

# Ultrasonic assisted polyol synthesis of highly dispersed Pt/MWCNT electrocatalyst for methanol oxidation

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**Abstract** A novel chemical method based on ultrasonic assisted polyol synthesis for the fabrication of highly dispersed Pt nanoparticles on multi-walled carbon nanotubes (MWCNTs) was developed. The simple and green method took only about 10 min at ambient temperature. The structure and chemical nature of the resulting Pt/MWCNT composites were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), and energy dispersive X-ray spectrometry (EDS). The results showed that the prepared Pt nanoparticles were uniformly dispersed on the MWCNT surface. The mean size of Pt nanoparticles was about 2.8 nm. Electrochemical properties of Pt/MWCNT electrode for methanol oxidation were examined by cyclic voltammetry (CV) and excellent electrocatalytic activities could be observed. The possible formation mechanism of Pt/MWCNTs was also discussed.

**Keywords** Ultrasonic · Polyol synthesis · Multi-walled carbon nanotubes · Electrocatalysts

## Introduction

Pt and Pt alloys are the most frequently employed catalyst materials on inert supports like carbon nanotubes, for the electrochemical reactions in direct methanol fuel cells

(DMFCs). It is well-known that the metal catalytic activity strongly depends on the particle size and distribution on supporting materials [1]. However, synthesis of highly dispersed supported metal particles with small and uniform size remains a challenge. Many efforts have recently been made to develop alternative methods for preparing Pt and Pt-based alloys electrocatalysts, such as chemical reduction [2, 3], electrochemical synthesis [4, 5], polyol process [6],  $\gamma$ -irradiation [7], etc. However, most of these are usually complicated, time-consuming, and have some limitation in practice. Although microwave synthesis introduces an alternative way to the rapid synthesis of electrocatalysts [8–12], the high reaction speed within 60 s could be difficult to control and the aggregation of metal nanoparticles always occurs on supporting materials.

Sonochemical method is fast and simple, uniform, energy efficient, and has been used extensively to generate novel materials with unusual properties since 1934. Recently, more successes have been reported in the use of sonochemical method to prepare single-dispersion metal nanoparticles (such as Pt, PtRu, Ag, Au, etc.) with narrow particle size distributions without supporting materials [13–19]. Tong and et al. [20] deposited catalytic Pt nanoparticles on multi-walled carbon nanotubes (MWCNTs) via ultrasonic synthesis. However, the reducing agents they used, such as  $\text{NH}_2\text{NH}_2$  and  $\text{NH}_3\text{OHCl}$ , are not environment-friendly because of the toxic quality. Therefore, it is necessary to explore simple and green ways to synthesis MWCNTs-based composites as electrocatalysts for DMFCs.

On the other hand, there has been a recent innovation to prepare metal powders using liquid polyols such as ethylene glycol [21–25], which was named the polyol process. It is a low-temperature process and is environmentally benign. Recently, Yang et al. [26] prepared acetate-stabilized Pt and Ru nanoparticles by the polyol process.

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In the present study, we used sonochemical technique in combination with the polyol process to deposit Pt nanoparticles on MWCNTs rapidly. To the best of our knowledge, this method is being reported for the first time. It is simple and effective. Moreover, it involves non-use of stabilizer, surfactant, or other toxic reagents that are commonly used for production of catalysts, so it is also an environment-friendly process. The as-prepared Pt/MWCNT catalyst exhibits a remarkable enhancement of catalytic activity for methanol oxidation compared to that of the commercially available Pt/C catalyst (E-TEK). It may have potential application in commercialization for preparing anodic material of DMFCs and proton exchange membrane fuel cell.

