

# Polyelectrolyte Functionalized Carbon Nanotubes as Efficient Metal-free Electrocatalysts for Oxygen Reduction

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**S** Supporting Information

**ABSTRACT:** Having a strong electron-withdrawing ability, poly(diallyldimethylammonium chloride) (PDDA) was used to create net positive charge for carbon atoms in the nanotube carbon plane via intermolecular charge transfer. The resultant PDDA functionalized/adsorbed carbon nanotubes (CNTs), either in an aligned or nonaligned form, were demonstrated to act as metal-free catalysts for oxygen reduction reaction (ORR) in fuel cells with similar performance as Pt catalysts. The adsorption-induced intermolecular charge-transfer should provide a general approach to various carbon-based efficient metal-free ORR catalysts for oxygen reduction in fuel cells, and even new catalytic materials for applications beyond fuel cells.

The activity of electrocatalysts for the oxygen reduction reaction (ORR) significantly affects the electrochemical performance of fuel cells and metal–air batteries.<sup>1</sup> In general, the ORR can proceed in two different pathways: (i) a two-electron process with the formation of H<sub>2</sub>O<sub>2</sub> as the intermediate; (ii) a more efficient four-electron process to directly produce H<sub>2</sub>O as the end product. Although Pt-based electrocatalysts have been traditionally used to catalyze the ORR with a high efficiency,<sup>2,3</sup> they still suffer from several serious problems, including the crossover and poisoning effects.<sup>4</sup> Besides, the high cost of the platinum catalysts, together with its limited reserves in nature, has precluded the large-scale commercialization of fuel cells. Therefore, efficient and low-cost ORR electrocatalysts are essential for mass marketing the fuel cell technology.

Along with the recent intensive research efforts in reducing or replacing Pt-based electrode in fuel cells,<sup>5,6</sup> we have found that vertically aligned nitrogen-containing carbon nanotubes (VA-NCNTs) could act as extremely effective metal-free ORR electrocatalysts.<sup>7</sup> The metal-free VA-NCNTs were shown to exhibit a 3 times higher electrocatalytic activity, smaller crossover effect, and better durability than the commercial Pt/C electrocatalysts in alkaline media.<sup>7</sup> On the basis of the experimental observations and quantum mechanics calculations, we attributed the improved electrocatalytic activity of the VA-NCNTs to the electron-withdrawing ability of the nitrogen atoms to create net positive charge on the adjacent carbon atoms in the carbon nanotube plane. In addition to the charge-induced favorable O<sub>2</sub> adsorption,<sup>7</sup> the positively charged carbon atoms can readily attract electrons from the anode to enhance the ORR. Uncovering this new ORR mechanism in nitrogen-doped carbon nanotube electrodes is

significant as the same principle could be applied to the development of various other metal-free efficient ORR catalysts for fuel cell and many other applications. In this regard, we have recently discovered that functionalization of carbon nanotubes (CNTs), simply through physical adsorption, with polyelectrolyte chains containing positively charged nitrogen moieties could also create net positive charge on carbon atoms of nitrogen-free CNTs via intermolecular charge-transfer. It was found that the polyelectrolyte adsorbed all-carbon CNTs, in either a vertically aligned or nonaligned form, possess remarkable electrocatalytic activities for ORR, similar to that of the commercially available Pt/C electrode (C2-20, 20% platinum on Vulcan XC-72R; E-TEK).<sup>2</sup> The ease with which all-carbon CNTs can be converted into efficient metal-free ORR electrocatalysts simply by the adsorption-induced intermolecular charge-transfer suggests considerable room for cost-effective preparation of various metal-free catalysts for oxygen reduction, and even new catalytic materials for applications beyond fuel cells. We believe that the results being reported in this communication will lead to new research areas of both fundamental and practical significance.

Various polyelectrolytes, including poly(diallyldimethylammonium chloride) (PDDA), have been used as interlinkers for depositing metal nanoparticles on CNTs<sup>2,8</sup> or fabricating multi-layer CNT thin films via the layer-by-layer (LBL) technique.<sup>9</sup> PDDA could effectively wrap around uncharged CNTs,<sup>10</sup> or adsorb onto negatively charged (e.g., acid oxidized) CNTs via electrostatic interaction.<sup>9</sup> Prior to our work, however, the intrinsic effect of polyelectrolyte on the CNT electronic structure (Scheme 1) and the possibility for the polyelectrolyte functionalized CNTs to be used as catalysts for the ORR process in fuel cells have not been exploited.

