

Synthesis and characterization of platinum nanoparticles on single-walled Carbon nanotube “nanopaper” support

Malka R Bromberg¹, Anitha Patlolla², Rebecca Segal¹, Yishai Feldman³, Qi Wang¹, Zafar Iqbal*² and Anatoly I Frenkel*¹

¹ Physics Department, Yeshiva University, New York, NY 10016, USA

² Department of Chemistry, New Jersey Institute of Technology, Newark, NJ 07102, USA

³ Weizmann Institute of Science, Rehovot, Israel

[*iqbal@njit.edu](mailto:iqbal@njit.edu); anatoly.frenkel@yu.edu

Abstract. We prepared several samples of carbon-nanotube-supported Pt nanoparticles that are potentially promising electrocatalysts for hydrogen fuel cells. Commercially obtained single-walled carbon nanotubes (SWNTs) were characterized by Raman Spectroscopy, SEM, TEM, EDS, and XANES. This multi-technique characterization allowed us to quantify the size and composition of metal impurities (Mo, Co) in SWNTs, to choose the best method to remove them, and characterize the effectiveness of their removal. After synthesizing a “nanopaper” (10-20 micrometer thick, free standing sheets of self-assembled SWNTs) we decorated it with Pt nanoparticles by electroless deposition. Formation of Pt nanoparticles was verified by EXAFS, and quantitative information about their size and structure was obtained.

1. Introduction

Single-walled carbon nanotubes (SWNTs) decorated with metals have recently attracted much interest due to their potential application as electric detectors or as templates for forming metal nanowires [1,2]. In this work we explored the properties of metal-nanotube systems that are important for understanding their high electrocatalytic activity and potential application as fuel cell catalyst support. While most previous studies focused on SWNTs that were not self-supported, we utilized synthetic procedures leading to self-assembled SWNTs in a “nanopaper” – a 10-20 micrometer thick free standing sheet of SWNTs. We studied different methods of synthesis and characterization of the nanopaper, and properties of platinum nanoparticles grown on it. A combination of different characterization techniques including synchrotron XANES and EXAFS was critical for understanding the quality, and optimizing the regimes, of our synthesis and purification methods.

2. Experiments

SWNTs were obtained from SouthWest Nanotechnologies. As-received SWNTs were known to contain some amount of Co and Mo due to catalysts used in the nanotube synthesis. Purification of SWNTs may damage the nanotubes and prevent their self-assembly into a nanopaper. Thus, to choose

the best purification method, one needs to monitor the quality of the nanotubes as well as the metal particle content. Our SWNTs were all purified using the acid oxidation method [3,4,5]: 1.5M HNO₃ was added to the as-received samples, which was bath-sonicated at 60 °C, then filtered, and finally rinsed with de-ionized (DI) water to remove the acid. Sonication time was varied from 30 to 120 min for different batches, to investigate the possible effects of sonication on nanotube damage. Raman spectroscopy was used to characterize the quality of the nanotubes. The size and composition of metal impurities were measured by SEM, EDS, TEM, and XANES. This multi-technique characterization allowed us to select a suitable purification method that resulted in the smallest amount of metal particles and the least detectable damage to the SWNTs.

After purification, a substrate for depositing Pt atoms was formed by synthesizing the carbon nanotube nanopaper (CNP): A 50mg/100ml suspension of SWNTs was prepared by dispersing SWNTs in DI water, to this suspension 1% Triton x-100 surfactant was added and it was sonicated for about 2hrs. This is followed by vacuum assisted filtration through a Teflonated filter paper (Millipore) with pore size of 10 μm. After filtration the filter paper was left for drying for about 4-5 hrs at room temperature and the CNP was peeled off as a free standing paper. Platinum was deposited onto the nanopaper by electroless deposition [6]. In this procedure, purified nanopapers were placed in a 5mM (50%-aq., 50%-ethanol) solution of Na₂PtCl₄ for 5 minutes. In this method, Pt nanoparticles deposit directly on the SWNTs, with the nanotubes acting as templates. Finally, the nanopaper decorated with Pt was washed with a mixture of water and ethanol to remove the surfactant and the unreduced precursor.