## Experimental

### Preparation of Pt/MWCNT composites

MWCNTs used in this work were purchased from Shenzhen Nanotech Port Co., Ltd (Shenzhen, China). The obtained MWCNTs were purified and shortened with a mixture of nitric and sulfuric acid (1:3 by volume), according to the literature [27]. The procedure employed for preparing Pt/MWCNTs (20 wt% metal content) was as follows: 20 mg surface-oxidized MWCNTs, 1.13 ml of 0.0046 M  $\text{H}_2\text{PtCl}_6$  solution, 0.075 ml of 2 M NaOH were mixed well in ethylene glycol (EG) by continuous stirring. Thereafter, the mixture was under sonication. The ultrasound irradiation was accomplished with a high-intensity ultrasonic probe (Xinzhi Co., China, JY92-2, 0.6 cm diameter, Ti-horn, 25 kHz, 0–1,000 W). The total ultrasonic time was 10 min. The resulting black solid sample was filtered, washed, and dried at 353 K for 12 h in a vacuum oven.

### Preparation of Pt/MWCNT catalyst electrode

Five milligrams of Pt/MWCNT catalyst sample, 0.25 ml of Nafion solution (0.1 wt%, Aldrich) and 0.5 ml of alcohol

were mixed together using ultrasonic bath. A measured volume (ca. 20  $\mu\text{l}$ ) of this mixture was transferred via a syringe onto a glassy carbon electrode (GCE) and heated under an infrared lamp to remove the solvent.

A commercial E-TEK Pt/C catalyst (20 wt% metal content) was chosen for the comparative experiment and characterized accordingly, and the E-TEK electrodes were also prepared in the same way with the Pt/MWCNT catalyst.

### Measurements

Morphology and microstructure of the synthesized materials were investigated by transmission electron microscope (TEM, FEI Tecnai G2 20 S-TWIN). The samples were prepared by dipping the Pt/MWCNT ethanol solution on the Cu grids and observed at 200 kV. X-ray diffraction (XRD) patterns of all the samples were obtained on a Bruker D8-ADVANCE diffractometer with  $\text{Cu K}\alpha$  radiation. Energy dispersive X-ray spectrometry (EDS, Quanta 2000 scanning electron microscope) was used to determine the metal mass fraction of catalysts.

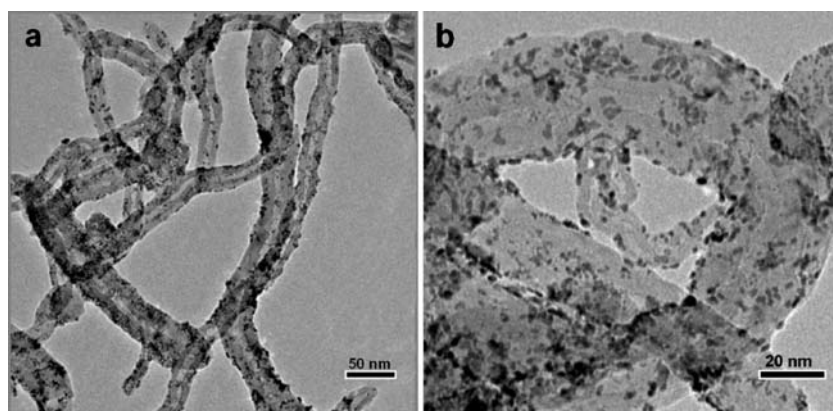
Electrochemical measurements were recorded using CHI660A electrochemical working station (Chenhua, Shanghai). A conventional cell with a three-electrode configuration was used throughout this work. The working electrode was catalyst-modified GCE (5 mm in diameter), a platinum foil was used as the counter electrode, and a saturated calomel electrode (SCE) was the reference electrode. All measurements were performed at room temperature. The electrolytes were 2.0 M  $\text{CH}_3\text{OH}$  in 1.0 M  $\text{H}_2\text{SO}_4$  solution, which had been purged with  $\text{N}_2$  for 30 min.

## Results and discussion

### TEM analysis of the Pt/MWCNT composites

Figure 1 shows transmission electron micrographs (a) and high-magnification view (b) of Pt/MWCNT composites.

