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Single Nanoparticle Voltammetry: Contact Modulation of the Mediated Current

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Abstract: *The cyclic voltammetric responses of individual palladium-coated carbon nanotubes are reported. Upon impact—from the solution phase—with the electrified interface, the nanoparticles act as individual nanoelectrodes catalyzing the hydrogen-oxidation reaction. At high overpotentials the current is shown to reach a quasi-steady-state diffusion limit, allowing determination of the tube length. The electrochemical response of the individual nanotubes also reveals the system to be modulated by the electrical contact between the electrode and carbon nanotube. This modulation presents itself as fluctuations in the recorded Faradaic current.*

Electrochemical reactions can be monitored at single nanoparticles impacting at an inert electrode.[1] One distinct aim of such investigations is to facilitate insight into the structure–activity relationship of specific nanoparticle systems.[2] Almost invariably, these mediated nanoparticle studies are performed using a single potential held upon the substrate electrode. However, extraction of physically significant kinetic and thermodynamic information from a single electrochemical potential is not feasible and repeat experiments performed over a range of potentials to yield statistically useful information must be undertaken.[3] Moreover, data analysis of the resulting currents assumes the process to not be influenced by the properties of the electrical contact between the inert electrode and the nanoparticle. Previous studies of the electrochemistry of single nanotubes have required the employment of complex fabrication techniques.[4] Conversely, in this work the hydrogen-oxidation reaction (HOR) is studied on individually impacting nitrogen-doped multi-walled carbon nanotubes supported on palladium nanoparticles (N-CNT-Pd) by cyclic voltammetry (CV) enabling the non-destructive sizing of single decorated CNTs. These studies clearly demonstrate that, for this experimental case, although at high overpotentials diffusion-limited currents are obtained, the mediated electrochemical process is modulated by the contact between the electrode and the nanoparticle. Consequently, extraction of physically significant data regarding the kinetics of the electrochemical process will require greater insight into properties of the electrical contact between the nanoparticle and the inert substrate.

The N-CNT-Pd were prepared by using the procedure described in the experimental section, and characterized with transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX) mapping, and scanning electron microscopy (SEM), respectively. Tube-shaped nanostructures are observed in both the TEM and SEM images (Figure 1 A,B), and highly dispersed spherical Pd nanoparticles (diameter 1.37 ± 0.30 nm) on the surface of the nanotube are shown in the TEM image. Typical SEM images were analyzed, giving the mean length and width of N-CNT-Pd to be 4.9 ± 4.0 μm (37 samples) and 128.6 ± 58.0 nm (28 samples), respectively. The corresponding length and width distribution of N-CNT-Pd and the diameter distribution of the Pd nanoparticles on the nanotube surface are displayed in Figure S1 and S2 in the Supporting Information, respectively. In Figure 1 C, the EDX maps evidence the presence of the elements C, N, O, and Pd on the N-CNT-Pd.

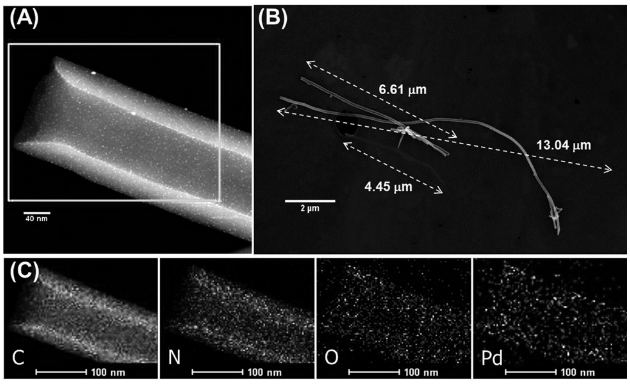

Figure 1. A) TEM (scale bar 40 nm), B) SEM image (scale bar 2 μm), and C) EDX maps of N-CNT-Pd (scale bars 100 nm).

