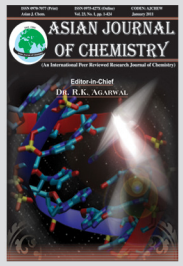
Asian Journal of Chemistry; Vol. 23, No. 12 (2011), 5311-5314

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Highly Dispersed Layered Double Hydroxide Crystals onto Carbon Nanotubes and its Catalytic Properties in Benzaldehyde Oxidation

XIAO LEI LIU[1,*], QIAN WANG[2], NAI QIU ZHAO[3], MIN WEI[3] and XUE DUAN[3]

[1]Chemical Engineering Department, Zibo Vocational Institute, Zibo 255314, P.R. China
[2]Automobile Engineering Department, Zibo Vocational Institute, Zibo 255314 P.R. China
[3]State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P.R. China

*Corresponding author: Tel: +86 533 2828221; E-mail: lxl5233@163.com

(*Received*: 3 November 2010; *Accepted*: 16 August 2011) AJC-10275

Nickel aluminum layered double hydroxide (LDH) was dispersed onto the surface of multi-walled carbon nanotubes (MWCNTs) by hydrothermal method and the resulting material shows superior catalytic activity in the oxidation reaction of benzaldehyde.

Key Words: Layered double hydroxide, Carbon nanotubes, Benzaldehyde, Immobilization.

INTRODUCTION

Layered double hydroxides (LDHs) are unusual layered materials consisting of positively charged layers with charge balancing anions between the layers. Layered double hydroxides can be represented by the formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-}_{x/n})\cdot mH_2O$ (M^{2+} divalent and M^{3+} trivalent metals, respectively, A^{n-}: *n*-valent anion)[1-6]. One of the most interesting features of these materials is their roles as catalysts or precursors in the field of catalysis[7,8].

Recent researches showed that the actually active sites in catalysis are mainly situated at the edges of the LDHs platelets[9-11]. Generally, the number of exposed edge active sites is limited by the lateral size of the LDH crystallites and increases with decreasing particle size. An effective solution to increase catalytic activity is to select appropriate materials as catalyst supports. Furthermore, the immobilized LDH nanocrystals can also provide more convenience for separation from product and reuse.

Carbon nanotubes (CNTs) constitute a novel material for application in the aerospace, textile and electronics industries, since this material possesses high chemical and thermal stability, mechanical strength, flexibility and electrical conductivity[12-14]. Although CNTs have been involved in a wide range of organic materials[15-18], research on inorganic coating onto CNTs is rather limited. Recently, surface coverage with a layer or particles of SiO_2, SnO_2, Al_2O_3, TiO_2, laponite and clay on CNTs has been reported[19-24]. In this paper, the NiAl-LDH crystals are highly dispersed onto the CNTs by the hydrothermal reaction and the composite shows superior catalytic activity in the oxidation reaction of benzaldehyde.

EXPERIMENTAL

The hydroxyl-functionalized multi-walled carbon nanotubes (OH-MWCNTs) were obtained from Chengdu Organic Chemicals Company Ltd. of Chinese Academy of Sciences. The hydroxy content of OH-MWCNTs is 20-26 mol % rate of surface carbon atom. The outside and inside diameters are 10-20 and 5-10 nm, respectively and the length is 10-20 μm. LDH-MWCNT was synthesized by the hydrothermal reaction from an aqueous solution. OH-MWCNTs (0.1 g) was dispersed in a 50 mL of NaOH solution (2 mol/L) for overnight stirring. A solution of $Ni(NO_3)_2\cdot 6H_2O$ (0.03 mol) and $Al(NO_3)_3\cdot 9H_2O$ (0.01 mol) in deionized water (12.5 mL) was added dropwise to the NaOH/OH-MWCNTs suspension in *ca.* 0.5 h and the pH was adjusted to 10 by using NaOH solution. The reaction was carried out in an autoclave at various temperatures for 24 h. The resulting solid product was filtrated and washed thoroughly with deionized water, centrifuged and dried at 70 ºC for 24 h.