**Fig. 1** TEM images of Pt/MWCNT composites: low magnification TEM image (a) and high magnification TEM image (b)



The carbon nanotubes exhibit a multi-walled microstructure with a diameter of about 15–30 nm. More importantly, very high particle densities for Pt particles are found at all MWCNT surfaces in the image. Consequently, the novel deposition method appears to be a very powerful and effective technique. The average Pt particle size is determined from the high-magnification images to be about 1–5 nm (Fig. 1b). Despite the small size of the Pt particles, particle agglomeration is very rare, probably because the ultrasound technique can effectively prevent the metal particles from congregating. It must be emphasized that the Pt particles appear to have a uniform distribution. This fact affects the electrode surface area, leading to an extension of the active surface area [28], thereby favoring the high performance of methanol oxidation, as discussed below.

#### XRD analysis of Pt/MWCNT composites

X-ray diffraction spectrum of Pt/MWCNT composites is shown in Fig. 2. All peaks can be indexed as the Pt face-centered cubic. The peak at 26.11° corresponds to the (002) planes of graphitized carbon and the peaks at 39.67°, 46.28°, 67.60°, and 81.48° can be assigned to (111), (200), (220), and (311) crystalline plane diffraction peaks, respectively. The average size of the Pt particles was calculated from the major diffraction peak (111) using the well-known Scherrer's formula (Eq. 1),

$$d = \frac{0.89\lambda}{B \cos \theta}, \quad (1)$$

where  $\lambda$  is the wavelength of X-rays used (0.154056 nm),  $B$  is the full width at half maximum of the peak, and  $\theta$  is the Bragg's angle of the XRD peak. The grain size was found to be about 2.8 nm, in good agreement with the mean particle size observed in the TEM micrograph.

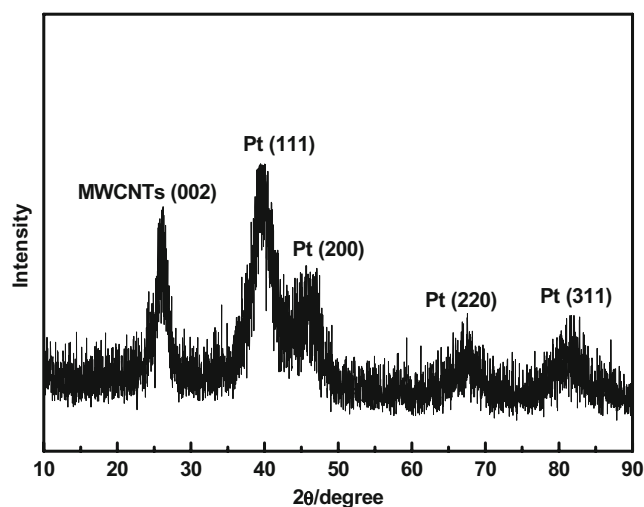


Fig. 2 XRD patterns of Pt/MWCNT composites

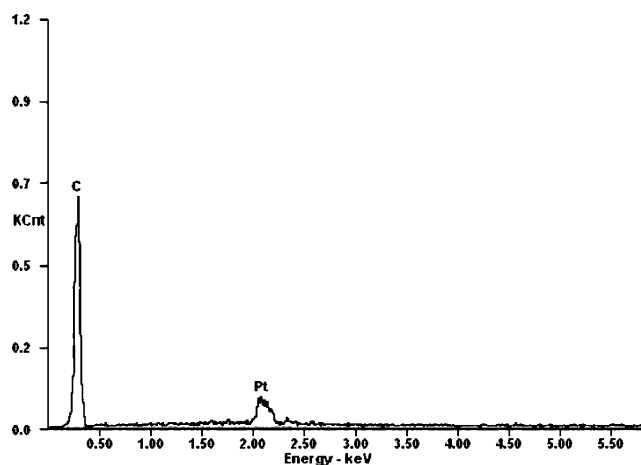


Fig. 3 EDS spectrum of Pt/MWCNT composites

#### EDS analysis of the Pt/MWCNT composites

Figure 3 shows the EDS pattern of Pt/MWCNT composites. It indicates that Pt and C are the major elements. The EDS result shows that the Pt metal weight percent of the final composite is about 19.8%.

