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Electrochemical Analysis of Single-Walled Carbon Nanotubes Functionalized with Pyrene-Pendant Transition Metal Complexes

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Single-walled carbon nanotubes (SWNTs) have received much attention due to their unique electronic and mechanical properties and their promise as building blocks for advanced materials and electronic devices.[1−4] Functionalization of SWNTs has been a strategy widely employed to modulate the properties and behavior of SWNT materials and devices, and a variety of chemical methodologies have been used to accomplish this.[5−12] In this work, electrochemical techniques were used to examine the functionalization, facilitated by noncovalent $\pi-\pi$ stacking interactions, of SWNTs with the pyrene-terminated cobalt(II) terpyridyl complex shown in Figure 1A. Not only does this work demonstrate a new system for the controllable functionalization of SWNT surfaces, but the electrochemical analyses described, unlike the spectroscopic, thermogravimetric, scanning probe and electron microscopy techniques often used to investigate these systems,[5−15] permit real-time in situ monitoring of the adsorption process without the complications and overhead that accompanies the fabrication and use of single-tube devices .

The synthesis and characterization of $[Co(\mathbf{tpy}\sim\mathbf{py})_2]^{2+}$, as well as the investigation of its adsorption on glassy carbon, has been described elsewhere.[16] To examine the functionalization of SWNTs with $[Co(\mathbf{tpy}\sim\mathbf{py})_2]^{2+}$, it was first necessary to devise an electrochemical setup where the carbon nanotubes would serve as the working electrode in a standard three-electrode cell. A home-built platinum working electrode, encased in glass, was polished and then heated to approximately 200 °C by wrapping the end of the electrode with heating tape. A 50 μL aliquot of an aqueous suspension of SWNTs (NanoIntegris PureTubes) was then dropped onto the hot Pt surface, and the water was evaporated, leaving a film of SWNTs adhered to the metallic electrode. The electrode was then rinsed with methanol to remove the proprietary surfactant used to disperse the nanotubes.[17] An AFM image of such a film of SWNTs, prepared on a silicon substrate, can be seen in Figure 1B and indicates that a dense, intertwined mat of carbon nanotubes, with minimal catalyst particles, is the result of this process. Since the SWNTs are in contact with each other and with the Pt electrode surface, this mat can act as an extension of the Pt working electrode. In Figure 1C, cyclic voltammograms (CVs) of neat supporting electrolyte and of 20 μM cobalt(II) bis (terpyridine) (without the pyrene functionality that can facilitate adsorption) at both a bare Pt working electrode and at a SWNT-coated Pt working electrode can be seen. The redox wave shown is that for the Co(II/III) oxidation/reduction process. As the SWNT sample used contained both metallic and semiconducting nanotubes, and because the points of contact between SWNTs are not necessarily ohmic, some uncompensated resistance would be expected and the "tilt" of the CV for the SWNT-coated electrode shown in Figure 1C is reflective of this.[18] A ΔE_{peak} of approximately 90 mV indicates that this system is not completely Nernstian,[18] consistent with a working electrode that is composed of a network of imperfectly connected SWNTs where swift and facile electron transfer is unlikely.

