J|A|C|S
COMMUNICATIONS

Published on Web 09/01/2009

Electrocatalytic Activity of Nitrogen-Doped Carbon Nanotube Cups

Yifan Tang, Brett L. Allen, Douglas R. Kauffman, and Alexander Star*

Department of Chemistry, University of Pittsburgh and the National Energy Technology Laboratory, Pittsburgh, Pennsylvania 15260

Received June 5, 2009; E-mail: astar@pitt.edu

Carbon-based nanomaterials, such as nanotubes[1] and graphene,[2] are currently at the forefront of materials research because they show outstanding electrocatalytic activity due to their unique electrical and chemical properties. Furthermore, the doping of these carbon nanostructures with nitrogen atoms has drawn much attention because conjugation between the nitrogen lone-pair electrons and the graphene π-system[3−5] may create nanomaterials with tailored electronic and mechanical properties. Recently, Dai and co-workers reported that nitrogen-doped carbon nanotube arrays demonstrate high electrocatalytic activity for the oxygen reduction reaction (ORR),[6] with a great potential for low-cost nonplatinum catalysts for fuel cell cathodes. However, the exact extent of the electrocatalytic activity of these nanomaterials and their application for other electrochemical reactions remained unknown. In this work we compare nitrogen-doped carbon nanotube cups (NCNCs) to commercial Pt-decorated multiwall carbon nanotubes (Pt-CNTs) as catalysts in ORR and demonstrate their applications for electrochemical detection of H_2O_2 and glucose.

NCNCs, also known as nanobells,[7] have been synthesized via chemical vapor deposition (CVD) as we reported previously[8] using MeCN, EtOH, and ferrocene as liquid precursors and Ar and H_2 as carrier gases. Transmission electron microscopy (TEM) images of NCNCs reveal that the nanomaterial is composed of individual nanocups stacked together to form long nanofibers (Figure 1a). Each nanocup has a proportional length and diameter of 12−40 nm, with a mean distribution of ∼20 nm. The nitrogen content of the nanocups was determined at 2−7% by electron energy loss spectroscopy (EELS).[8] For electrochemical comparison, we used commercial Pt-CNTs with a tube diameter of 10 to 15 nm with a Pt particle size of ∼1.5 nm (Figure 1b). The platinum content in Pt-CNTs was measured at 11.5% by thermogravimetric analysis (TGA) (Supporting Information (SI)). Analogous to the previous study,[6] we have conducted cyclic voltammetry (CV) of stacked nanocups and Pt-CNTs in O_2 saturated 0.1 M KOH aqueous solutions (Figure 1c). We observed ORR peaks for NCNCs and Pt-CNTs at −0.438 and −0.386 V, respectively. These peaks were absent in N_2 saturated solutions (SI).

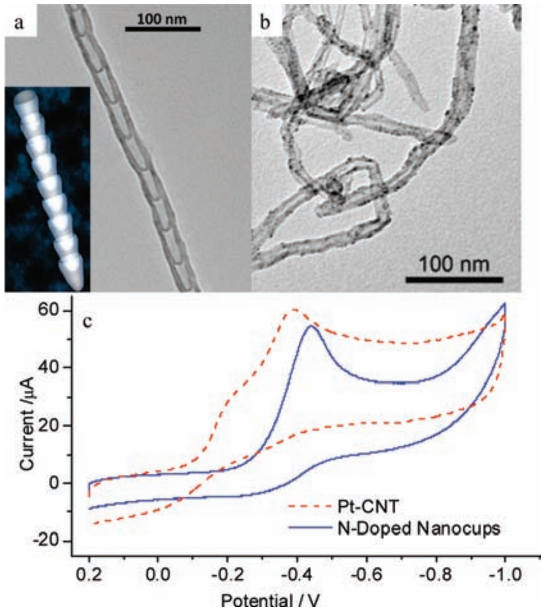

Figure 1. (a) Transmission electron microscopy (TEM) image of stacked nitrogen-doped carbon nanotube cups (NCNCs). Inset: cartoon illustrating orientation of the nanocups in stacked NCNC. (b) TEM image of commercial Pt-CNTs. (c) Cyclic voltammograms (CV) of stacked NCNCs versus commercial Pt-CNTs in oxygen saturated 0.1 M KOH aqueous solution both showing the oxygen reduction reaction (ORR) peaks.

Comparison of the ORR CVs reveals that NCNCs and Pt-CNTs have similar peak shapes, intensities, and positions. This similarity indicates that NCNCs have electrochemical activity for ORR comparable to that of Pt catalyst. To rule out the possibility that traces of Pt metal (from glassware or Pt-counter electrode) might be responsible for the observed electrocatalytic activity of NCNCs, we have confirmed these CV results using brand new glassware and Cu foil as the counter electrode (SI). NCNCs showed similar durability (∼$^1/_3$ current loss after 20 000 s) to Pt-CNTs in ORR when tested under constant cathode potential (SI). Furthermore, rotating ring disk electrode (RRDE) voltammetry was performed to study oxygen reduction under steady-state conditions. Transferred electron number (*n*) per oxygen molecule suggested that while Pt-CNTs follow a four-electron pathway, the NCNCs' reduction process is a combination of two-electron and four-electron pathways (SI).