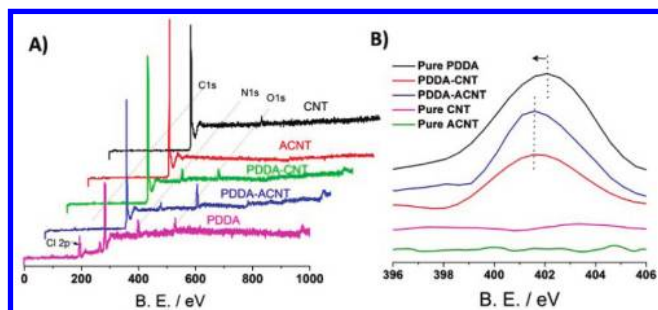
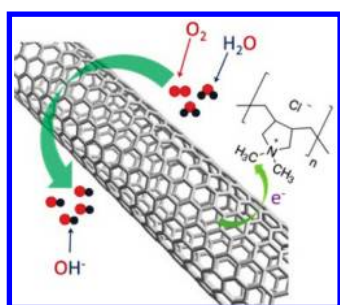
In this study, we found that quaternary ammonium functional groups along the PDDA backbone have a strong electron-accepting ability to withdraw electrons from carbon atoms in the nanotube carbon plane to induce the net positive charge, facilitating the ORR catalytic activity of the nitrogen-free CNTs adsorbed with the PDDA chains.<sup>7</sup>

In a typical experiment, the functionalization of nonaligned and vertically aligned CNTs with PDDA (denoted as: PDDA-CNT and PDDA-ACNT, respectively) was carried out by simply dispersing CNTs in an aqueous solution of PDDA<sup>10</sup> and by spin-coating/infiltrating PDDA chains into the nanotube array, respectively (see Experimental Section and Scheme S2 in Supporting Information [SI]).<sup>11</sup> X-ray photoelectron spectroscopy

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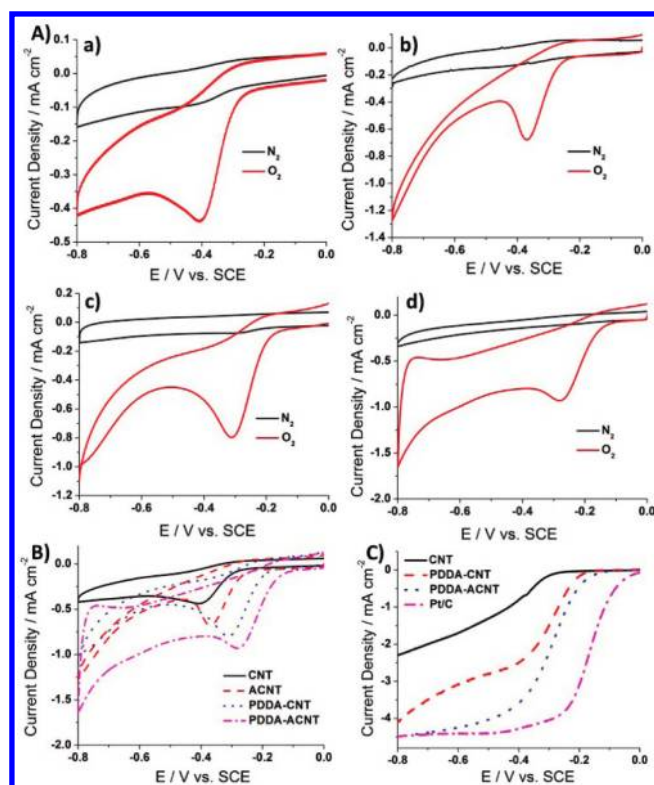
## Scheme 1. Illustration of Charge Transfer Process and Oxygen Reduction Reaction on PDDA-CNT



**Figure 1.** XPS (A) survey and (B) the high-resolution N1s spectra for vertically aligned and nonaligned carbon nanotubes before and after the functionalization with PDDA. Also included are the corresponding spectra for PDDA as reference; the O 1s peak is from adsorbed moisture.<sup>10</sup>

(XPS) and Raman measurements were performed to confirm the adsorption of PDDA chains onto CNTs and ACNTs as well as the associated intermolecular charge transfer.