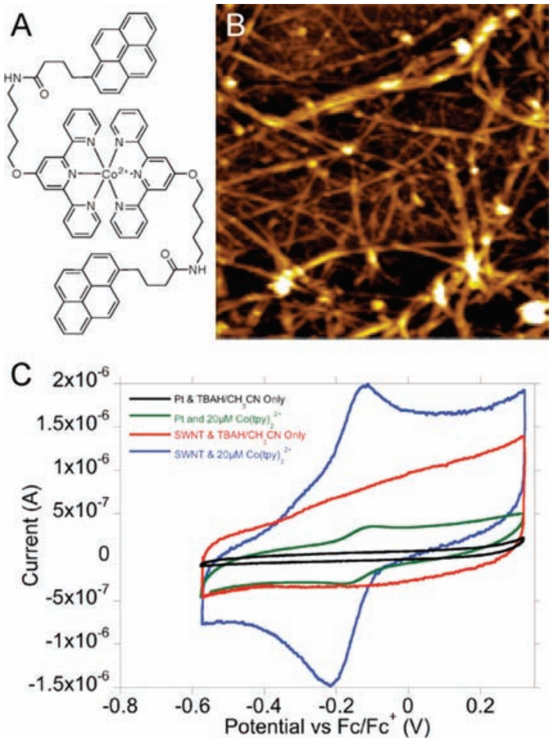

Figure 1. (A) Cobalt bis (4-Pyren-1-yl-*N*-[5-([2,2′;6′,2″]terpyridin-4′-yloxy)-pentyl]-butyramide) ($[Co(\mathbf{tpy}\sim\mathbf{py})_2]^{2+}$). (B) Noncontact mode atomic force microscope image (3 × 3 μm) of SWNTs dispersed on silicon substrate. (C) CVs of 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH)/CH_3CN and of 20 μM $[Co(tpy)_2]^{2+}$ in (TBAH)/CH_3CN at bare Pt and SWNT-coated Pt working electrodes; all with a potential sweep rate of 100 mV/s.

Nevertheless, it is clear that a well-defined electrochemical response can be obtained from this SWNT electrode. A comparison of the anodic peak current of the Co (II/III) redox process, at the bare and at the SWNT-coated electrode, indicates that the electrochemically active surface area of the SWNT-coated Pt electrode is approximately 8 times larger than that of the platinum surface.[18] This is the result of a significant quantity of SWNTs functioning as a working electrode, and it is clear that the electrochemical response observed from such an electrode can be primarily considered reflective of processes occurring at the surface of SWNTs. While the possible role of catalyst particles in the observed electrochemical response cannot be ignored, their miniscule surface area compared to that of the SWNTs and their lack of well-defined redox chemistry in the potential window of interest make it highly

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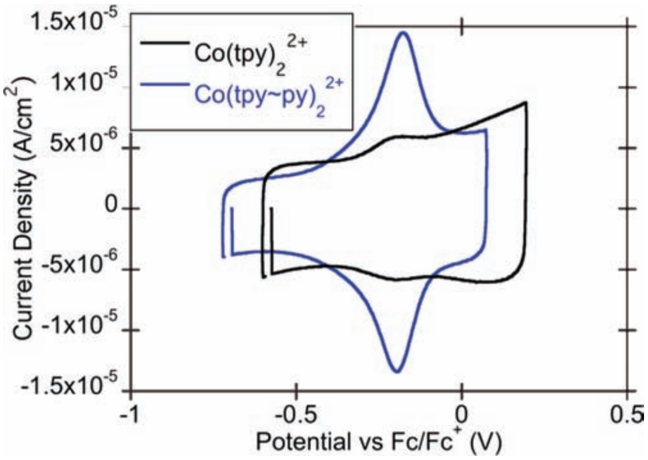

Figure 2. Overlaid cyclic voltammograms of 5 μM [Co(tpy)$_2$]$^{2+}$ and 5 μM [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$, each in 0.1 M TBAH/CH$_3$CN at the same SWNT-coated Pt working electrode with a potential sweep rate of 100 mV/s.

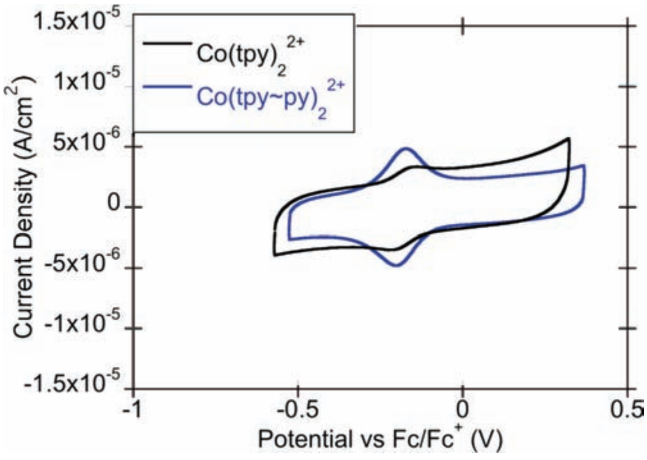

Figure 3. Overlaid cyclic voltammograms of 5 μM [Co(tpy)$_2$]$^{2+}$ and 5 μM [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$, each in 0.1 M TBAH/CH$_3$CN at the same Pt working electrode with a potential sweep rate of 100 mV/s.

