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# Template-free electrochemical nanofabrication of polyaniline nanobrush and hybrid polyaniline with carbon nanohorns for supercapacitors

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**Abstract**

Polyaniline (PANI) nanobrushes were synthesized by template-free electrochemical galvanostatic methods. When the same method was applied to the carbon nanohorn (CNH) solution containing aniline monomers, a hybrid nanostructure containing PANI and CNHs was enabled after electropolymerization. This is the first report on the template-free method to make PANI nanobrushes and homogeneous hybrid soft matter (PANI) with carbon nanoparticles. Raman spectroscopy was used to analyze the interaction between CNH and PANI. Electrochemical nanofabrication offers simplicity and good control when used to make electronic devices. Both of these materials were applied in supercapacitors and an improvement capacitive current by using the hybrid material was observed.

## 1. Introduction

In the processing of soft matter such as conducting polymers, traditional spin-casting cannot guarantee homogeneous nanostructures due to the fast speed of solvent evaporation. Electrochemical techniques provide an innovative, versatile and economic way of nanofabrication. It especially offers a better alternative for constructing soft-matter nanostructures in a controllable manner. A simple and completely nonlithographic preparation technique for free-standing nanostructured conducting polymer films with defined arrays of nanoembossments had been developed by template methods using a porous anodic aluminum oxide (AAO) membrane [1–3], polystyrene latex [4–6], etc. Such methods always require removing the templates at the end step, which may introduce contaminants and limit their applications in electronic devices. Thus the assembly of nanostructured polymers without using a template was needed. Large arrays of uniform and oriented nanowires can be prepared through controlled nucleation and growth during a stepwise electrochemical galvanostatic deposition process, in which a large number of nuclei were first deposited on the substrate using a large current density. After the initial nucleation, the current density was reduced stepwise in order to grow the oriented nanowires from the nucleation sites created in the first step [7]. Carbon nanomaterials such as carbon nanotubes (CNTs) have attracted significant attention since their discovery [8]. There has been much effort in the development of hybrid materials containing CNTs and conducting polymers. Composite films of CNTs with polyaniline (PANI), polypyrrole (PPy) or poly(3,4-ethylenedioxythiophene) (PEDOT) were prepared via electrochemical co-deposition from solutions containing acid-treated CNTs and the corresponding monomer [9]. The hybrid CNT and conducting polymer composites show promising applications in photovoltaics [10], sensors [11] and electrochemical energy storage devices [12]. However, the extremely low solubility of CNTs in solutions

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makes their functionalization a challenge. A derivative of CNTs, CNHs have an irregular horn-like shape and can be viewed as being formed from the crushing or origami-like contortion of a graphene sheet. They can be easily prepared with high purity as a low-cost raw material [13]. Unlike CNTs, the advantage of using CNHs lies not only in their large surface area but also easy permeation of gas and liquid, i.e. CNHs can form homogeneous dispersions in aqueous solutions [14].

This paper describes a novel method to make PANI nanobrushes by stepwise galvanostatic electrochemical deposition. A hybrid material containing CNHs and PANI was also synthesized in the same way. This approach is highly efficient and scalable, while meeting the current requirements for nanoelectronics technologies with bottom-up production methods. Both materials were thereafter used in supercapacitors and the hybrid material shows an improvement in capacitive current.

## 2. Experimental details

All chemicals including sulfuric acid ($H_2SO_4$, ACS reagent, 95.0–98.0%), hydrochloric acid (HCl, ACS reagent, 37%) and aniline (ACS reagent, $\geqslant$99.5%) were purchased from Sigma Aldrich. High surface area nanoporous CNHs were produced by an arc discharge in liquid nitrogen using a graphite anode and cathode, which are 3 and 12 mm in diameter with an arc current of 100 A [13]. At the end of the discharge process, CNHs were collected and subsequently dispersed in the aniline monomer solution with a weight concentration of 0.5 g $l^{-1}$.

