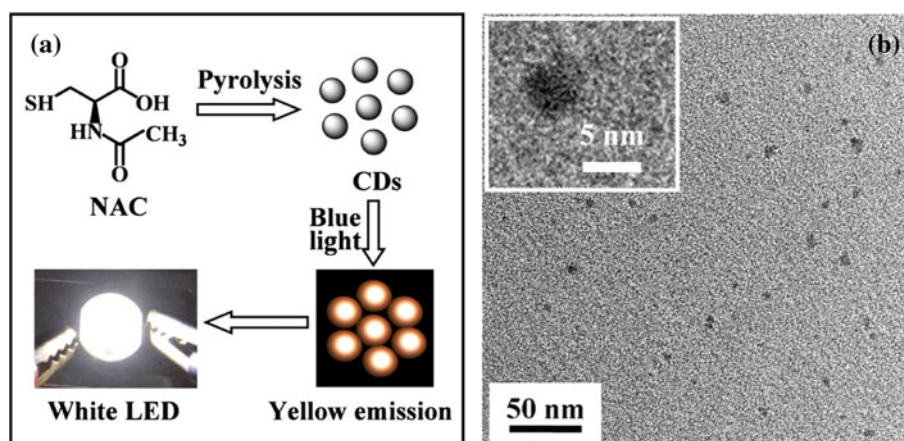
Preparation of the white LEDs

The blue GaN-based LED chips with the peak wavelength centered on 460 nm were used and attached on the bottom of the LED bases. The two threads on LED were prepared to connect to the power supply. Afterward, epoxy resin A and epoxy resin B were mixed with the CDs phosphor and put in a vacuum chamber to remove the bubbles. About $30 \mu\text{L}$ of the phosphor mixture was dispensed into the conventional cup-shaped void on the LED chip and thermally cured at $120 \text{ }^\circ\text{C}$ for 1 h. Finally, the optical lenses were placed on the bottom of the LED chips.

Characterization

High-resolution transmission electron microscope (HRTEM) observation was performed with a JEOL JEM-2010 transmission electron microscope. X-ray diffraction (XRD) was

Fig. 1 **a** Schematic representation of the formation of CDs and their application in white LEDs. **b** HRTEM image of fluorescent CDs. *Inset*: the enlargement HRTEM image of an individual CD



performed on a Rigaku Corporation D/max-rC rotating anode X-ray powder diffractometer using a copper target. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 FT-IR spectrometer. Ultraviolet–visible (UV–vis) absorption spectra were taken with a Perkin-Elmer Lambda 900 UV–vis spectrometer. PL measurements were carried out on a Varian Cary Eclipse spectrophotometer. Time-correlated single-photon counting (TCSPC) data were performed on SLM 48000 spectrofluorometer using a 400 nm laser as the excitation source. The element analysis of the product was measured on an Elementar Vario EL-III (Germany). The emission spectrum of the white LED was measured by a USB4000 Miniature Fiber Optic Spectrometer of Ocean Optics. All the spectra were measured at room temperature.

Results and discussion

The schematic representation of the formation of CDs is illustrated in Fig. 1a. The calcination of NAC at 300 °C for 2 h under carrier gas of nitrogen directly obtain CDs with bright yellow fluorescence under blue light, which could be used as the yellow phosphor to apply in producing white LEDs with blue-LED chips. This one-step route avoids time-consuming multi-step procedures and complicated particles separation step, opening a simple rapid way to fabricate CDs with novel photoluminescent properties.

Figure 1b shows the HRTEM image of CDs. The as-prepared CDs have well dispersion with particle size of 3–5 nm. No crystalline lattices were observed in the HRTEM measurement. XRD pattern of the CDs displays a broad diffraction peak located at $2\theta = 24^\circ$ (Fig. 2b), which further confirms an amorphous nature of the CDs [37]. FT-IR spectra were acquired to determine the surface chemistry of as-prepared CDs (Fig. 2a). The spectrum of CDs shows obvious peaks around 3437 and 1634 cm^{-1} , which can be ascribed to the stretching vibrations of O–H and C=O, respectively. In addition, the absorption peaks in the spectrum of CDs around 1285 and 1070 are referred to

C–O and C–N stretching vibrations. However, the characteristic absorption peaks around 1717 and 2547 cm^{-1} for carboxylate group and S–H stretching vibration observed in the spectrum of NAC are disappeared in the spectrum of CDs. Although there are no data in the literature describing in detail the pyrolysis of NAC, we speculate that the carboxyl and sulfhydryl in NAC molecules had decomposed during high-temperature treatment. The elemental analysis reveals the composition of CDs as follows: C 55.7 wt%, H 4.7 wt%, N 14.6 wt%, S 7.2 wt%, O (calculated) 17.8 wt%. Compared to the parent precursor, the contents of H, S, and O are remarkably reduced during the pyrolysis process.