As shown by the XPS spectra in Figure 1A, only a pronounced C 1s peak was observed for the pristine CNT and ACNT. The presence of a trace amount of O in the CNT sample is possibly due to the incorporation of physically adsorbed oxygen.<sup>12</sup> Upon PDPA functionalization, a N 1s peak appeared and the intensity of the O 1s peak increased for both PDPA-CNT and PDPA-ACNT. The newly appeared N 1s peak comes from the adsorbed PDPA chain while the observed intensity increase in the O 1s peak for both PDPA-CNT and PDPA-ACNT indicates an enhanced oxygen absorption onto the PDPA functionalized CNTs, suggesting an additional advantage as the ORR electrode.<sup>15</sup> The absence of any metal peak in the XPS spectra for the unfunctionalized CNTs clearly indicates that the metal catalyst residues, if any, have been completely removed by electrochemical purification (Experimental Section [SI]).<sup>7</sup> Figure 1B shows the N1s XPS spectra, in which the principle peak at around  $\sim 402$  eV for pure PDPA is attributed to the charged nitrogen,  $N^+$ . Compared to the N1s XPS peak in pure PDPA, the PDPA N1s peak position for PDPA-CNT and PDPA-ACNT shifted negatively to lower binding energy by  $\sim 0.5$  eV (Figure 1B), which indicates the occurrence of charge transfer from CNT or ACNT to the N species of PDPA. The observed charge-transfer related binding energy shift clearly establishes that PDPA acts as a *p*-type dopant to positively charge carbon atoms in the conjugated electron-rich nanotube carbon plane.<sup>13</sup> The N/C atomic ratio calculated for the PDPA-ACNTs (3.8 atom %) from XPS is much lower than that



**Figure 2.** (A) Cyclic voltammograms of ORR on CNT (a), ACNT (b), PDPA-CNT (c), and PDPA-ACNT (d) in  $N_2$  (black curve)- and  $O_2$  (red curve)-saturated 0.1 M KOH solutions at a scan rate of 50 mV/s. (B) The cyclic voltammograms for oxygen reduction in the  $O_2$ -saturated 0.1 M KOH solution. (C) Linear sweep voltammograms of ORR in an  $O_2$ -saturated 0.1 M KOH solution at a scan rate of 10 mV  $s^{-1}$ . The rotation rate is 1600 rpm.

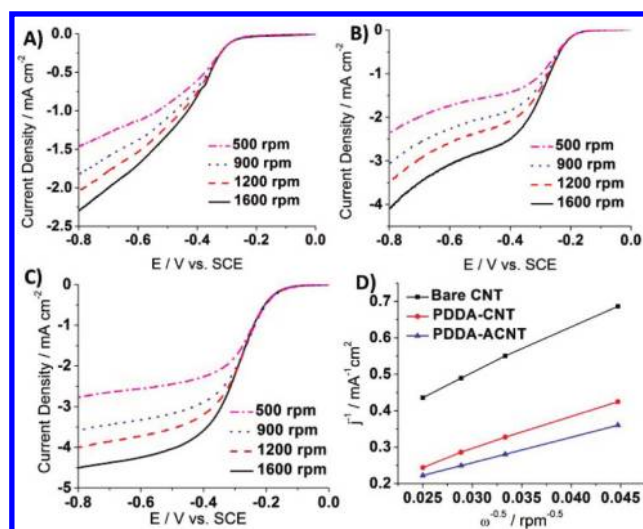
(13 atom %) of the pure PDPA, indicating a low adsorption degree as contributions from carbon atoms on the nanotube substrate are substantial. Thermogravimetric analyses (TGA) indicate about 8 and 12 wt % PDPA chains adsorbed on the CNTs and ACNTs, respectively (Figure S1 [SI]). Other evidence for functionalization of CNTs through adsorption of PDPA and the associated intermolecular charge-transfer come from FTIR (Figure S2 [SI]) and/or Raman (Figure S3 [SI]) measurements.<sup>14</sup>