ITO quartz glasses (Prazisions Glas&Optik GmbH) with a thickness of 1 mm were cleaned by ultrasonication in separate solutions of acetone, ethanol and water for 10 min individually. Afterwards they were further cleaned in a plasma cleaner (Harrick, PDC-001) for another 10 min for both sides before being used as working electrodes. Electropolymerization was carried out in an aqueous solution containing 0.5 M aniline and 1.0 M HCl. The three-electrode electrochemical cell set-up was used for the galvanostatic electropolymerization of PANI and the PANI–CNH hybrids. The working electrode is ITO coated on quartz glass, the reference electrode is Ag/AgCl and the counter electrode is Pt foil. Firstly, a constant current (0.12 mA $cm^{-2}$) was applied for 0.5 h to introduce the PANI nuclei onto the ITO-coated quartz glass working electrode. The current was then reduced to 0.06 mA $cm^{-2}$ for 3 h. In the last step, the current was decreased to 0.03 mA $cm^{-2}$ for 3 h. The stepwise growth produced nanobrushes of PANI. By the same method, the hybrid CNH–PANI material was also produced. The electrochemical polymerization and electrochemical properties of the assembled supercapacitors were studied by galvanostatic and cyclic voltammetry measurements using Autolab (PGSTAT 302N). In testing the supercapacitors, electrodes (size 1 cm × 1 cm) were made with PANI nanobrushes and with PANI–CNH hybrids. When assembling the device, 1 M $H_2SO_4$ aqueous solution was used as the electrolyte and high-fiber cellulose paper was used as the separator. The high-fiber cellulose paper provides environmental friendliness and proves to be an effective ionic transfer material whilst it is an electronic insulator in supercapacitors [15]. The electrochemical window was kept from $-0.5$ to 0.5 V with a scan rate of 50 mV $s^{-1}$ during the cyclic voltammetry.

The excitation wavelength of 780 nm (Renishaw, NIR diode laser) was used for Raman analysis. The spectrometer was always calibrated against an Si standard (520 $cm^{-1}$) before measurements.

## 3. Results and discussion

The PANI nanobrushes were fabricated on ITO-coated quartz glass by well-controlled nucleation and growth without templates. Figure 1 shows the scanning electron microscopy (SEM) images. The thickness of ITO coated on quartz is about 10 $\mu$m as shown in figure 1(a). Figure 1(b) is the surface morphology of the ITO. After the stepwise galvanostatic electropolymerization, PANI nanobrushes were formed (figure 1(c)). Following the initiation of nucleation of the conducting polymer at high current densities (0.12 mA $cm^{-2}$), the current density is reduced to 0.06 mA $cm^{-2}$ and then 0.03 mA $cm^{-2}$ to avoid formation of further nuclei. The existing nuclei preferentially grew vertically to the surface. Since the ITO substrate surface is not smooth, it grows and forms the 3D brush-like structure and the tips having fairly uniform diameters ranging from 20 to 50 nm (figure 1(d)). This size range is very similar to the tip size range of the aligned PANI nanowires synthesized using similar methods (50–70 nm) [16]. The SEM image of CNHs (figure 1(e)) is taken after they were dried from their suspension of water without the presence of aniline. The diameter of the CNHs is around 20–100 nm. CNHs have a graphene sheet in an irregular horn-like shape with open ends and can be homogeneously dispersed in aqueous solutions with a concentration of 0.5 g $l^{-1}$. They form a uniform solution with 0.5 M aniline and 1.0 M HCl as figure 2 shows. Electrochemical polymerization at low and constant current levels was used to fabricate both PANI nanobrushes and PANI–CNH hybrid material with uniform diameter. The surface morphology of the PANI–CNH hybrid material is illustrated in figure 1(f). There are two possible interactions between CNHs and PANI. Firstly, during the initial electropolymerization process, the positively charged aniline radicals can be covalently bonded to the carbon surface of CNHs like in the case of CNTs [17, 18] (figure 3(a)). Secondly, the charge-induced negative pi electrons in the bending sheet of grapheme along CNHs as well as CNTs may be incorporated as doping anions in the PANI backbone [19] as figure 3(b) shows.

Raman spectroscopy was employed to verify the interaction, and the spectra have been separated from each other in order to clarify the changes. CNHs have characteristic G and D bands in the Raman spectra (figure 4(a)). The G band belongs to the tangential modes at about 1590–1300 $cm^{-1}$ [20]. The bands at approx. 1592 $cm^{-1}$ in figures 4(a) and (b) are assigned to G bands. Another characteristic of CNHs, the D band, is always in the range around 1270–1300 $cm^{-1}$. It is caused by disorder-inducing parameters, mainly from covalent modification. The bands of 1315 $cm^{-1}$ in figures 4(a) and (b) are assigned to D bands. The Raman spectra of the