The as-prepared CDs exhibit excellent photoluminescent properties. Figure 3 depicts the UV–vis absorption and PL spectra of CDs in ethanol. An intense absorption characteristic peak at ~ 320 nm is observed in the UV–vis absorption spectrum. As frequently reported, the PL emission wavelength of the CDs is dependent on the excitation, with PL peaks red-shift from 480 to 600 nm by increasing excitation wavelength (λ_{ex}) from 370 to 550 nm. Excited at 460 nm, a PL peak centering at 530 nm with maximum intensity and a full width at half maximum of about 110 nm is observed, suggesting the CDs could exhibit broad yellow fluorescence and are favorable as the yellow phosphor toward white LEDs. Quantum yield was calculated using quinine sulfate in 0.10 M H_2SO_4 solution as the standard [12]. The quantum yield of the as-prepared CDs was determined to be 13 % (see details in Fig. S1 and Table S1). CDs in most cases present quantum yield less than 10 %, and this value is comparable to those for desirable CDs prepared previously [17–29]. It is worth noting that NAC precursor does not exhibit any detectable fluorescence. Thus, the fluorescence in the products should be engendered from the nanoparticles, where a widely recognized explanation is the radiative recombination of excitons at the particle surfaces [13].

Another indication is the fluorescent stability of CDs. Time-resolved fluorescence was performed to access the

Fig. 2 FT-IR spectra (a) and powder XRD pattern (b) of the fluorescent CDs

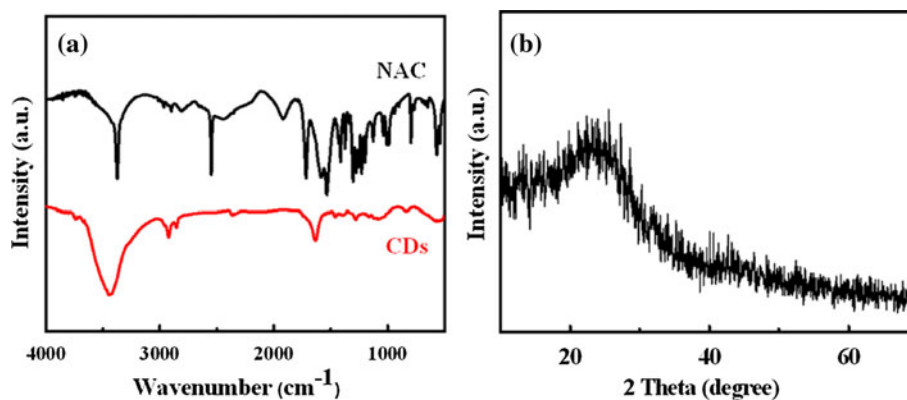


Fig. 3 **a** UV–vis absorption and PL emission spectra of CDs in ethanol. **b** Normalized PL emission spectra of CDs in ethanol at different excitation wavelengths

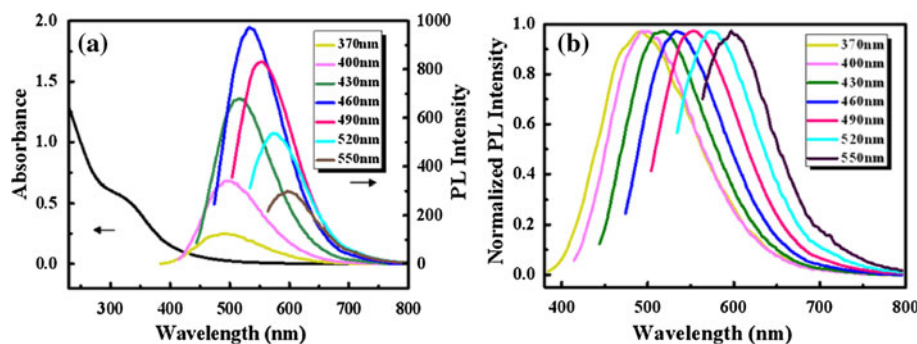
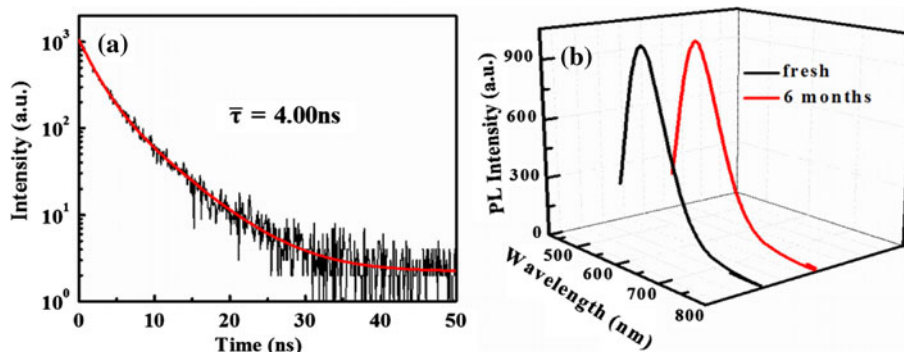