The cyclic voltammograms (CVs) of oxygen reduction in  $O_2$ - or  $N_2$ -saturated 0.1 M KOH solutions at different electrodes (bare CNT, bare ACNT, PDPA-CNT, and PDPA-ACNT) at a constant active mass loading (0.01 mg) are shown in Figure 2. Figure 2A clearly shows the ORR peaks for all of the nanotube electrodes in the  $O_2$ -saturated, but not  $N_2$ -saturated, 0.1 M KOH solution. For the bare CNT electrode, the onset potential of ORR is at  $-0.29$  V (versus SCE) with a single cathodic reduction peak around  $-0.4$  V (versus SCE, Figure 2A(a),B), indicating a two-electron ( $2e^-$ ) process for reduction of  $O_2$  to peroxide ( $HO_2^-$  in 0.1 M KOH). Upon functionalization of the CNT with PDPA, both the onset potential and the reduction peak potential of ORR shifted positively to around  $-0.12$  V and  $-0.30$  V, respectively, with a concomitant increase in the peak current density (Figure 2A(c),B). These results clearly indicate a significant enhancement in the ORR electrocatalytic activity for the PDPA adsorbed CNTs (i.e., PDPA-CNT). Compared with the PDPA-CNT electrode (Figure 2A(c)), the PDPA-ACNT

electrode (Figure 2A(d),B) shows even a more positive shift in both the onset potential ( $-0.07$  V) and the peak potential ( $-0.28$  V) with a more pronounced increase in the current density. Apart from the charge-transfer effect, therefore, the alignment structure has also played a role in the ORR process by facilitating the electrolyte diffusion, as previously demonstrated for the VANCNT electrode.<sup>7</sup> On the other hand, it cannot be ruled out that the relatively high amount of PDDA adsorbed onto the ACNTs with respect to CNTs (Figure S1 [SI]) could have also contributed to the observed higher electrocatalytic activity for PDDA-ACNTs. However, the ORR electrocatalytic activity for the bare vertically aligned CNTs (ACNTs) (Figure 2A(b),B) is still lower than that of the PDDA functionalized nonaligned CNT (PDDA-CNT), albeit higher than that of the bare nonaligned CNT electrode (Figure 2B). As a control, we have also performed the ORR test on a solution-cast PDDA/GC electrode and bare GC electrode (Figure S4 [SI]), showing no ORR activity. Therefore, the observed enhancement in the ORR electrocatalytic activity for the PDDA functionalized CNT electrodes could be attributed exclusively to the intermolecular charge transfer schematically shown in Scheme 1. In view of the fact that polyethyleneimine (PEI) has been widely used as an electron donor to modify CNTs for various device applications (e.g., FETs),<sup>16</sup> we have also functionalized CNTs with PEI (PEI-CNTs, Scheme S3 [SI]) and compared the ORR electrocatalytic activity of the PEI-CNTs with the bare CNT electrode (Figure S5 [SI]). As expected, the ORR onset potential at the PEI-CNT electrode shifted negatively from that of the bare CNT electrode, indicating a reduced ORR electrocatalytic activity for the CNTs after being functionalized with the electron-donating PEI chains.

To further investigate the ORR performance, we carried out the linear sweep voltammetry (LSV) measurements on a rotating disk electrode (RDE) for each of the electrode materials, including the CNT-based and commercial Pt/C electrocatalysts, in  $O_2$ -saturated 0.1 M KOH at a scan rate of  $10 \text{ mV s}^{-1}$  and a rotation rate of 1600 rpm. As can be seen in Figure 2C, the ORR at the bare CNT electrode commenced around  $-0.24$  V (onset potential), followed by a continuous increase in the current density with no current plateau. The ORR onset potential at the PDDA-CNT electrode significantly shifted positively to  $-0.14$  V and the limiting diffusion current at  $-0.4$  V became about 3 times stronger with a relatively wide plateau in respect to the bare CNT electrode. Compared to both the PDDA-CNT and bare CNT electrodes, the strongest limiting diffusion current with a very wide current plateau was observed for ORR at the PDDA-ACNT electrode due, most probably, to an efficient four-electron pathway. The ORR current density at  $-0.4$  V at the PDDA-ACNT electrode is 1.5 and 4.5 times that at the PDDA-CNT and bare CNT electrode, respectively, indicating that the combined effects of the PDPA adsorption and the aligned CNT structure are responsible for the high ORR electrocatalytic activity observed for the PDDA-ACNT electrode. Although the onset potential of ORR on PDDA-ACNT ( $-0.09$  V) is still lower than that of the Pt/C electrode, its limiting diffusion current density is close to that of the Pt/C catalyst. Thus, our results should be sufficiently promising to warrant further research efforts in developing novel metal-free catalysts through intermolecular charge transfer.