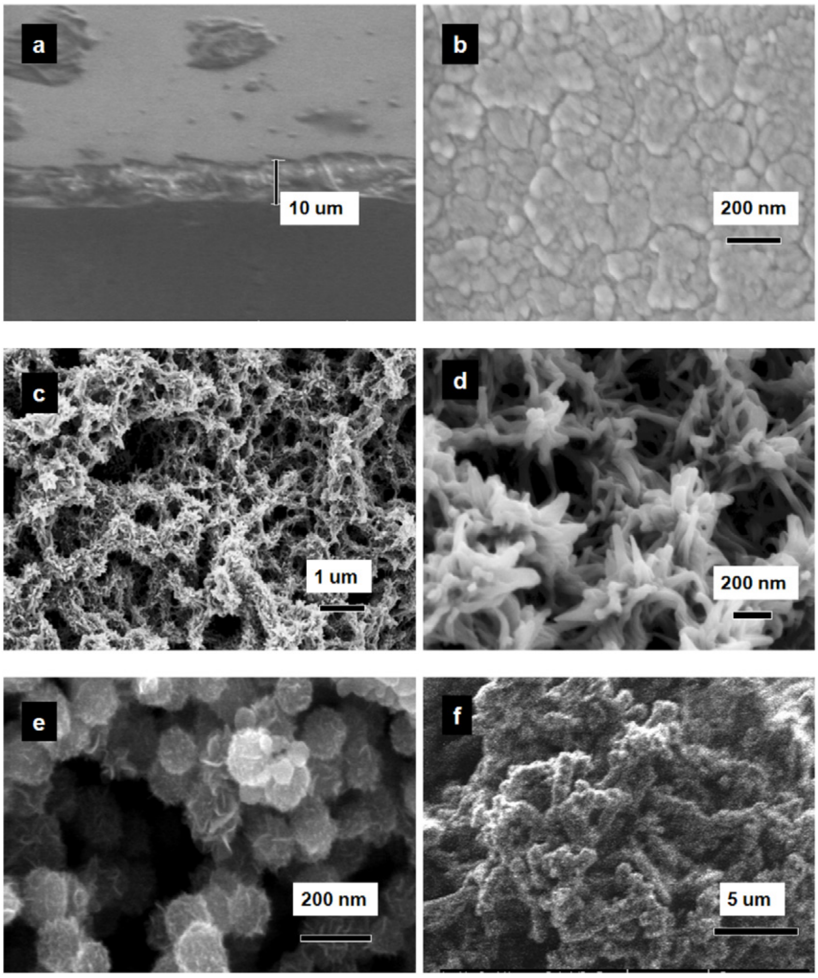

**Figure 1.** Scanning electron microscopy (SEM) images of (a) ITO view, (b) enlarged view of the ITO surface, (c) nanostructured polyaniline, (d) enlarged view of nanostructured polyaniline, (e) carbon nanohorns (CNHs), (f) carbon nanohorns and polyaniline nanocomposites (CNH–PANI).

CNH exhibited noticeable changes upon modification, most importantly an increase in the relative intensity of the D band versus G band. This is known to be sensitive to disorder mainly caused by covalent bonding. In order to get a detailed overview of the changes upon modification, the intensity ratio ($I_D/I_G$) of the D band ($I_D$) and the G band ($I_G$) was calculated. The $I_D/I_G$ ratio for pure CNH (figure 4(a)) is 1.1 and for figure 4(b) is 1.4. This implies covalent bonding happens upon modification of CNHs with PANI. The $I_D$ is usually comparable to or even larger than $I_G$ in covalent functionalization [21, 22]. Lefrant *et al* [23] have reported that the band at approx. 1165 cm$^{-1}$ confirms the presence of a covalently functionalized single-walled carbon nanotube composite with PANI. The strong Raman bands at 1150 cm$^{-1}$ in figure 4(b) may possibly be from the covalent functionalization of CNHs with conducting PANI. The Raman spectra (figures 4(b) and (c)) were taken after electropolymerization. In figure 4(c), all Raman bands belong to PANI. The existence of peaks at 1555 and 1469 cm$^{-1}$ are associated with C=C ring stretching and C=N stretching from the quinoid unit [24]. The C–N$^{+\cdot}$ stretching vibrations of the semiquinone radicals give a strong Raman band at approx. 1328 cm$^{-1}$, which confirms that the obtained PANI is in the conducting form [25]. C–H in-plane bending of the quinoid rings at 1150 cm$^{-1}$ and the quinoid ring deformation at 802 cm$^{-1}$ can also be observed [24]. It has to be pointed out that there are also Raman signals from PANI after electropolymerization in the presence of CNHs. However, PANI does not fully cover the surface and the spectrum shown in figure 4(b) is taken at a spot where PANI is not interfering with the CNH signal since the G band of 1592 cm$^{-1}$ can still be observed in figure 4(b). The results show that PANI may have been covalently bonded to the CNH, which is shown by the change in the intensity ratio ($I_D/I_G$) in Raman spectra. However, the doping effect from CNHs as large anions might coexist.