RESULTS AND DISCUSSION

The morphology of OH-MWCNTs and as-prepared LDH-MWCNT sample was examined by SEM (Fig. 1). It can be seen that the surface of OH-MWCNTs is smooth with the average diameter of *ca.* 20 nm (Fig. 1A). The LDH nanocrystals exhibit uniform hexagonal morphology with the particle size of *ca.* 50 nm (Fig. 1B). In this work, synthesis of LDH-MWCNT at various temperatures (70, 80, 90, 100, 110 and 120 ºC) was also studied and both the SEM and TEM images are shown in Fig. S1 and Fig. S2. It was found that the particle size of LDH

nanocrystals can be controlled by the hydrothermal temperature: the higher the temperature, the larger the size of LDH particles obtained. The EDX spectrum in Fig. S3 reveals that

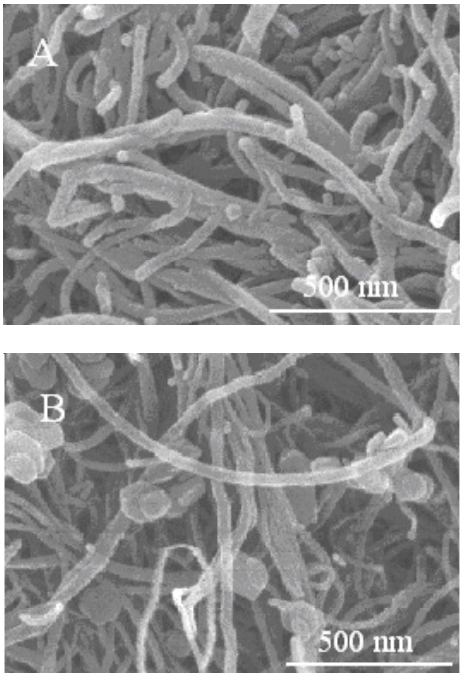
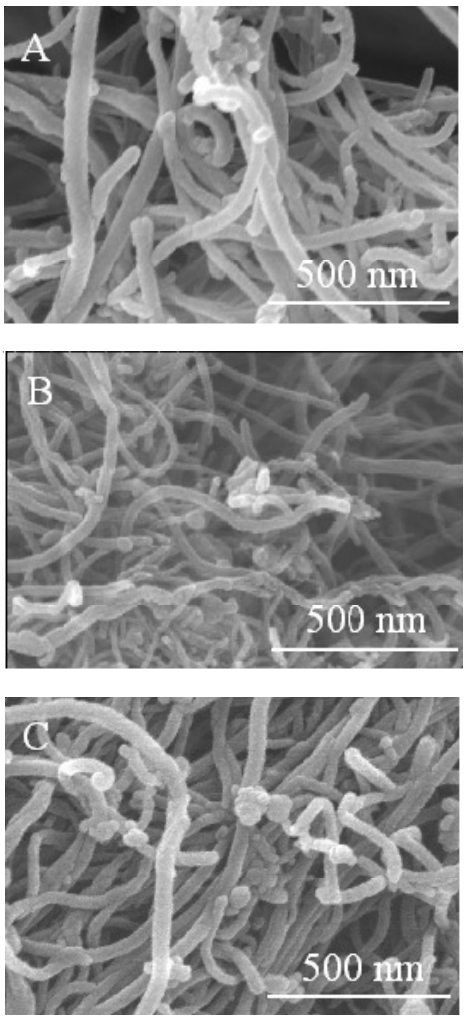