Fig. 4 **a** Time-resolved fluorescence decay curves for ethanol solution of CDs ($\lambda_{ex} = 460$ nm) measured at emission-peak maxima of 530 nm. **b** PL spectra of fresh and 6-month-stored solutions of CDs ($\lambda_{ex} = 460$ nm)



fluorescent lifetime of CDs using TCSPC methodology, as seen in Fig. 4a. The decay lifetime of CDs was evaluated by biexponential fit process [38], using the expression (1)

$$Y(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2) \quad (1)$$

where α_1, α_2 are fractional contributions of time-resolved decay lifetimes τ_1, τ_2 . And, average lifetime $\bar{\tau}$ could be concluded from the Eq. (2)

$$\bar{\tau} = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2} \quad (2)$$

The best fit gives the decay lifetime of 4.00 ns for CDs (see Table 1), similar to those of CDs obtained by other groups [13, 14]. In addition, after being stored under ambient conditions for 6 months, the CDs showed no significant change in PL spectra (see Fig. 4b), revealing the excellent photoluminescent stability of the as-prepared CDs. The excellent PL properties in terms of brightness and stability make the as-prepared benign CDs useful in various applications.

The effect of various organic solvents on the PL spectra of CDs was investigated. Figure 5a shows the different PL intensity of CDs dispersed in cyclohexane, water, toluene, ethanol, DMF, and cyclohexanone, from which we can see

Table 1 Biexponential fit values of the CDs in ethanol

	α_1	τ_1	α_2	τ_2	Average τ
Value	764.31	2.00	290.05	5.81	4.00

that CDs exhibit excellent fluorescence in water and various organic solvents except cyclohexane (see original PL emission spectra in Fig. S2). As evidenced in the FT-IR spectra (Fig. 2a), there are abundant organic functional groups on the surfaces of CDs (–OH, C=O, C–O and C–N). These functional groups confer the CDs with excellent dispersibility in diverse solvents, which might be responsible for the strong PL intensity and is highly desirable for practical applications of CDs.

Figure 5b shows the effect of pH on PL intensity of the CDs in aqueous solution. As depicted in Fig. 5b, the PL intensity of the CDs is pH-dependent. The PL is relatively stable in the pH range of 5–9, while the PL intensity decreased significantly for either a strong acidic or a strong basic solution. Meanwhile, there is an interesting phenomenon that the PL intensity of CDs decreased linearly with the increase of the pH from 9 to 14. These pH-sensitive CDs could be exploited to monitor reactions which may cause a minor change in pH values.

Perhaps more importantly, we directly employed as-prepared solid CDs as the yellow phosphor for incorporation into solid-state lighting applications in the form of white LEDs. As we know, the development of LEDs continues to be a topic of intense interest for their great potential in lighting and display [35]. The prototype white LED was made by coating CDs encased in epoxy resin on the solid-state lighting unit comprised of a blue-LED chip with 460 nm excitation. The light-emissive property of the prototype white LED was investigated. As shown in

Fig. 5 **a** Solvent effect on PL intensity of CDs with the same concentration ($\lambda_{\text{ex}} = 370$ nm). **b** Effect of the solution pH on the PL intensity of CDs in aqueous solution ($\lambda_{\text{ex}} = 370$ nm)