The capacitive behavior of PANI nanowire electrodes have shown great potential in application to electrochemical energy storage devices such as supercapacitors and rechargeable batteries [26]. Supercapacitors store energy either by a pure electrostatic attraction occurring between the ions and the charged surface of the electrode (e.g. carbon), which is known as an electrochemical double-layer capacitor (EDLC), or by fast surface Faradaic redox reactions (pseudocapacitors) [27]. Electrode materials with pseudocapacitance properties are

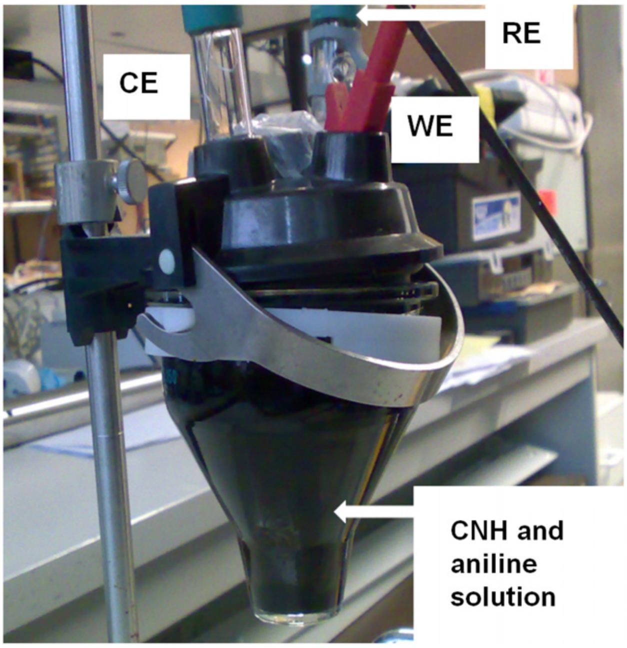

**Figure 2.** Three-electrode electrochemical cell set-up. WE: working electrode, RE: reference electrode, CE: counter electrode. Aniline monomer was dissolved homogeneously in the CNH dispersion.

(This figure is in colour only in the electronic version)

generally metal oxides ($RuO_2$, $MnO_2$, etc) or conducting polymers [28, 29]. Ordered PANI nanowires tailored by stepwise electrochemical deposition showed remarkably enhanced capacitance [12]. Figure 5(a) shows the cyclic voltammogram from a plain EDLC made of ITO electrodes. When the ITO surface is coated with PANI nanobrushes, the capacitive current increases (figure 5(b)) and it is attributed to the pseudocapacitance current. There are many parameters that will influence the specific capacity of PANI including the substrate of the working electrode and the electropolymerization methods [23]. The specific capacity is about 48 F $g^{-1}$ in this device. As aniline was electropolymerized in the CNH dispersion, the new composite material is formed. When such a PANI–CNH composite is used as electrodes in supercapacitors the capacitive current improves significantly (figure 5(c)) with a specific capacity of 168 F $g^{-1}$. Such a current is considered as the combination of pseudocapacitance current and the EDLC current, which carbon nanomaterials contribute. For high EDLC capacitance,