Based on the electrocatalytic performance of N-doped nanocups in ORR, it is worthwhile to investigate if NCNCs can catalyze other electrochemical reactions where Pt catalyst is currently used. Electrochemical detection of H_2O_2 is a basis for detection of many medically important analytes[9] including glucose, which currently dominates the biosensor market.[10]

Figure 2 shows the amperometric response of a stacked NCNC-modified glassy carbon (GC) electrode upon successive addition of different concentrations of H_2O_2 in 50 mM phosphate buffer solution (PBS) (pH = 7.2) at 500 mV vs Ag/AgCl reference electrode. The NCNC-modified GC electrode exhibits a linear range from 0.1 to 10 mM (R = 0.9936) with a sensitivity of 0.19 μA/mM. Above 10 mM H_2O_2, the electrode response deviates from linearity as it saturates.

The detection of glucose was performed by further modification of the NCNC-GC electrode with glucose oxidase (GOx) and Nafion. The amperometric response upon successive addition of glucose in 50 mM PBS (pH = 7.2) at 500 mV vs Ag/AgCl is shown in Figure 3. The response was proportional to the glucose concentration in a range from 0.3 to 7 mM with a sensitivity of 0.033 μA/mM and a correlation coefficient of 0.9999. The limit of detection

10.1021/ja904595t CCC: $40.75 © 2009 American Chemical Society

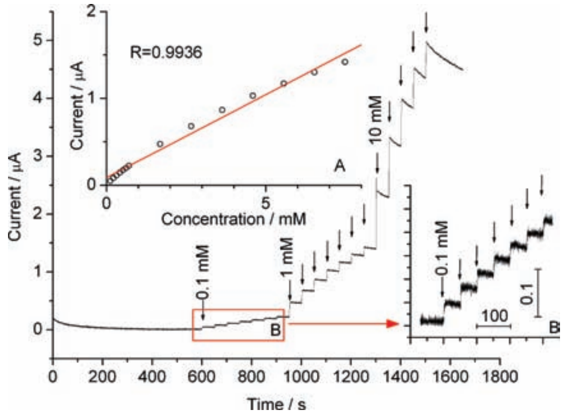

Figure 2. Current versus time curve of the stacked NCNC-modified GC electrode for successive addition of H_2O_2 (indicated by arrows with marked concentrations) to 50 mM pH = 7.2 PBS at 0.50 V vs Ag/AgCl. Inset A: Calibration curve for H_2O_2. Inset B: Amplification of curve B.

was estimated from the slope to be 0.3 mM at a signal-to-noise ratio of 3. Above 10 mM glucose the electrode is saturated and we observed a sluggish response with further addition. The results from this unoptimized glucose sensor were inferior to the performance of Pt-CNT electrodes (SI). In our setup, electrodes modified with Nafion-GOx-Pt-CNTs showed a response to glucose with a lower detection limit of 0.01 mM and deviation from linearity at ∼10 mM, which is comparable to the literature values.[9]

The observed catalytic activity of NCNCs toward oxidation of H_2O_2, which is a reversed process to ORR where O_2 is reduced to H_2O_2, can be explained by the strong electronic affinity of the nitrogen atoms and the substantially high positive charge density on the adjacent carbon atoms.[6] These sites are favorable for the side-on O_2 adsorption, which could effectively weaken O−O bonding to facilitate ORR.[6] Furthermore, the unique structure of NCNCs can also contribute to the catalytic activity. Unlike N-doped carbon nanotubes or N-doped graphene, where N atoms are distributed along the whole surface, in NCNCs the nitrogen atoms are concentrated primarily on the basal edges of individual cups within the stacked fiber.[8] Such nitrogen enrichment might provide a higher density of catalytically active centers with low stereohindrance for binding redox species. It has been recently proposed[11] that binding of the reduction intermediate, OOH, on pyridinic edge sites in nitrogen-treated graphite is optimal for two-electron reduction of O_2 to H_2O_2.

Another possible explanation for the catalytic activity of NCNCs could be related to the presence of residual Fe catalyst in nanocups remaining from their CVD synthesis (SI). Although we have observed no Fe peak in the CV of stacked NCNCs (Figure 1c), Fe was evident in the nanocups after they were physically separated and electrochemically purified (SI). We hypothesize that the residual iron can interact with nitrogen atoms, to form iron-porphyrin-like structures,[12] and such Fe/N/C electrocatalysts[13] can be responsible for ORR and H_2O_2 oxidation. The catalytic activity of separated nanocups toward ORR (SI) suggests that it is the intrinsic catalytic property of isolated nanocups, rather than the stacked form. It has been previously shown[14] that the Fe species in N-doped carbon nanotubes could be dissolved and/or passivated during electrochemical potential cycling and were not the primary catalytically active site for ORR. However, similar treatment of NCNCs resulted in only a slight dissolution/passivation of the Fe (SI), indicating that Fe is bound more strongly in NCNCs and results in improved stability and catalytic activity as the Fe/N/C structure. Without completely ruling out the possible effect of Fe species,[15] both mechanisms might explain the electrocatalytic activity of NCNCs. Further studies are needed to reveal the exact mechanism of the catalytic activity of nitrogen-doped carbon nanomaterials.