Fig. 1. (A) MWCNT and (B) LDH-MWCNT



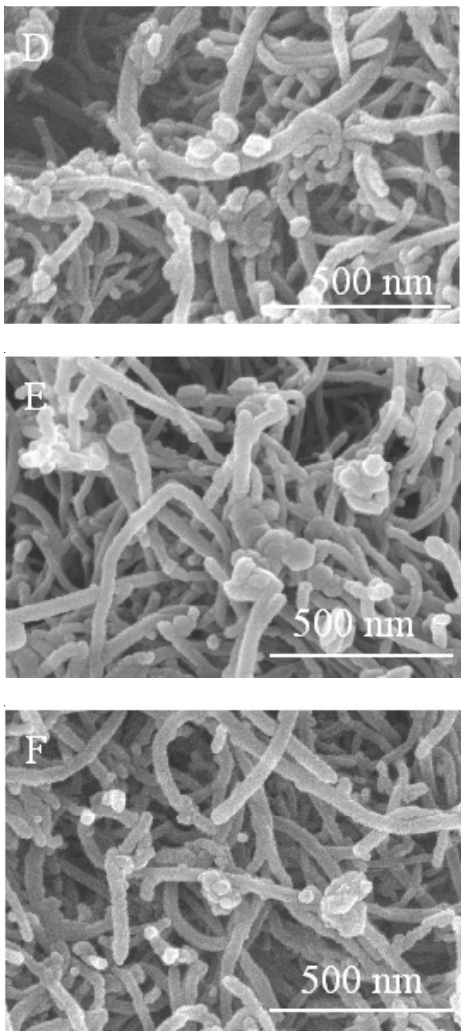
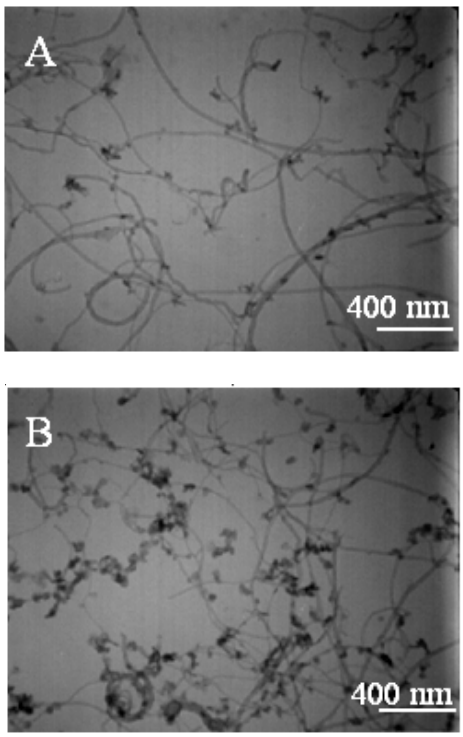


Fig. S1. SEM images of the LDH-MWCNT synthesized at various temperatures: (A) 70 ºC, (B) 80 ºC, (C) 90 ºC, (D) 100 ºC, (E) 110 ºC and (F) 120 ºC, respectively



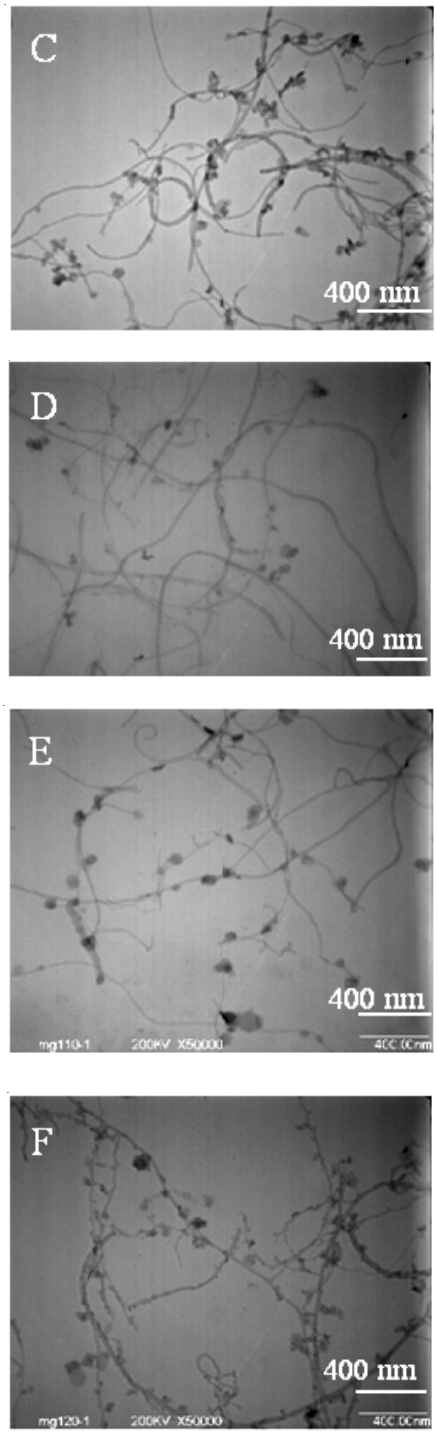


Fig. S2. TEM images of the LDH-MWCNT synthesized at various temperatures: (A) 70 ºC, (B) 80 ºC, (C) 90 ºC, (D) 100 ºC, (E) 110 ºC and (F) 120 ºC, respectively

the composite material is composed of C, O, Ni and Al. Moreover, the quantitative analysis results indicate that the atomic ratio of Ni to Al is very close to that of the precursor solution (3:1), suggesting that the coprecipitation process was essentially complete. Fig. 2 depicts the X-ray diffraction (XRD) patterns for the raw OH-MWCNTs as well as LDH-MWCNTs at various temperatures. The XRD pattern of the OH-MWCNTs (curve a) shows a reflection at 2θ 25.9º attributed to the (002) plane of hexagonal graphite structure[25]. In the case of LDH-MWCNT samples however, two sets of superposed reflections