Raman spectroscopy measurements were taken at the New Jersey Institute of Technology (NJIT) with a Mesophotonics SE1000 Raman Spectrometer using a 130 μm beam spot with a laser emitting at a wavelength of 785 nm. Scans were typically run for 60-80 s. SEM measurements were performed in NJIT using a Gemini Leo 1530 VP microscope. TEM measurements were performed in the Weizmann Institute of Science, Israel, using a CM120 Phillips microscope operated at 120 kV and equipped with an EDS detector (EDAX-Phoenix Microanalyzer) for elemental analysis.

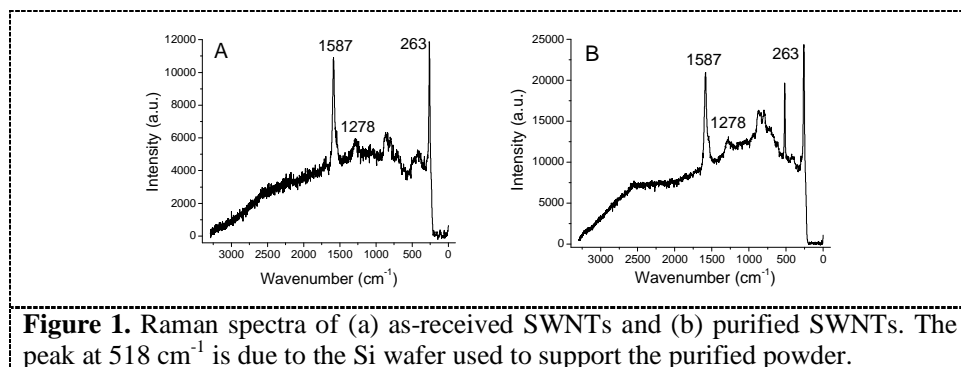
Synchrotron x-ray absorption spectroscopy measurements were performed at the beamline X18B at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory in Upton, New York, USA. To detect the metal content in the as-received and purified SWNTs, Mo and Co K-edge measurements in the fluorescence mode were used. SWNT powder was deposited on adhesive tape which was then folded several times to maximize fluorescence intensity. Gas-filled Oxford ionization chambers for initial, transmission, and reference beam detection, as well as the Lytle detector, were used. Synchrotron EXAFS measurements were made on the Pt-CNP samples before and after washing to detect Pt nanoparticles and quantitatively characterize their size and structure. Pt foil and the K₂PtCl₄ precursor compound were used for analysis calibration purposes, in transmission. We have also used this technique to characterize the homogeneity of the system and evaluate the quality of the precursor removal process.

3. Results

3.1 Raman spectroscopy characterization.

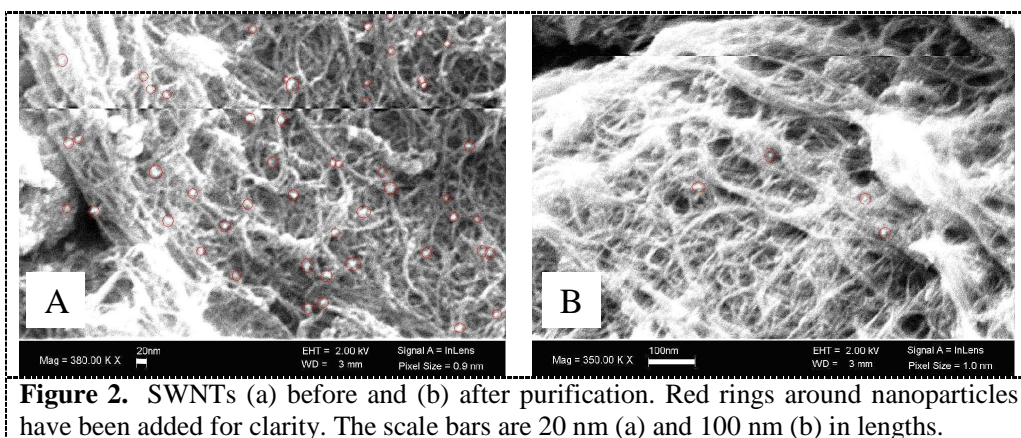
Raman spectra (figure 1) were collected from the as-received and from the purified SWNTs. The common peaks present in both samples are due to the SWNTs: the peak at ca. 1587 cm⁻¹ with a lower frequency component is due to the graphitic mode (G-band), the line at 263 cm⁻¹ is due to the diameter-dependent radial breathing mode, and the broad peak at ca. 1278 cm⁻¹ is due to the disorder mode (D-band) associated with defects on the nanotube walls [5,7,8]. The ratio of the D- to the G-band peak height allows one to quantify the amount of defects in the SWNTs and hence the quality of the nanotube sample. We find that there is no significant change in this ratio before and after purification. Thus, the purification procedure showed negligible damage to SWNTs in terms of the formation of disordered carbon or defects. However, purification may cause other damage, such as