#### Electrochemical properties of Pt/MWCNT composites

In general, the real surface area of Pt particles is one of the important parameters to determine the catalytic properties of electrocatalysts for methanol oxidation, as this reaction is surface-sensitive. The active specific surface area of Pt particles for Pt-based catalysts could be estimated from the hydrogen adsorption curves [29]. The cyclic voltammogram of the GCE modified by Pt/MWCNT catalyst in 1.0 M  $\text{H}_2\text{SO}_4$  at a scan rate of  $50 \text{ mV s}^{-1}$  between  $-0.25$  and  $1.0 \text{ V}$  is shown in Fig. 4. For comparison, the cyclic voltammogram of the E-TEK catalyst is also presented. It can be seen that the area of hydrogen adsorption and

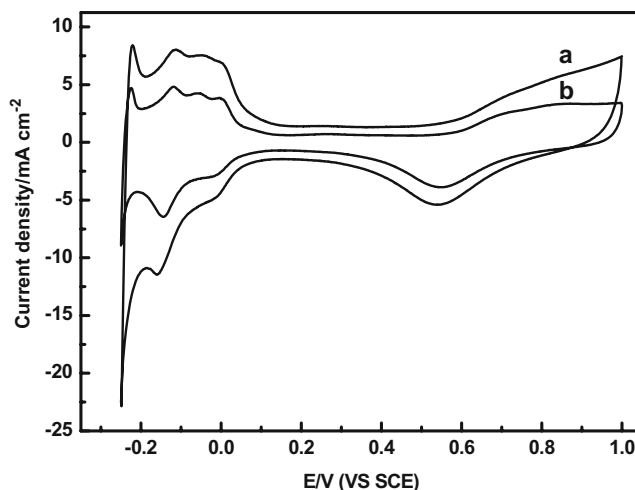
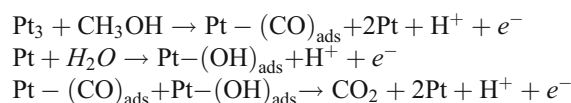


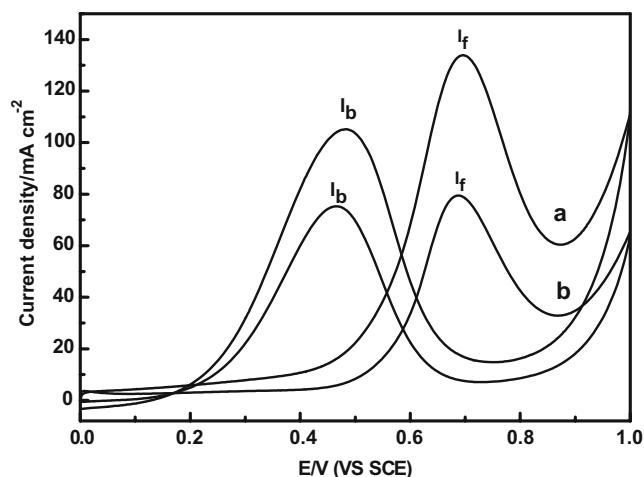
Fig. 4 Cyclic voltammetry curves of Pt/MWCNT (a) and E-TEK (b) catalysts in 1.0 M  $\text{H}_2\text{SO}_4$  solution. Scan rate:  $50 \text{ mV s}^{-1}$

desorption peak for the Pt/MWCNT catalyst is much bigger than that of the E-TEK catalyst, which means that the Pt/MWCNT catalyst has a relative larger active surface area in comparison with the E-TEK. The high active surface area may be owing to the high dispersion and small size of Pt nanoparticles on the MWCNTs.