First, the oxidation of hydrogen at the N-CNT-Pd was studied by drop-casting the material onto a macro glassy carbon (GC) electrode. As shown in Figure 2, in the potential

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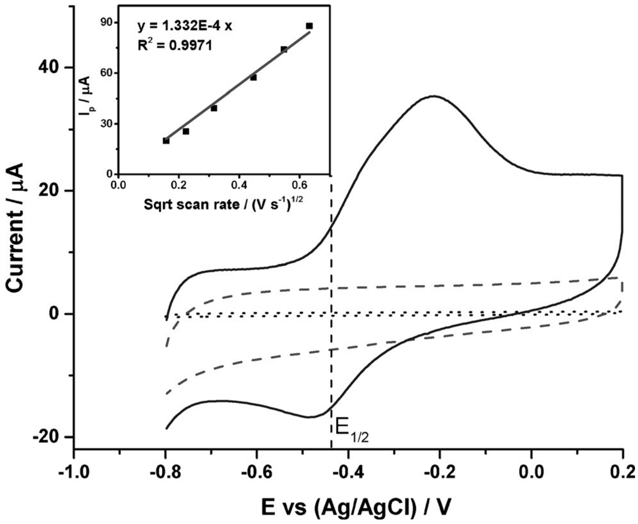

Figure 2. Voltammogram of the bare GC electrode ($d = 3.0$ mm) in H_2-saturated KNO_3 (0.20 M) solution (dotted line); voltammogram of the N-CNT-Pd-modified GC electrode in 0.20 M KNO_3 solution with (solid line) and without (dashed line) H_2, 50 mVs^{-1}. Vertical dashed line represents the reversible half-wave potential ($E_{1/2}$) for the HOR (−0.194 V vs. SHE). Inset: plot of peak current and square root of scan rate.

window of study and in a hydrogen-saturated solution, 0.77 mM (Henry's law constant: $K_{H2} = 1292$ dm^3 bar mol^{-1}),[5] the bare GC electrode shows no voltammetric feature corresponding to the HOR. A 20 μL suspension of N-CNT-Pd (4.6×10^{-12} M) was then drop-cast onto the GC electrode and left to dry in a N_2 atmosphere. Assuming a homogeneous coverage over the surface this amount of material would constitute about five layers of carbon nanotubes on the surface. The CV response of the N-CNT-Pd-modified electrode was recorded in the presence (solid line) and absence (dashed line) of saturated hydrogen. The voltammogram shows a quasi-irreversible peak ($E_{\text{mid-point}} = -0.348$ V vs. Ag/AgCl) for hydrogen oxidation in the presence of saturated hydrogen at the N-CNT-Pd-modified electrode. The minimized reductive peak likely reflects the apparently sluggish electron-transfer kinetics of the redox reaction. The expected half-wave potential for reversible hydrogen oxidation in this system is −0.449 V versus Ag/AgCl (Section S3),[6] and is marked on the voltammogram in Figure 2 (vertical dashed line). The characteristic potential for a reversible CV is the mid-point potential; however, for the present experimental case the analytically determined half-wave potential provides a close approximation to the predicted reversible mid-point potential.[7] The oxidative peak current was studied as a function of scan rate as shown in the inlay of Figure 2, where its magnitude was found to scale linearly with the square-root of the scan rate. Moreover, analysis of this peak yields a measured diffusion coefficient for hydrogen (D_{H2}) of $5.7 \pm 0.3 \times 10^{-9}$ m^2 s^{-1}, this is in close agreement with the reported literature value of 5.0×10^{-9} m^2 s^{-1}.[8]

Having evidenced the ability of the N-CNT-Pd to effectively catalyze the HOR, the work now turns to focus upon the detection of individual impacting carbon nanotubes. A clean carbon fiber microwire (length: ca. 1 mm; diameter 7 μm) in a H_2-saturated solution containing 0.2 M KNO_3 and 7.0×10^{-14} M N-CNT-Pd. A potential of 0.1 V (vs. Ag/AgCl) was applied to the microwire and the resulting current recorded. In the absence of N-CNT-Pd within the solution the chronoamperometric response showed a monotonic decrease in the current corresponding to capacitative charging of the electrode. In the presence of the carbon nanotubes and after about 10 chronoamperometric scans had been run clear steps in the current were recorded (Figure 3 A–D). This increased current is ascribed to being due to catalysis of the hydrogen-oxidation reaction at the carbon fiber surface because of arrival of N-CNT-Pd. Moreover, the sharp onsets (as a function of time) of the current features are strongly indicative of the arrival of single entities at the electrode surface. The transport of the carbon nanotubes from solution to the carbon fiber electrode is taken to occur solely by virtue of Brownian motion, such that, the N-CNT-Pd randomly and stochastically collide with the electrified interface. It was found that once in electrical contact with the electrode, the N-CNT-Pd were relatively stable and remained immbolized for tens of seconds. After an initial impact event repeat chronoamperograms can be recorded exhibiting the catalytic current. Figure 3 E and F show two chronoamperometric profiles in which the current is observed to step-off, indicating the loss of the catalytic material from the surface.