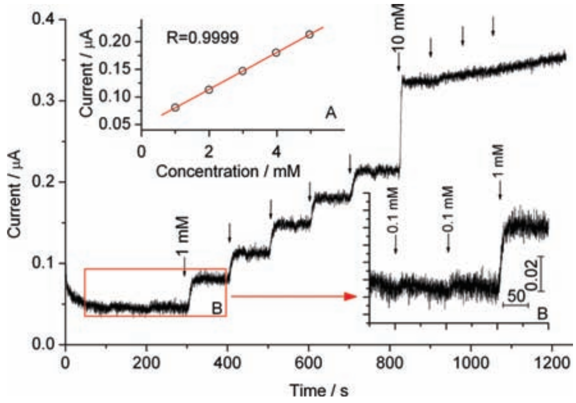

Figure 3. Current−time curve of Nafion-GOx-NCNC-modified GC electrode for successive addition of glucose (indicated by arrows with marked concentrations) to 50 mM pH = 7.2 PBS at 0.50 V vs Ag/AgCl. Inset A: Calibration curve for glucose. Inset B: Amplification of curve B.

In conclusion, we demonstrated that the stacked NCNCs have similar catalytic ability in ORR as Pt-CNTs and also could be used in the electrochemical detection of H_2O_2 and glucose. By comparison with commercial Pt-CNTs catalyst, the N-doped nanocups have shown the potential to replace the costly Pt-based catalyst in fuel cells and sensors.

Acknowledgment. This work was supported by the Pennsylvania NanoMaterials Commercialization Center through funding provided by DCED. We thank John Baltrus at the National Energy Technology Laboratory for access to the XPS instrumentation and Shigeru Amemiya for access to RRDE.

Supporting Information Available: Experimental procedures; TGA of commercial Pt-CNTs; XPS and additional CVs of stacked, separated NCNCs and Pt-CNTs; amperometric response of Nafion-GOx-Pt-CNT-modified GC electrode. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Wang, J. *Electroanalysis* **2005**, *17*, 7.
(2) Alwarappan, S.; Erdem, A.; Liu, C.; Li, C. *J. Phys. Chem. C* **2009**, *113*, 8853.
(3) Terrones, M.; Terrones, H.; Grobert, N.; Hsu, W. K.; Zhu, Y. Q.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M.; Kohler-Redlich, P.; Rühle, M.; Zhang, J. P.; Cheetham, A. K. *Appl. Phys. Lett.* **1999**, *75*, 3932.
(4) Han, W. Q.; Kohler-Redlich, P.; Seeger, T.; Ernst, F.; Rühle, M.; Grobert, N.; Hsu, W. K.; Chang, B. H.; Zhu, Y. Q.; Kroto, H. W.; Walton, D. R. M.; Terrones, M.; Terrones, H. *Appl. Phys. Lett.* **2000**, *77*, 1807.
(5) Wang, X.; Li, X.; Zhang, L.; Yoon, Y.; Weber, P. K.; Wang, H.; Guo, J.; Dai, H. *Science* **2009**, *324*, 768.
(6) Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. *Science* **2009**, *323*, 760.
(7) Wang, E. G. *J. Mater. Res.* **2006**, *21*, 2767.
(8) Allen, B. L.; Kichambare, P. D.; Star, A. *ACS Nano* **2008**, *2*, 1914.
(9) Hrapovic, S.; Liu, Y.; Male, K. B.; Luong, J. H. T. *Anal. Chem.* **2004**, *76*, 1083.
(10) Wang, J. *Chem. Rev.* **2008**, *108*, 814–825.
(11) Kurak, K.; Anderson, A. B. *J. Phys. Chem. C* **2009**, *113*, 6730.
(12) Lefèvre, M.; Dodelet, J. P.; Bertrand, P. *J. Phys. Chem. B* **2002**, *106*, 8705.
(13) Lefèvre, M.; Proietti, E.; Jaouen, F.; Dodelet, J. P. *Science* **2009**, *324*, 71.
(14) Lyon, J. L.; Stevenson, K. J. *Langmuir* **2007**, *23*, 11311.
(15) Kruusma, J.; Mould, N.; Jurkschat, K.; Crossley, A.; Banks, C. E. *Electrochem. Commun.* **2007**, *9*, 2330.

JA904595T