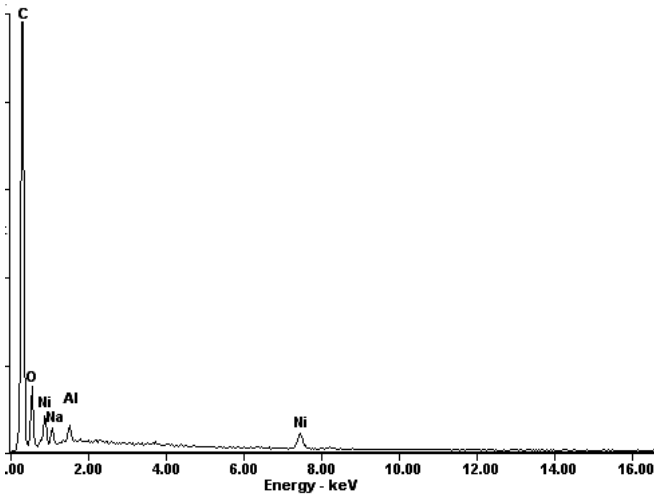


Fig. S3. EDX spectrum of LDH-MWCNT sample

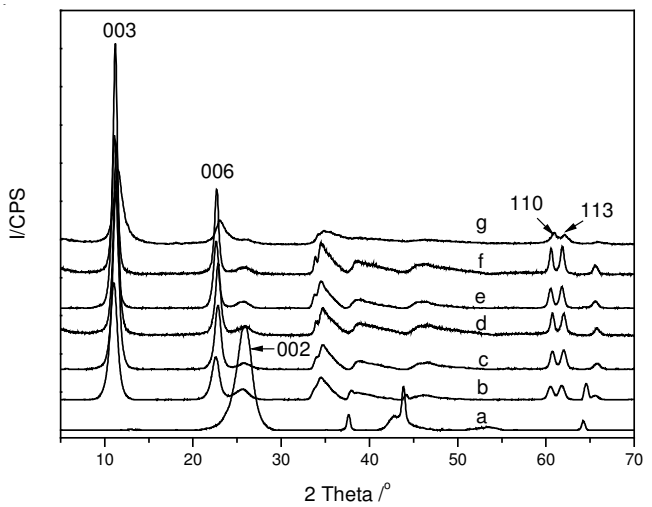


Fig. 2. XRD patterns of (a) OH-MWCNTs and LDH-MWCNT samples synthesized at various temperatures: (b) 70 ºC, (c) 80 ºC, (d) 90 ºC, (e) 100 ºC, (f) 110 ºC, (g) 120 ºC

were observed: one is due to MWCNTs and the other can be indexed to a hexagonal lattice with R-3m rhombohedral symmetry, commonly used for the description of LDH structure. The two intense lines in XRD patterns at low 2θ angle correspond to (003) and (006) reflection and the peaks between 60º and 65º (2θ) are due to (110) and (113) plane, respectively. Moreover, the relative intensity of reflection at 2θ 25.9º of MWCNTs decreases from curve b to g, indicating the improvement in the LDH crystallineity upon increasing the synthesis temperature. XRD results demonstrate the formation of composite between MWCNTs and well-crystallized NiAl-LDH.

X-Ray photoelectron spectroscopy (XPS) has been approved to be a particularly useful method in the study of the changes in the chemical states[26]. In this work, it can be seen from Fig. S4 that the NiII 2p3/2 peak of LDH-MWCNT appears at 856.9 eV, which is 1.0 eV higher than that of the pristine LDH. Furthermore, the Al(III) 2p3/2 peak of LDH-MWCNT was higher than that of the pristine NiAl-LDH. It is suggested that in the crystallized process, the LDHs was induced by the hydroxyl of OH-MWCNT. Moreover, the LDH and MWCNT was interacted through hydrogen bond, which increased the Ni, Al XPS value.