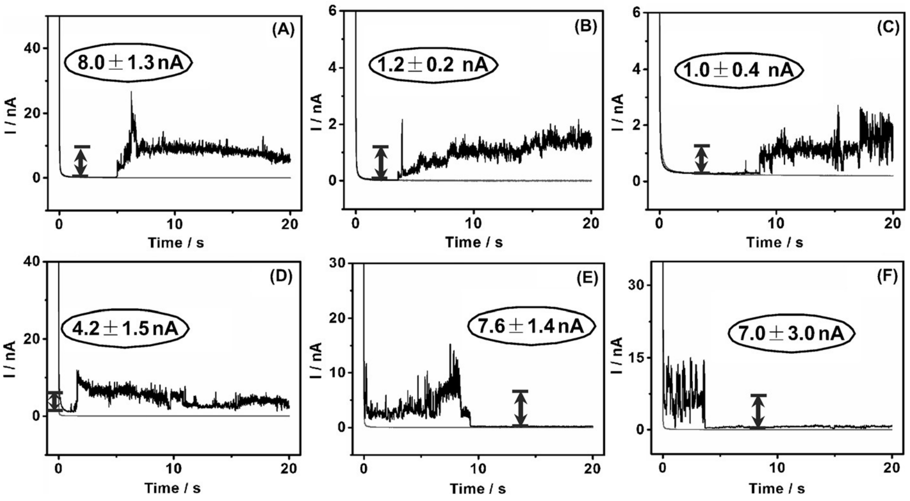

Figure 3. Chronoamperometric profiles showing catalytic oxidative Faradaic steps of N-CNT-Pd in 0.77 mM H_2, 0.2 M KNO_3 at 0.1 V (vs. Ag/AgCl). Profiles A, B, C, and D show the collision of N-CNT-Pd with the wire electrode, while E and F show the falling off of N-CNT-Pd from the wire electrode.

Due to the long residence times (immobilization) of the N-CNT-Pd at the carbon microwire electrode, as evidenced by the duration of the Faradaic "steps" observed on the chronoamperograms, it is possible—after the arrival of the N-CNT-Pd—to experimentally record a cyclic voltammogram at individual CNTs. A known concentration of N-CNT-Pd suspension was added into a H_2-saturated solution containing 0.2 M KNO_3, followed immediately by CV scanning. The CV signals of hydrogen oxidation caused by the collision and immobilization of the N-CNT-Pd was normally observed after a few scans. Figure 4 shows six examples (from a total of 30 recorded events) of cyclic voltammograms measured for individual impact events. The scale bars give an indication of the magnitude of the Faradaic current above the background capacitative signal.

Modeling the carbon nanotubes as cylindrical electrodes allows the cyclic voltammetric responses to be readily quantitatively analyzed.[9] Simulation of the voltammetric response using a fixed carbon nanotube radius of 64 nm, allows it to be concluded that for each micron in nanotube length the expected current for an individual tube is 0.55 nA. Due to the small Pd interparticle distance on the nanotube surface (cf. the diffusion layer thickness), under diffusion-limited conditions the reaction rate will not be sensitive to the surface coverage of the palladium on the carbon nanotubes. Consequently, comparison of the quasi-steady-state currents measured from cyclic voltammetry of the impacted N-CNT-Pd allows assessment of the nanotube lengths. These electrochemically measured lengths were compared to the data obtained from SEM and the corresponding size distributions are shown in Figure 5. The excellent correspondence between the SEM and electrochemical sizing allows the conclusion that the observed impacts are associated with the arrival and immobilization of individual N-CNT-Pd at the carbon fiber electrode surface.