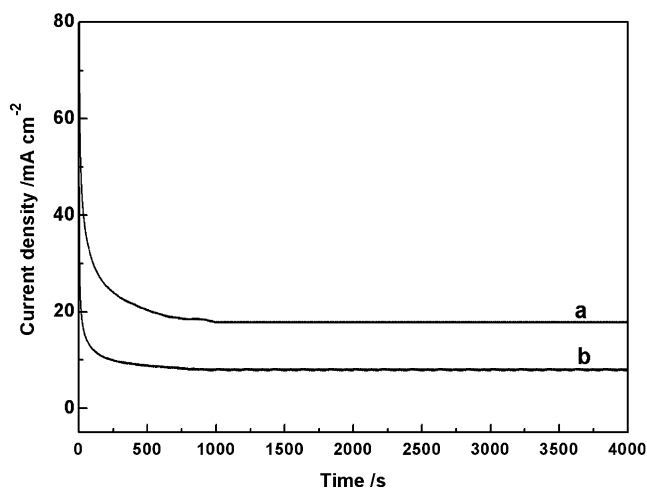
Figure 5 shows the typical cyclic voltammograms of methanol oxidation under acidic conditions (1.0 M H<sub>2</sub>SO<sub>4</sub> + 2.0 M CH<sub>3</sub>OH) catalyzed by the Pt/MWCNT and E-TEK catalysts, respectively. The voltammetric features are in good agreement with most published work [30, 31]. The scans in both the positive and negative directions show CV characteristic peaks of methanol oxidation. The oxidation mechanism of methanol on Pt catalyst, which can be shortly written as follows [32, 33]:



This reaction involves adsorption steps with the formation of chemisorbed residues leading to a decrease of the activity of the catalyst surface, and the adsorption takes place by dehydrogenation reactions forming different adsorbate species. The peak around 0.69 V in the forward scan ( $I_f$ ) resembles the methanol electrooxidation. In the reverse scan, the removal of the incompletely oxidized carbonaceous species formed in the forward scan promotes the appearance of an asymmetric anodic peak ( $I_b$ ) at 0.47 V [34]. The ratio of the forward anodic peak current density to the reverse of the anodic peak current density ( $I_f/I_b$ ) has been used to describe the catalyst tolerance to carbonaceous species accumulation. A low  $I_f/I_b$  ratio indicates poor oxidation of methanol to carbon dioxide during the anodic



**Fig. 5** Cyclic voltammetry curves of Pt/MWCNT (a) and E-TEK (b) catalysts in 1 M H<sub>2</sub>SO<sub>4</sub> + 2 M CH<sub>3</sub>OH solution. Scan rate: 50 mV s<sup>-1</sup>



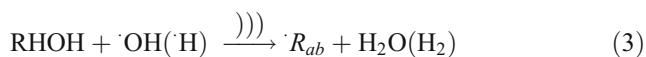
**Fig. 6** Plot of specific current vs time of the catalyst Pt/MWCNT (a) and E-TEK (b), recorded at 0.6 V in 1 M H<sub>2</sub>SO<sub>4</sub> + 2 M CH<sub>3</sub>OH solution