To examine the possible crossover effect in the presence of other fuel molecules (e.g., methanol), the current–time ( $i-t$ ) chronoamperometric responses for ORR at the PDDA-CNT and PDDA-ACNT electrodes were given in Figure S6 ([SI]). For comparison, the corresponding current–time ( $i-t$ ) chronoamperometric



**Figure 3.** Linear sweep voltammetry curves of ORR at various rotation rates at (A) bare CNT, (B) PDDA-CNT, and (C) PDDA-ACNT. (D) Koutecky–Levich plots for the three electrode materials at  $-0.8$  V.

response for a Pt/C catalyst is also included in Figure S6 ([SI]) that shows a sharp decrease in current upon the addition of 3.0 M methanol. However, the amperometric responses from the PDDA-CNT and PDDA-ACNT electrodes remained unchanged even after the addition of methanol. This result confirms that the PDPA functionalized CNT electrocatalysts have a higher selectivity toward ORR and better methanol tolerance than the commercial Pt/C electrode. In addition, the durability of the PDDA-CNT, PDDA-ACNT, and the commercial Pt/C electrodes for ORR was evaluated via a chronoamperometric method<sup>5b</sup> at  $-0.25$  V in  $O_2$ -saturated 0.1 M KOH at a rotation rate of 1600 rpm. As seen in Figure S7 ([SI]) the current density loss on PDDA-CNT and PDDA-ACNT is much less than that on Pt/C after continuous reaction for 20000 s, and then the  $i-t$  chronoamperometric responses for the PDDA-CNT and PDDA-ACNT electrodes seem to level off, indicating that the PDPA adsorbed nanotube electrocatalysts are more stable than the commercial Pt/C electrode.

RDE voltammetry measurements were also carried out to gain further insight on the ORR performance of the CNT electrodes before and after adsorption with PDPA. Figure 3A–C shows RDE current–potential curves at different rotation rates for various CNT-based electrodes. As can be seen, the limiting current density increases with increasing rotation rate. Once again, the limiting current densities obtained from the PDDA-ACNT electrode are higher than those at the bare CNT and PDDA-CNT electrodes at a constant rotation rate. The transferred electron number per oxygen molecule involved in the oxygen reduction at each of the CNT electrodes was determined by the Koutecky–Levich equation given below:<sup>6,15</sup>

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{0.5}} \quad (1)$$

where  $j_k$  is the kinetic current and  $\omega$  is the electrode rotating rate.  $B$  could be determined from the slope of K–L plots (Figure 3D) based on Levich equation as follows:<sup>15</sup>

$$B = 0.2nF(D_{O_2})^{2/3}v^{-1/6}C_{O_2} \quad (2)$$

where  $n$  represents the number of electrons transferred per oxygen molecule,  $F$  is the Faraday constant ( $F = 96485$

$C \text{ mol}^{-1}$ ),  $D_{\text{O}_2}$  is the diffusion coefficient of  $\text{O}_2$  in 0.1 M KOH ( $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ),  $\nu$  is the kinetic viscosity ( $0.01 \text{ cm}^2 \text{ s}^{-1}$ ), and  $C_{\text{O}_2}$  is the bulk concentration of  $\text{O}_2$  ( $1.2 \times 10^{-6} \text{ mol cm}^{-3}$ ). The constant 0.2 is adopted when the rotation speed is expressed in rpm.

As shown in Figure 3D, a linear relationship between  $j^{-1}$  and  $\omega^{-0.5}$  was observed for all the three CNT-based electrodes at  $-0.8 \text{ V}$ . The numbers of electrons transferred per  $\text{O}_2$  molecule ( $n$ ) were calculated from the slope of the K–L plots to be 2.21, 3.08, and 3.72 for the bare CNT, PDDA-CNT, and PDDA-ACNT electrode, respectively. While the electron transfer number (2.21) of ORR at the bare CNT electrode is close to the classical two-electron process, as is the case for many other carbon-based electrode materials,<sup>7</sup> the corresponding number of 3.72 for the PDDA-ACNT electrode indicates an efficient four-electron process similar to the Pt/C electrode. On the other hand, the electron transfer number of 3.08, which lies between the two-electron and four-electron processes, for the PDDA-CNT electrode suggests that the oxygen reduction on PDDA-CNT electrocatalysts may proceed by a coexisting pathway involving both the two-electron and four-electron transfers.