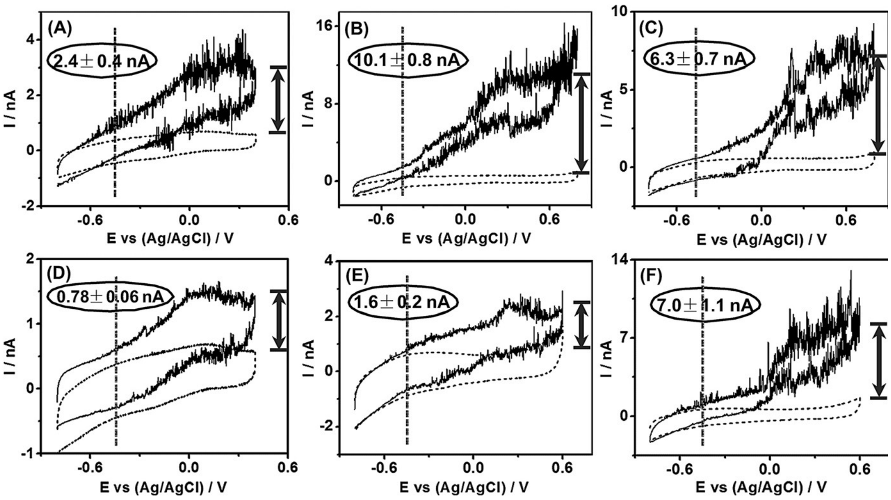

Figure 4. Cyclic voltammetric profiles of H_2 (0.77 mM) oxidation in 0.2 M KNO_3 of an immobilized N-CNT-Pd on the carbon fiber microwire electrode. The vertical dashed lines depict the analytically calculated half-wave potential for HOR.

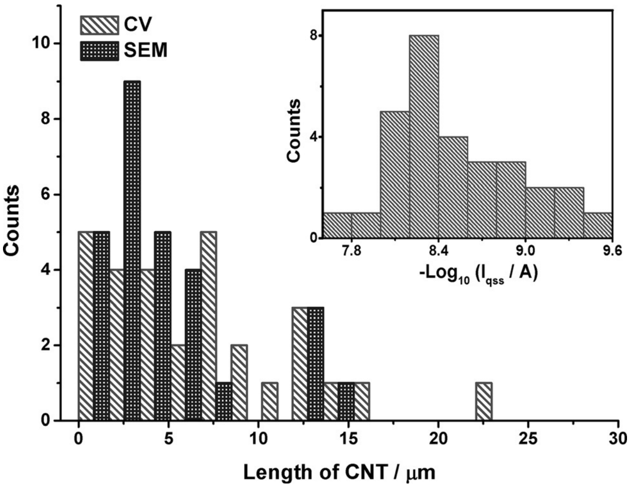

Figure 5. Comparison of length distribution of N-CNT-Pd from the CV method (30 samples) and SEM analysis (37 samples). Inset: I_{qss} distribution from 30 CV profiles of single immobilized N-CNT-Pd in 0.77 mM H_2, 0.2 M KNO_3.

Both the chronoamperometic and voltammetric profiles for the single carbon nanotubes exhibit distinct fluctuations in the mediated Faradaic signal. The cyclic voltammograms of the individual tubes evidence that the noise in the current is intimately associated with the Faradaic charge transfer and is not capacitative in origin. Due to the magnitude of the currents involved it is unlikely that these fluctuations are due to shot noise associated with the discrete nature of the charge carrier (hydrogen in the present case).[10] Second, the use of multi-walled carbon nanotubes renders it unlikely that the fluctuations arise due to conduction along the length of the tube.[11] Consequently, it is concluded that the electrochemical response reflects the modulation of the mediated current by the contact between the nanotube and electrode surface. This modulation will be presented as a variable and uncompensated resistance on the system, which will serve to distort the voltammetric response and lead to the measurement of apparently slower electron-transfer kinetics.

By recording the voltammetry of single carbon nanotubes the stochastic detection and sizing of the material can be readily obtained from the diffusion-limited current. However, extraction of meaningful kinetic data will require greater insight into the nanotube/electrode contact. Finally, it is highlighted that the mechanism causing the Faradaic fluctuations may be operative in a range of experimental reports employing drop-cast electrodes; the direct observation of the phenomena is only attainable in the present case due to the study of individual carbon nanotubes.

Experimental Section

Preparation of nitrogen-doped carbon nanotubes decorated with palladium nanoparticles (N-CNT-Pd): N-CNT-Pd were prepared by the following route: functionalization was first carried out on carbon nanotubes (CNTs) by oxidation in HNO_3. Gaseous NH_3 was then flowed over oxidized CNTs (O-CNTs) in a tubular quartz reactor at 600 °C for 4 h to introduce nitrogen-containing functional groups on the CNTs (N-CNTs). Palladium ions were added to a solution of functionalized CNTs for coordination with functionalities as anchoring sites. Appropriate hydrolysis treatment was applied to the impregnated materials to crystallize the precursors to achieve a 2.4 wt % loading (measured by inductively coupled plasma, ICP) of Pd-supported N-CNTs (N-CNT-Pd) with a high dispersion scale.

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Keywords: carbon nanotubes · catalysis · electrochemistry · hydrogen-oxidation reaction · palladium

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