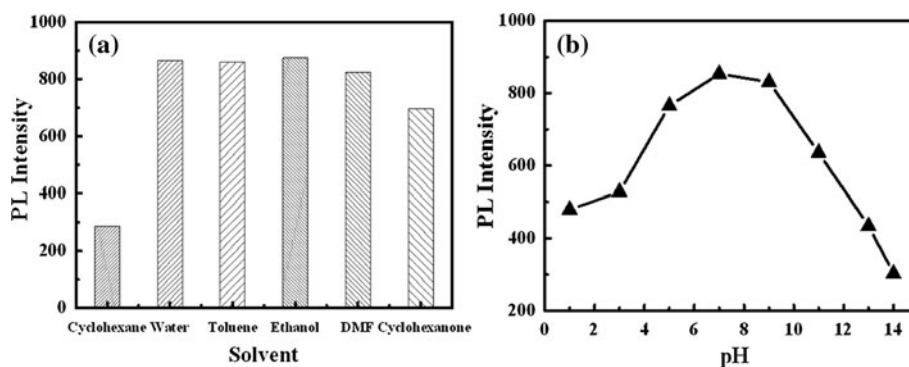


Fig. 6 **a** Emission spectrum of a prototype white LED. **b** The photograph of a prototype white LED operated at 3.0 V. **c** Placement of the LED emission spectrum on the CIE 1931 chromaticity chart

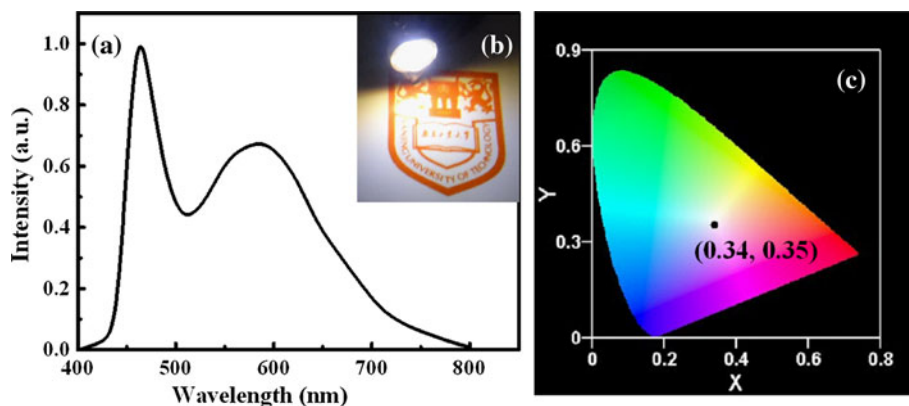


Fig. 6a, the emission spectra of the white LED consists of two emission bands, blue emission centering at 460 nm from the LED chip and broad yellow emission from CDs. These two emission bands are combined to give a spectrum that produces white light. As seen in Fig. 6b, the device provided a bright white illumination. The prepared white LED displays the Commission Internationale d'Eclairage (CIE) chromaticity coordinates of (0.34, 0.35) (Fig. 6c), which is close to those of balanced white-light emission (0.33, 0.33), and hence it exhibits warm white light approximating natural sunlight. These results demonstrate the success in white LEDs' fabrication based on yellow emission of CDs, which has not been reported previously. In previous report, white LEDs were constructed by white emission of CDs stimulated by UV light. The UV-LED chips have smaller power rating and more cost than blue-LED chips. Thus, the white LEDs comprised of yellow-emitting CDs and blue-LED chips are more practical than those reported previously. Meanwhile, the CDs also possess advantages of easy fabrication, lower cost, and lower toxicity over conventional YAG:Ce and semiconductor QDs.

Conclusions

We have developed a simple route to fabricate CDs derived from NAC precursor by a simple pyrolysis process.

Interestingly, the obtained CDs exhibit unique yellow-emitting fluorescence, overcoming the drawback of the dull blue fluorescence of traditional CDs. The as-prepared CDs are well-dispersed in various hydrophilic and hydrophobic solvents and possess high quantum yield of 13 % without further surface treatment. Also, we applied these CDs as the yellow phosphor in combination with blue-LED chips to construct white LEDs for the first time. The environmentally friendly white LEDs exhibited warm white light with the color coordinates of (0.34, 0.35). Consequently, coupled with their low cost, low toxicity, and PL stability, the CDs as a promising alternative yellow phosphor for white LEDs may further widen the applicability of CDs.

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References

- Schubert EF, Kim JK (2005) *Science* 308(5726):1274
- Pan YX, Wu MM, Su Q (2004) *Mater Sci Eng, B* 106(3):251