scan and excessive accumulation of carbonaceous residues on the electrode surface. A high  $I_f/I_b$  ratio shows the reverse case [30, 31]. From qualitative analysis of these voltammetric profiles, three aspects are immediately evident. First, the  $I_f/I_b$  ratio of 1.28 for the Pt/MWCNT is higher than that of E-TEK ( $I_f/I_b=1.06$ ), which indicates more intermediate carbonaceous species are oxidized to carbon dioxide in the forward scan on the Pt/MWCNT electrode surface than on the E-TEK electrode surface. Second, the Pt/MWCNT electrode has a much lower onset potential (ca. 0.10 V) than the one on the E-TEK electrode (ca. 0.42 V), indicating better electrocatalytic activity of the Pt/MWCNT electrode. Third, the current density at the Pt/MWCNT electrode is higher than that of the E-TEK electrode. The above analysis results confirm that the Pt/MWCNT composites have a better electrocatalytic activity than that of E-TEK for methanol oxidation. This can be attributed to several factors, including (1) the as-prepared Pt/MWCNT electrocatalyst possesses appropriate Pt nanoparticle sizes and good distribution that enhance its electrocatalytic activity; (2) better electrical conductance of the MWCNT compared with the classical carbonaceous supports such as carbon black and so on [35]. More importantly, this result proves that the novel deposition method is effective in the preparation of Pt/MWCNT anode electrocatalyst with high catalytic activity for methanol oxidation.

To test the stability of the as-prepared catalysts, the chronoamperometry curves were recorded at 0.6 V for 4,000 s as shown in Fig. 6. The decay of current is in similar model for two catalysts during the process going; however, the methanol oxidation current at the electrode of Pt/MWCNT is found to be kept to the higher than E-TEK in the whole process. The result shows that Pt/MWCNT is much more efficient than E-TEK, which is consistent with the CV results.

The mechanism for the synthesis of Pt/MWCNT composites

While in the high-intensity ultrasonic field, carbon nanotubes could absorb ultrasound irradiation. In addition, the homogeneous ultrasonic wave in the liquid samples shortens the reaction time, providing a more uniform environment for the growth and nucleation of nanoparticles on supports. In this case, the cavitation would form the collapsing bubbles with elevated temperature and high pressure on the surface of MWCNTs as the reaction active sites, where the reaction among Pt (IV), EG, and other reducing species would occur. The ultrasonic field possessing the high energy could accelerate the mass transport and the reactant diffusion speed, resulting in the high reacting speed. Meanwhile, it can also increase the isolation of MWCNT bundles. Consequently, the highly dispersed Pt nanoparticles with narrow size distribution could be deposited on the side wall of MWCNTs. The formation of Pt nanoparticles on MWCNTs is speculated from the reactions as follows [36, 37]:



where the mark ))) and RHOH denote a sonolysis and an EG additive, respectively. Equations 2–4 indicate the sonochemical formation of the reducing radicals and reductants: (1)  $\cdot\text{H}$  is formed from sonolysis of water; (2)  $\cdot\text{R}_{\text{ab}}$  is formed from the abstraction reaction of RHOH with  $\cdot\text{OH}$  or  $\cdot\text{H}$ ; (3)  $\cdot\text{R}_{\text{py}}$  is formed via RHOH pyrolysis. Finally, the reduction of Pt (IV) proceeds by the interaction with various reducing species and involves a number of complex reaction steps, as seen in Eq. 5.

## Conclusion

In summary, we have demonstrated a simple, effective and green method of preparing carbon-supported Pt nanoparticles as electrocatalysts for DMFCs. The Pt nanoparticles, which were uniformly dispersed on MWCNTs, were about 2.8 nm in diameter. The as-prepared Pt/MWCNT catalyst exhibits a remarkable enhancement of catalytic activity for methanol oxidation compared to that of the commercially E-TEK catalyst. Therefore, it is expected

to have potential for the preparation of commercial catalysts. We believe that this synthetic strategy is useful for the synthesis of other metal/carbon catalysts. Intensive investigation is under progress in our laboratory.