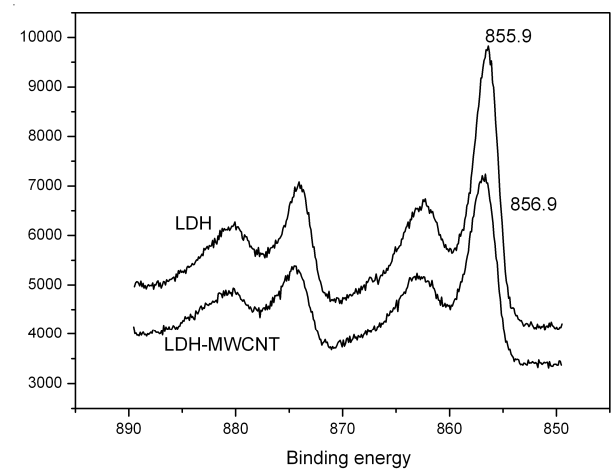


Fig. S4. XPS of NiII 2p3/2 peak for NiAl-LDH and LDH-MWCNT

Since the LDH nanocrystals were highly dispersed onto MWCNTs surface, the composite material should exhibit high stability and catalytic activity. The catalytic behaviour was evaluated by the benzaldehyde oxidation as a probe reaction. Fig. 3 shows the plots of benzaldehyde conversion against reaction time, which were catalyzed by the pristine LDH, OH-MWCNTs, physical mixed of LDHs and MWCNT, LDH-MWCNT as well as the corresponding blank test, respectively. It was found that benzaldehyde can be slowly oxidized by the oxygen in air with the absence of catalyst. Interestingly, the sample of OH-MWCNTs itself accelerates the oxidation reaction. It has been reported that the dispersed MWCNTs can effectively enhance the oxygen solubility in the aqueous solution[27], which is beneficial for the oxidation of benzaldehyde. In this experiment, the pristine NiAl-LDH can efficiently catalyze the oxidation reaction. After a short induction period of *ca*. 10 min, the conversion of benzaldehyde increased up to approximately 80 % during the first 40 min and then increased to 98 % over 50 min. Compared with the LDHs, the activity of LDH-MWCNT on the LDH-weight basis for the oxidation reaction is obviously higher. The reaction was almost complete within 40 min. Moreover, no induction period was observed, which is the same as the case of MWCNTs used as catalyst.

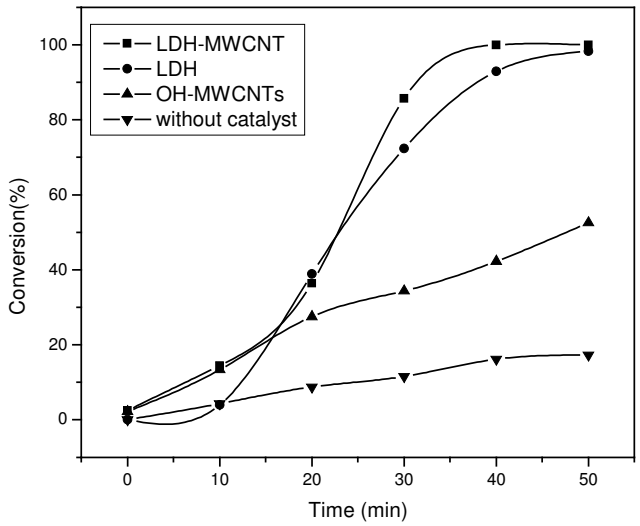


Fig. 3. Catalytic activity of LDH-MWCNT for the oxidation reaction of benzaldehyde to benzoic acid

This high activity of LDH-MWCNT can be attributed to the synergistic effect between the high dispersibility of LDH crystallites on the surface of MWCNTs and the enhanced solubility of oxygen resulted from MWCNTs.

Conclusion

The MWCNT-supported LDH nanoparticle catalyst can be prepared with high yields using hydrothermal method. It was found that the LDH nanocrystals were immobilized onto OH-MWCNTs surface. Based on the results, it is expected that a wide variety of LDH nanocrystals could be attached onto MWCNTs by a similar methodology. Moreover, the LDH-MWCNTs exhibits superior catalytic activity in the oxidation reaction of benzaldehyde. This novel and simple synthetic technique for the preparation of LDH-MWCNT may potentially have a wide range of catalytic applications for chemical syntheses.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China, the Program for New Century Excellent Talents in University (Grant No. NCET-05-121), 973 Program (Grant No. 2009CB939802) and the Program for Changjiang Scholars and Innovative Research Team in University (Grant No. IRT0406).