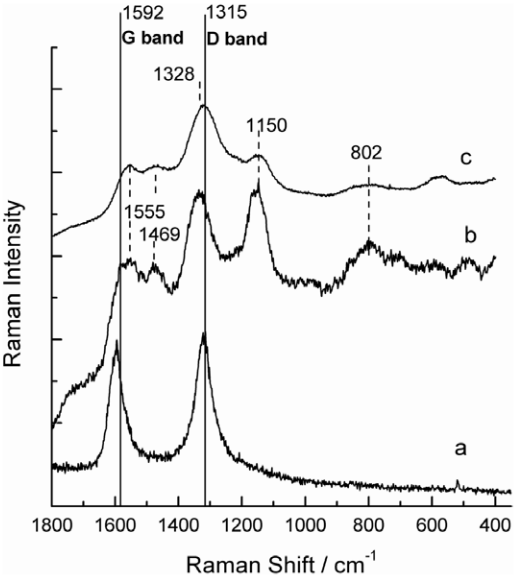

**Figure 4.** Raman spectra of (a) pure CNHs, (b) CNHs functionalized with polyaniline and (c) polyaniline.

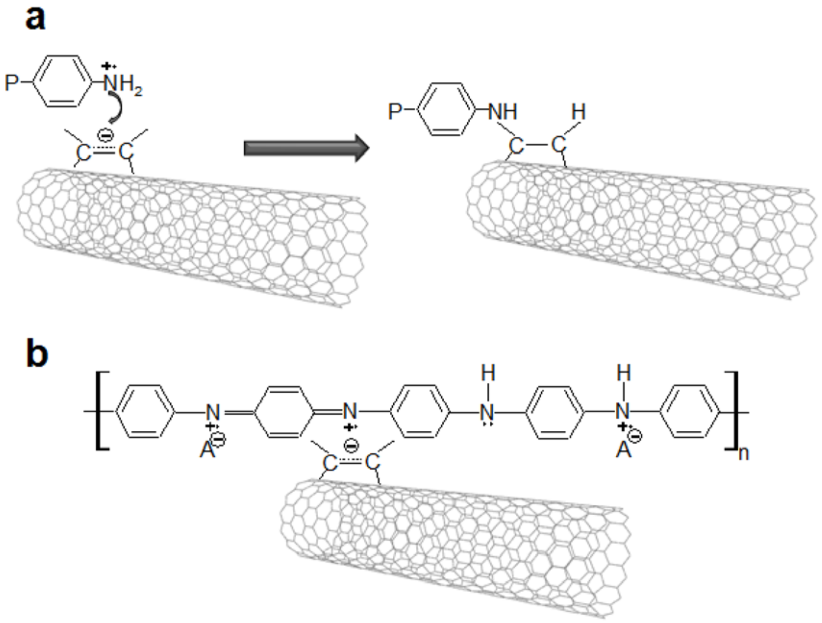

**Figure 3.** Two possible interactions of polyaniline with CNHs: (a) chemical covalent bonding and (b) electrochemical doping.

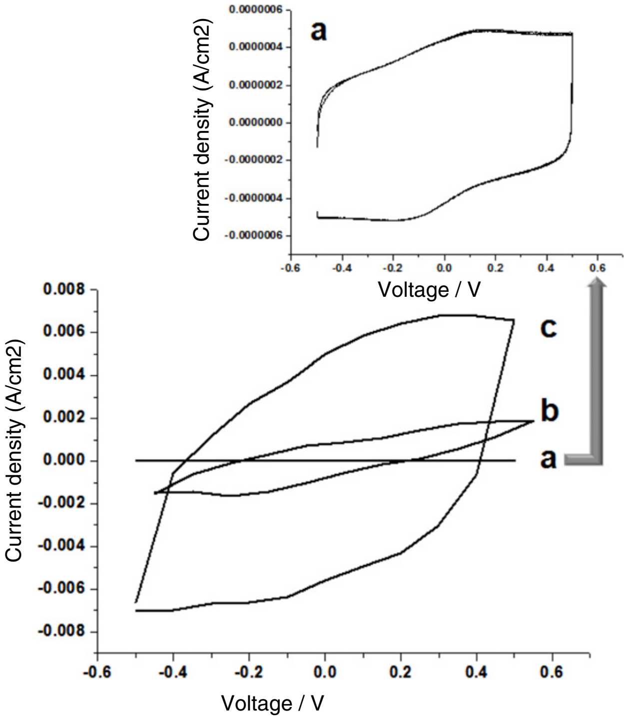

**Figure 5.** Cyclic voltammetry (CV) characterization of the supercapacitors made of (a) pure ITO, (b) nanostructured polyaniline on ITO and (c) nanostructured polyaniline and CNH nanocomposites on ITO. Inset is an enlarged CV diagram for supercapacitor made of pure ITO.

the carbon electrodes should have a high specific surface area that can be easily accessed by electrolytes. CNHs, when dried from a water suspension, become particles and cannot adhere to the ITO substrate. The PANI polymer is also acting as a matrix to hold the CNHs in the supercapacitor electrodes.

In summary, electrochemical nanofabrication generally offers simplicity, efficiency, low-temperature processing, cost-effectiveness, the possibility of preparing large-area deposits and precise control of the deposit thickness, which are essential advantages compared to other nanofabrication techniques to date. This paper describes a stepwise galvanostatic electrochemical deposition method to make PANI nanobrushes and PANI–CNH hybrid material. Both materials were thereafter used in supercapacitors and the hybrid material showed significant improvement in capacitive current. Deposition of electrochromic PANI on optically transparent electrodes may enable the visualization of energy charge by a color change of PANI when the supercapacitor is cycled between charging and discharging. With improvements in the conductance in transparent electrodes, further improved supercapacitive and electrochromic devices made of PANI–CNH may be realized.