3. Park JK, Kim CH, Park SH, Park HD, Choi SY (2004) *Appl Phys Lett* 84(10):1647
4. Jang HS, Jeon DY (2007) *Appl Phys Lett* 90(4):041906
5. Shioi K, Hirosaki N, Xie RJ, Takeda T, Li YQ (2010) *J Mater Sci* 45:3198
6. Park JK, Lim MA, Choi KJ, Kim CH (2005) *J Mater Sci* 40:2069
7. Sapra S, Mayilo S, Klar TA, Rogach AL, Feldmann J (2007) *Adv Mater* 19(4):569
8. Ziegler J, Xu S, Kucur E, Meister F, Batentschuk M, Gindele F, Nann T (2008) *Adv Mater* 20(21):4068
9. Bowers MJ II, McBride JR, Rosenthal SJ (2005) *J Am Chem Soc* 127(44):15378
10. Lita A, Washington AL II, van de Burgt L, Strouse GF, Stiegman AE (2010) *Adv Mater* 22(36):3987
11. Jang HS, Yang H, Kim SW, Han JY, Lee SG, Jeon DY (2008) *Adv Mater* 20(14):2696
12. Xu XY, Ray R, Gu YL, Ploehn HJ, Gearheart L, Raker K, Scrivens WA (2004) *J Am Chem Soc* 126(40):12736
13. Sun YP, Zhou B, Lin Y, Wang W, Fernando KAS, Pathak P, Meziani MJ, Harruff BA, Wang X, Wang HF, Luo PJG, Yang H, Kose ME, Chen BL, Veca LM, Xie SY (2006) *J Am Chem Soc* 128(24):7756
14. Wang X, Cao L, Lu FS, Meziani MJ, Li H, Qi G, Zhou B, Harruff BA, Kermarrec F, Sun YP (2009) *Chem Commun* (25):3774
15. Li XY, Wang HQ, Shimizu Y, Pyatenko A, Kawaguchi K, Koshizaki N (2011) *Chem Commun* 47(3):932
16. Wang X, Cao L, Yang ST, Lu FS, Meziani MJ, Tian LL et al (2010) *Angew Chem Int Ed* 49(31):5310
17. Zhou JG, Booker C, Li RY, Zhou XT, Sham TK, Sun XL et al (2007) *J Am Chem Soc* 129(4):744
18. Zhao QL, Zhang ZL, Huang BH, Peng J, Zhang M, Pang DW (2008) *Chem Commun* (41):5116
19. Peng H, Travas-Sejdic J (2009) *Chem Mater* 21(23):5563
20. Qiao ZA, Wang YF, Gao Y, Li HW, Dai TY, Liu YL et al (2010) *Chem Commun* 46(46):8812
21. Liu HP, Ye T, Mao CD (2007) *Angew Chem Int Ed* 46(37):6473
22. Tian L, Ghosh D, Chen W, Pradhan S, Chang XJ, Chen SW (2009) *Chem Mater* 21(13):2803
23. Liu RL, Wu DQ, Liu SH, Koynov K, Knoll W, Li Q (2009) *Angew Chem Int Ed* 48(25):4598
24. Zong J, Zhu YH, Yang XL, Shen JH, Li CZ (2011) *Chem Commun* 47(2):764
25. Bourlino AB, Stassinopoulos A, Anglos D, Zboril R, Karakassides M, Giannelis EP (2008) *Small* 4(4):455
26. Bourlino AB, Stassinopoulos A, Anglos D, Zboril R, Georgakilas V, Giannelis EP (2008) *Chem Mater* 20(14):4539
27. Zhu H, Wang XL, Li YL, Wang ZJ, Yang F, Yang XR (2009) *Chem Commun* (34):5118
28. Wang QL, Zheng HZ, Long YJ, Zhang LY, Gao M, Bai WJ (2011) *Carbon* 49(9):3134
29. Wang XH, Qu KG, Xu BL, Ren JS, Qu XG (2011) *J Mater Chem* 21(8):2445
30. Cao L, Wang X, Meziani MJ, Lu FS, Wang HF, Luo PJG et al (2007) *J Am Chem Soc* 129(37):11318
31. Yang ST, Cao L, Luo PGJ, Lu FS, Wang X, Wang HF et al (2009) *J Am Chem Soc* 131(32):11308
32. Yang ST, Wang X, Wang HF, Lu FS, Luo PJG, Cao L et al (2009) *J Phys Chem C* 113(42):18110
33. Li Q, Ohulchanskyy TY, Liu RL, Koynov K, Wu DQ, Best A et al (2010) *J Phys Chem C* 114(28):12062
34. Zheng LY, Chi YW, Dong YQ, Lin JP, Wang BB (2009) *J Am Chem Soc* 131(13):4564
35. Wang F, Chen YH, Liu CY, Ma DG (2011) *Chem Commun* 47(12):3502
36. Guo X, Wang CF, Yu ZY, Chen L, Chen S (2012) *Chem Commun* 48(21):2692
37. Wang F, Kreiter M, He B, Pang SP, Liu CY (2010) *Chem Commun* 46(19):3309
38. Yang SY, Wang CF, Chen S (2011) *J Am Chem Soc* 133(22):8412