unlikely that they would contribute in a meaningful way to the observed electrochemical signals. Further, instrumental neutron activation analysis of the SWNT material, commissioned by NanoIntegris, has shown that there is considerably less than 1% by mass of any potential catalyst impurities remaining in the SWNTs.[17]

To examine the adsorption of [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$ on SWNTs, a SWNT-coated Pt electrode was first placed into a 5 μM solution of [Co(tpy)$_2$]$^{2+}$ in 0.1 M TBAH/CH$_3$CN. After soaking for 2 h, the cyclic voltammogram, shown in black in Figure 2, was obtained; the relatively small current is due to the low concentration of the analyte. The electrode was then removed from this solution, rinsed with copious amounts of CH$_3$CN and placed into a 5 μM solution of [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$ in 0.1 M TBAH/CH$_3$CN. After soaking for 2 h in this solution, the cyclic voltammogram shown in blue in Figure 2 was obtained. Despite the concentrations of each analyte being the same, the current response for [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$ was almost 10 times greater than that for [Co(tpy)$_2$]$^{2+}$. Additionally, the ΔE_{peak} for [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$ was less than 20 mV (compared with 90 mV for [Co(tpy)$_2$]$^{2+}$), giving a strong indication that the [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$ was specifically adsorbed to the surface of the SWNTs.[19]

Using the Randles−Sevcik equation and the previously measured diffusion coefficient of [Co(tpy)$_2$]$^{2+}$, the surface area of the SWNT electrode and subsequently the coverage of [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$ on the surface of the SWNTs was determined.[16,18,19] For the CV shown above, the coverage of [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$ is estimated at 1.0×10^{-10} mol/cm^2. As the [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$ complex is relatively large, the possibility of it nonspecifically adsorbing onto all surfaces (including a bare Pt electrode) was considered. In Figure 3 the experiment shown above in Figure 2 was repeated at a bare Pt electrode. If [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$ did not adsorb at all on platinum, the two CVs in Figure 3 would be nearly identical. What is evident from the size of the electrochemical response of [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$ at a platinum electrode is that there is some degree of adsorption. However, the coverage of [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$ on platinum, determined as described previously, was found to be only 2.1×10^{-11} mol/cm^2, approximately a factor of 5 smaller than that on SWNTs.

This comparatively small degree of adsorption is suggestive of a weak nonspecific interaction between [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$ and the platinum surface, and this is confirmed by the total disappearance of any redox wave upon rinsing the electrode and placing it in fresh supporting electrolyte.

It is well-known that the dependence of current on the potential sweep rate is different for surface-confined redox processes than for redox events resulting from material freely diffusing in solution.[18,19] Consequently, a set of experiments in which the potential sweep rate varied was carried out using a SWNT-coated Pt electrode that had soaked for 2 h in 5 μM [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$, to unambiguously demonstrate that [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$ was specifically adsorbed to the surface of the SWNTs. Shown in Figure 4 are the results of this study, and the linear relationship between the anodic peak current and the potential sweep rate shown in the inset is the hallmark of a surface-confined redox couple.[19]

The increase in ΔE_{peak} with the increase of potential sweep rate that can be observed in Figure 4 is indicative of kinetic barriers to electron transfer.[19,20] However, the kinetic limitations are more likely related to the nonohmic, imperfect electrical connections between the SWNTs serving as the working electrode than to inherent barriers to electron transfer.