## References

[1] Cheng F, Tang W, Li C, Chen J, Liu H, Shen P and Dou S 2006 *Chem.—Eur. J.* **12** 3082
[2] Kim B H, Park D H, Joo J, Yu S G and Lee S H 2005 *Synth. Met.* **150** 279
[3] Drury A, Chaure S, Kroell M, Nicolosi V, Chaure N and Blau W J 2007 *Chem. Mater.* **19** 4252
[4] Park S H and Xia Y 1998 *Adv. Mater.* **10** 1045
[5] Johnson S A, Ollivier P J and Mallouk T E 1999 *Science* **283** 963
[6] Tian S, Wang J, Jonas U and Knoll W 2005 *Chem. Mater.* **17** 5726
[7] Liu J, Lin Y, Liang L, Voigt J A, Huber D A, Tian Z R, Coker E, Mckenzie B and Mcdermott M J 2003 *Chem. Eur. J.* **9** 604
[8] Iijima S 1991 *Nature* **354** 56
[9] Peng C, Jin J and Chen G Z 2007 *Electrochim. Acta* **53** 525
[10] Bhattacharyya S, Kymakis E and Amaratunga G A J 2004 *Chem. Mater.* **16** 4819
[11] Gooding J J 2005 *Electrochim. Acta* **50** 3049
[12] Zou X, Zhang S, Shi M and Kong J 2007 *J. Solid State Electrochem.* **11** 317
[13] Wang H, Chhowalla M, Sano N, Jia S and Amaratunga G A J 2004 *Nanotechnology* **15** 546
[14] Yang C M, Kim Y J, Endo M, Kanoh H, Yudasaka M, Lijima S and Kaneki K 2007 *J. Am. Chem. Soc.* **129** 20
[15] Pushparaj V L, Manikoth S M, Kumar A, Murugesan S, Ci L, Vajtai R, Linhardt R J, Nalamasu O and Ajayan P M 2007 *Proc. Natl Acad. Sci.* **104** 13574
[16] Liang L, Liu J, Windisch C F Jr, Exarhos G J and Lin Y 2002 *Angew. Chem. Int. Edn* **41** 3665
[17] Baibarac M, Baltog I, Lefrant S, Mevellec J Y and Chauvet O 2003 *Chem. Mater.* **15** 4149
[18] Wei D, Kvarnstrom C, Lindfors T and Ivaska A 2007 *Electrochem. Commun.* **9** 206
[19] Zengin H, Zhou Z, Jin J, Czerw R, Smith D W, Echegoyen L, Caroll D L, Foulger S H and Ballato J 2002 *Adv. Mater.* **14** 1480
[20] Paloniemi H, Aaritalo T, Laiho T, Liuke H, Kocharova N, Haapakka K, Terzi F, Seeber R and Lukkari J 2005 *J. Phys. Chem.* B **109** 8634
[21] Bahr J L, Yang J P, Kosynkin D V, Bronikowski M J, Smalley R E and Tour J M 2001 *J. Am. Chem. Soc.* **123** 6536
[22] Balasubramanian K, Friedrich M, Jiang C, Fan Y, Mews A, Burghard M and Kern K 2003 *Adv. Mater.* **15** 1515
[23] Lefrant S, Baibarac M, Baltog I, Mevellec J Y, Godon C and Chauvet O 2005 *Diamond Relat. Mater.* **14** 867
[24] Lindfors T and Ivaska A 2005 *J. Electroanal. Chem.* **580** 320
[25] Quillard S, Berrada K, Louarn G, Lefrant S, Lapkowski M and Pron A 1995 *New. J. Chem.* **19** 365
[26] Gupta V and Miura N 2005 *Electrochem. Solid State Lett.* **8** A630
[27] Conway B E 1999 *Electrochemical Supercapacitors—Scientific Fundamentals and Technological Applications* (New York: Kluwer)
[28] Zhang H, Cao G, Wang Z, Yang Y, Shi Z and Gu Z 2008 *Nano Lett.* **8** 2664
[29] Mastragostino M, Arbizzani C and Soavi F 2002 *Solid State Ion.* **148** 493