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## References

1. Armadi IS, Wang ZL, Green TC, Henglein A, El-Sayed MA (1996) *Science* 272:1924
2. Huang JE, Guo DJ, Yao YG, Li HL (2005) *J Electroanal Chem* 577:93
3. Li WZ, Liang CH, Zhou WJ, Qiu JS, Zhou ZH, Sun GQ, Xin Q (2003) *J Phys Chem B* 107:6292
4. Guo DJ, Li HL (2006) *J Power Sources* 160:44
5. Guo DJ, Li HL (2005) *Electroanalysis* 17:869
6. Bock C, Paquet C, Couillard M, Botton GA, MacDougall B (2004) *J Am Chem Soc* 126:8028
7. Oh SD, So BK, Choi SH, Gopalan A, Lee KP, Yoon KR, Choi IS (2005) *Mater Lett* 59:1121
8. Boxall DL, Lukehart CM (2001) *Chem Mater* 13:806
9. Komarneni S, Li DS, Newalkar B, Katsuki H, Bhalla AS (2002) *Langmuir* 18:5959
10. Chen WX, Lee JY, Liu ZL (2002) *Chem Commun* 21:2588
11. Liu ZL, Lee JY, Chen WX, Han M, Gan LM (2004) *Langmuir* 20:181
12. Liu ZL, Hong L, Thama MP, Lim TH, Jiang H (2006) *J Power Sources* 161:831
13. Mizukoshi Y, Oshima R, Maeda Y, Nagata Y (1999) *Langmuir* 15:2733
14. Okitsu K, Yue A, Tanabe S, Matsumoto H (2000) *Chem Mater* 12:3006
15. Li Q, Ding Y, Shao MW, Wu J, Yu GH, Qian YT (2003) *Mater Res Bull* 38:539
16. Jiang LP, Wang AN, Zhao Y, Zhang JR, Zhu JJ (2004) *Inorg Chem Commun* 7:506
17. Okitsu K, Ashokkumar M, Grieser F (2005) *J Phys Chem B* 109:20673
18. Vinodgopal K, He YH, Ashokkumar M, Grieser F (2006) *J Phys Chem B* 110:3849
19. Nemamcha A, Rehspringer JL, Khatmi D (2006) *J Phys Chem B* 110:383
20. Tong H, Li HL, Zhang XG (2007) *Carbon* 45:2424
21. Kurihara LK, Chow GM, Schoen PE (1995) *Nanostruct Mater* 5:607
22. Komarneni S, Li D, Newalkar B, Katsuki H, Bhalla AS (2002) *Langmuir* 18:5959
23. Yan X, Liu H, Liew KY (2001) *J Mater Chem* 11:3387
24. Viau G, Brayner R, Poul L, Chakroune N, Lacaze E, Fiévet-Vincent F, Fiévet F (2003) *Chem Mater* 15:486
25. Cushing BL, Kolesnichenko VL, O'Connor CJ (2004) *Chem Rev* 104:3893
26. Yang J, Deivaraj TC, Too HP, Lee JY (2004) *Langmuir* 20:4241
27. Chen J, Hamon MA, Hu H, Chen YS, Rao AM, Eklund PC, Haddon RC (1998) *Science* 282:95
28. Zhang FB, Li HL (2006) *Carbon* 44:3195
29. Babic BM, Vracar LM, Radmilovic V, Krstajic NV (2006) *Electrochim Acta* 51:3820
30. Liu ZL, Ling XY, Su XD, Lee JY (2004) *J Phys Chem B* 108:8234

31. Mu YY, Liang H, Hu J, Jiang L, Wan LJ (2005) *J Phys Chem B* 109:22212
32. Bagotzky VS, Vassiliev YB, Khazova OA (1977) *J Electroanal Chem* 81:229
33. Petry OA, Podlovchenko BI, Frumkin AN, Lal H (1965) *J Electroanal Chem* 10:253
34. Manohara R, Goodenough JB (1992) *J Mater Chem* 2:875
35. Hsin YL, Hwang KC, Yeh CT (2007) *J Am Chem Soc* 129:9999
36. Price GJ, Ashokkumar M, Hodnett M, Zequiri B, Grieser F (2005) *J Phys Chem B* 109:17799
37. Fujimoto T, Terauchi S, Umehara H, Kojima I, Henderson W (2001) *Chem Mater* 13:1057