In summary, we have demonstrated that certain polyelectrolyte (e.g., PDDA) functionalized carbon nanotubes, either in an aligned or nonaligned form, could act as metal-free electrocatalysts for ORR. It is notable that the PDDA adsorbed vertically aligned CNT electrode possesses remarkable electrocatalytic properties for ORR—similar to that of commercially available Pt/C electrode but a better fuel selectivity and long-term durability. Furthermore, this work clearly indicates that the important role of intermolecular charge transfer to ORR for nitrogen-free carbon nanotubes can be applied to other carbon materials for the development of various other metal-free efficient ORR catalysts for fuel cell applications, even new catalytic materials for applications beyond fuel cells. Therefore, the methodology developed in this study could serve as a general approach to the development of various metal-free catalysts.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** The experimental section, details of material preparation, electrode fabrication, and supplementary results and discussion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ REFERENCES

- (1) (a) Stamenkovic, V. R.; Fowler, B.; Mun, B. S.; Wang, G. J.; Ross, P. N.; Lucas, C. A.; Markovic, N. M. *Science* **2007**, *315*, 493. (b) Zhang, J. D.; Vukmirovic, M. R.; Xu, Y.; Mavrikakis, M.; Adzic, R. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 2132.
- (2) Wang, S. Y.; Jiang, S. P.; White, T. J.; Guo, J.; Wang, X. J. *Phys. Chem. C* **2009**, *113*, 18935.

- (3) Yano, H.; Song, J. M.; Uchida, H.; Watanabe, M. *J. Phys. Chem. C* **2008**, *112*, 8372.
- (4) (a) Arenz, M.; Mayrhofer, K. J. J.; Stamenkovic, V.; Blizanac, B. B.; Tomoyuki, T.; Ross, P. N.; Markovic, N. M. *J. Am. Chem. Soc.* **2005**, *127*, 6819. (b) Kowal, A.; Li, M.; Shao, M.; Sasaki, K.; Vukmirovic, M.; Zhang, J.; Marinkovic, N. S.; Liu, P.; Frenkel, A. I.; Adzic, R. R. *Nat. Mater.* **2009**, *8*, 325.
- (5) (a) Xiao, L.; Zhuang, L.; Liu, Y.; Lu, J. T.; Abruna, H. D. *J. Am. Chem. Soc.* **2009**, *131*, 602. (b) Liu, R. L.; Wu, D. Q.; Feng, X. L.; Mullen, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 2565. (c) Yu, D. S.; Nagelli, E.; Du, F.; Dai, L. M. *J. Phys. Chem. Lett.* **2010**, *1*, 2165. (d) Xiong, W.; Du, F.; Liu, Y.; Perez, A.; Supp, M.; Ramakrishnan, T. S.; Dai, L.; Jiang, L. *J. Am. Chem. Soc.* **2010**, *132*, 15127.
- (6) Yu, D.; Zhang, Q.; Dai, L. *J. Am. Chem. Soc.* **2010**, *132*, 15839.
- (7) Gong, K. P.; Du, F.; Xia, Z. H.; Durstock, M.; Dai, L. M. *Science* **2009**, *323*, 760.
- (8) Alexeyeva, N.; Tammeveski, K. *Anal. Chim. Acta* **2008**, *618*, 140.
- (9) Zhang, M. N.; Yan, Y. M.; Gong, K. P.; Mao, L. Q.; Guo, Z. X.; Chen, Y. *Langmuir* **2004**, *20*, 8781.
- (10) Yang, D. Q.; Rochette, J. F.; Sacher, E. *J. Phys. Chem. B* **2005**, *109*, 4481.
- (11) Chen, W.; Qu, L.; Chang, D.; Dai, L.; Ganguli, S.; Roy, A. *Chem. Commun.* **2008**, 163.
- (12) Collins, P. G.; Bradley, K.; Ishigami, M.; Zettl, A. *Science* **2000**, *287*, 1801.
- (13) Choudhury, D.; Das, B.; Sarma, D. D.; Rao, C. N. R. *Chem. Phys. Lett.* **2010**, *497*, 66.
- (14) Rao, A. M.; Eklund, P. C.; Bandow, S.; Thess, A.; Smalley, R. E. *Nature* **1997**, *388*, 257.
- (15) Qu, L. T.; Liu, Y.; Baek, J. B.; Dai, L. M. *ACS Nano* **2010**, *4*, 1321.
- (16) Shim, M.; Javey, A.; Kam, N. W. S.; Dai, H. J. *J. Am. Chem. Soc.* **2001**, *123*, 11512.