REFERENCES

1. C. Taviot-Gueho, Y.J. Feng, G.R. Williams, F. Leroux and D. O'Hare, *Chem. Mater*., **18**, 4312 (2006).
2. G.R. Williams, T.G. Dunbar, A.J. Beer, A.M. Fogg and D. O'Hare, *J. Mater. Chem*., **16**, 1222 (2006).
3. X.Q. Hou and R.J. Kirkpatrick, *Chem. Mater*., **14**, 1195 (2002).
4. L. Moyo, N. Nhlapo and W.W. Focke, *J. Mater. Sci*., **43**, 6141 (2008).
5. X.Q. Hou and R.J. Kirkpatrick, *Chem. Mater*., **12**, 1890 (2000).
6. B. Sels, D.D. Vos, M. Buntinx, F. Pierard, A.K. Mesmaeker and P. Jacobs, *Nature*, **400**, 855 (1999).
7. N. Das, D. Tichit, R. Durand, P. Graffin and B. Coq, *Catal. Lett*., **71**, 181 (2001).
8. S. Abello, F. Medina, D. Tichi, J. Pe´rez-Ramirez, Y. Cesteros, P. Salagre and J.E. Sueiras, *Chem. Commun*., 1453 (2005).
9. F. Winter, V. Koot, A.J. Van Dillen, W.G. John and K.P. De Jong, *J. Catal*., **236**, 91 (2005).
10. L. Li and J.L. Shi, *Chem. Commun*., 996 (2008).
11. X.C. Chen, J.H. He, C.X. Yan and H.M. Tang, *J. Phys. Chem. B*, **110**, 21684 (2006).
12. J. Sun, L. Gao and M. Iwasab, *Chem. Commun*., 832 (2004).
13. E. Artukovic, M. Kaempgen, D.S. Hecht, S. Roth and G. Gruner, *Nano. Lett*., **5**, 757 (2005).
14. M. Zhang, S. Fang, A.A. Zakhidov, S.B. Lee, A.E. Aliev and C.D. Williams, *Science*, **309**, 1215 (2005).
15. X. Lu and T. Imae, *J. Phys. Chem. C*, **111**, 2416 (2007).
16. Y. Sun, S.R. Wilson and D.I. Schuster, *J. Am. Chem. Soc*., **123**, 5348 (2001).
17. C.A. Dyke and J.M. Tour, *J. Am. Chem. Soc*., **125**, 1156 (2003).
18. T. Inada, H. Masunaga, S. Kawasaki, M. Yamada, K. Kobori and K. Sakurai, *Chem. Lett*., **34**, 524 (2005).
19. K.J.D. Mackenzie and M.J. Bolton, *J. Mater. Sci*., **44**, 2851 (2009).
20. J. Sun, L. Gao and W. Li, *Chem. Mater*., **14**, 5169 (2002).
21. E.A. Whitsitt and A.R. Barron, *Nano. Lett*., **3**, 775 (2003).
22. T. Seeger, Th. Kohler, Th. Frauenheim, N. Grobert, M. Ruhle, M. Terrones and G. Seifert, *Chem. Commun*., 34 (2002).
23. V. Georgakilas, A. Bourlinos, D. Gournis, T. Tsoufis, C. Trapalis, A. Mateo-Alonso and M. Prato, *J. Am. Chem. Soc*., **130**, 8733 (2008).
24. W.D. Zhang, I.Y. Phang and T. Liu, *Adv. Mater*., **18**, 73 (2006).
25. L. Liu and J.C. Grunlan, *Adv. Funct. Mater*., **17**, 2343 (2007).
26. C. Battocchio, I. Fratoddi, M.V. Russo and G. Polzonetti, *J. Phys. Chem. A*, **112**, 7365 (2008).
27. Z.H. Ai, T.M. Mei, J. Liu, J.P. Li, F.L. Jia, L.Z. Zhang and J.R. Qiu, *J. Phys. Chem. C*, **111**, 14799 (2007).