To demonstrate the power of the electroanalytical methodology described herein, the adsorption of [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$ on SWNTs was monitored in real time by the acquisition of CVs at regular time intervals after placing a clean SWNT-coated Pt electrode into a 5 μM solution of the analyte. The amount of material adsorbed to the SWNTs was determined from the peak anodic current[19] and is shown in Figure 5. In the absence of surfactant (i.e., after methanol rinsing), the adsorption is rapid and equilibrium coverage is reached after approximately 1 h, but for electrodes that were not rinsed to remove the surfactant, the adsorption process is very slow. This observation emphasizes the importance of surfactant removal and indicates how crucial the molecular details of the interface are in such a noncovalent adsorption process.

In conclusion we have demonstrated that the complex [Co(**tpy**$\sim$**py**)$_2$]$^{2+}$, with pendant pyrene functional groups that enable $\pi-\pi$ stacking interactions, can specifically adsorb to the surface of SWNTs. While this large and somewhat insoluble complex also shows some adsorption on platinum electrode surfaces, this interaction appears to be relatively weak and

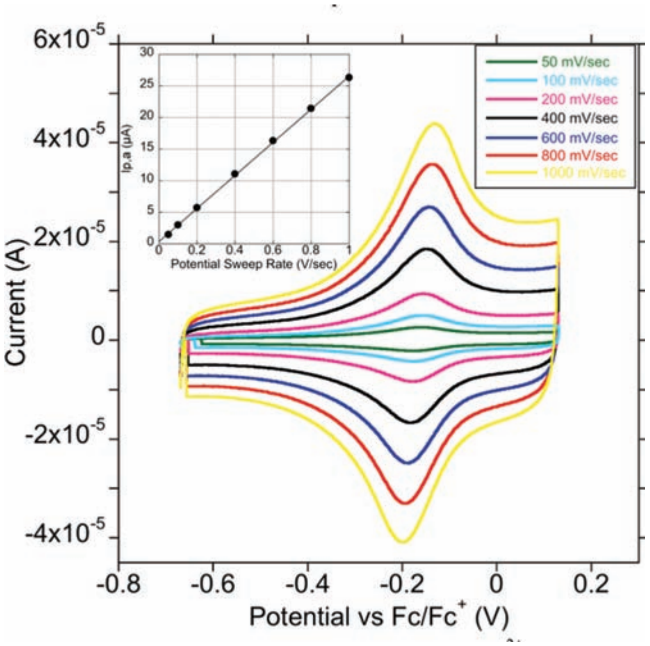

Figure 4. Cyclic voltammetry of [Co(**tpy**∼**py**)$_2$]$^{2+}$ adsorbed to SWNT-coated Pt working electrode at a range of potential sweep rates. Supporting electrolyte is 0.1 M TBAH/CH$_3$CN, and plot of anodic peak current vs potential sweep rate is shown in inset.

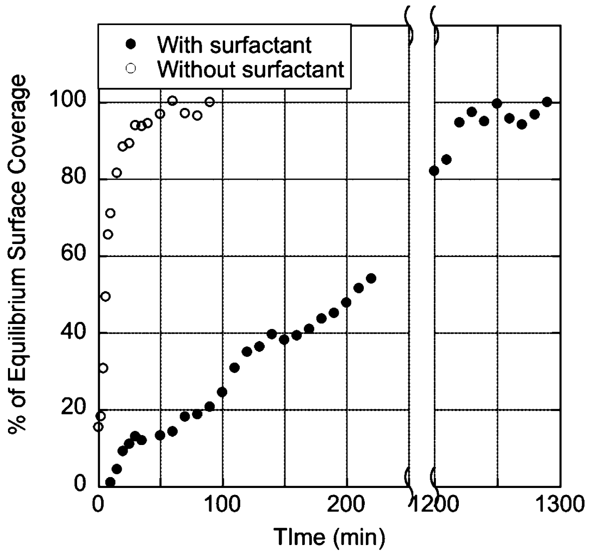

Figure 5. Surface coverage vs time for 5 μM [Co(**tpy**∼**py**)$_2$]^2 in 0.1 M TBAH/CH$_3$CN at SWNT-coated Pt electrode with and without surfactant present.

nonspecific compared to the SWNT/[Co(**tpy**∼**py**)$_2$]$^{2+}$ interaction. Unlike many other approaches, the electrochemical techniques employed in this work permit this adsorption process to be examined in situ. Further, this electrochemical methodology is robust and experimentally straightforward and can be used in any instance where a redox-active probe is a part of the moiety used to functionalize SWNTs. Future work will involve correlating the observed electrochemical response with Raman spectroscopy, utilizing SWNT samples that contain exclusively metallic or semiconducting nanotubes and examining the functionalization of nanoscale SWNT field effect transistor devices. Currently work is ongoing to examine both the kinetics and the thermodynamics of adsorption, to enable deliberate and specific functionalization, at arbitrary levels of surface coverage, of SWNTs with pyrene-terminated transition metal complexes such as [Co(**tpy**∼**py**)$_2$]$^{2+}$.

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Supporting Information Available: Experimental details for electrode preparation and electrochemical techniques, the calculations for determining the coverage of [Co(**tpy**∼**py**)$_2$]$^{2+}$, and the full citation for ref 8. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Tans, S. J.; Verschueren, A. R. M.; Dekker, C. *Nature* **1998**, *393*, 49–52.
(2) Baughman, R. H; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787–92.
(3) Avouris, P.; Appenzeller, J.; Martel, R.; Wind, S. J. *Proc. IEEE* **2003**, *91* (11), 1772–1784.
(4) Avouris, P.; Chen, Z.; Perebeinos, V. *Nat. Nanotechnol.* **2007**, *2*, 605–615.
(5) Dyke, C. A.; Tour, J. M. *J. Phys. Chem. A* **2004**, *108* (51), 11151–11159.
(6) Usrey, M. L.; Lippmann, E. S.; Strano, M. S. *J. Am. Chem. Soc.* **2005**, *127* (46), 16129–16135.
(7) Prato, M.; Kostarelos, K.; Bianco, A. *Acc. Chem. Res.* **2008**, *41* (1), 60–68.
(8) Guo, X.; et al. *Science* **2006**, *311*, 356–359.
(9) Star, A.; Liu, Y.; Grant, K.; Ridvan, L.; Stoddart, J. F.; Steuerman, D. W.; Diehl, M. R.; Boukai, A.; Heath, J. R. *Macromolecules* **2003**, *36* (3), 553–560.
(10) Chen, R. J.; Zhang, Y.; Wang, D.; Dai, H. J. *J. Am. Chem. Soc.* **2001**, *123* (16), 3838–3839.
(11) Zhao, Y.-L.; Stoddart, J. F. *Acc. Chem. Res.* **2009**, *42* (8), 1161–1171.
(12) Staii, C.; Chen, M.; Gelperin, A.; Johnson, A. T. *Nano Lett.* **2005**, *5* (9), 1774–1778.
(13) Ballesteros, B.; de la Torre, G.; Ehli, X.; Rahman, G. M. A.; Agullo-Rueda, F.; Guldi, D. M.; Torres, T. *J. Am. Chem. Soc.* **2007**, *129*, 5061–5068.
(14) Prencipe, G.; Tabakman, S. M.; Welsher, K.; Liu, Z.; Goodwin, A. P.; Zhang, L.; Henry, J.; Dai, H. *J. Am. Chem. Soc.* **2009**, *131*, 4783–4787.
(15) Stephenson, J. J.; Hudson, J. L.; Azad, S.; Tour, J. M. *Chem. Mater.* **2006**, *18*, 374–377.
(16) Smith, H. L.; Usala, R. L.; McQueen, E. W.; Goldsmith, J. I. *Langmuir*, accepted for publication.
(17) Personal communication, NanoIntegris technical staff.
(18) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; J. Wiley & Sons: New York, 2001; Chapter 6.
(19) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; J. Wiley & Sons: New York, 2001; Chapter 14.
(20) Laviron, E. *J. Electroanal. Chem.* **1979**, *101* (1), 19–28.

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