shortening of the individual nanotube lengths and functionalization of the nanotube walls, which cannot be monitored directly by Raman spectroscopy.



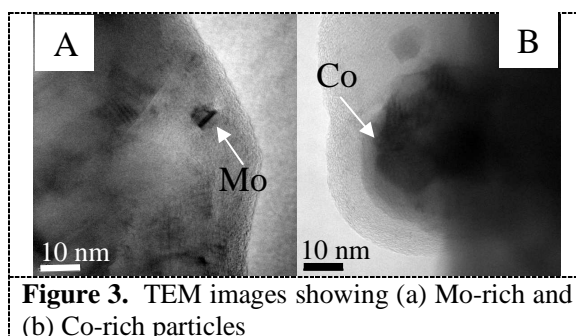
3.2 SEM characterization.

SEM images in figure 2 demonstrate removal of significant amount of metal particles from the nanotubes following their purification. The question remains how to quantitatively characterize the loss of each metal by our purification procedure. This will be described later by using EXAFS and EDS/TEM measurements.



3.3 TEM characterization.

EDS measurements demonstrated that metal composition varied between the particles (figure 3). Specifically, the smaller particles were predominantly Mo-rich and the larger particles were found to be mostly Co-rich.



3.4 XANES and EXAFS characterization.

Mo and Co K-edge XANES measurements were taken in the as-received and purified SWNTs. It was found that the ratio of Mo to Co edge steps decreased after purification (figure 4) indicating that the purification procedure is more effective in removing Mo.

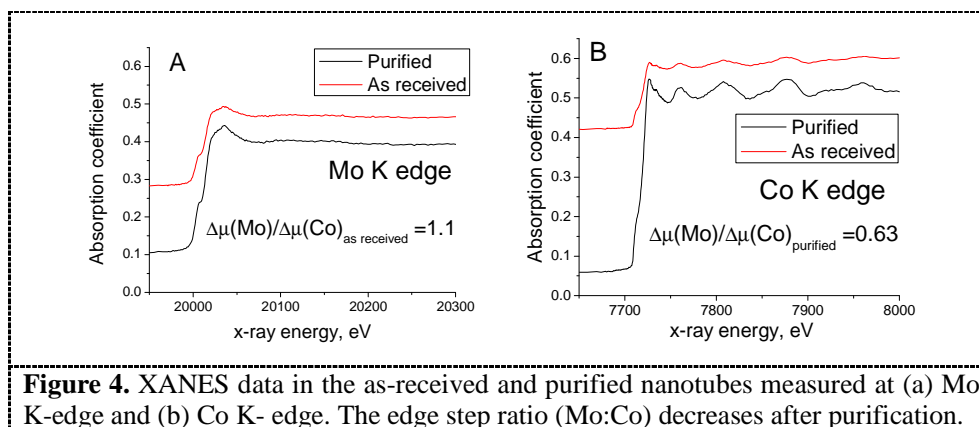
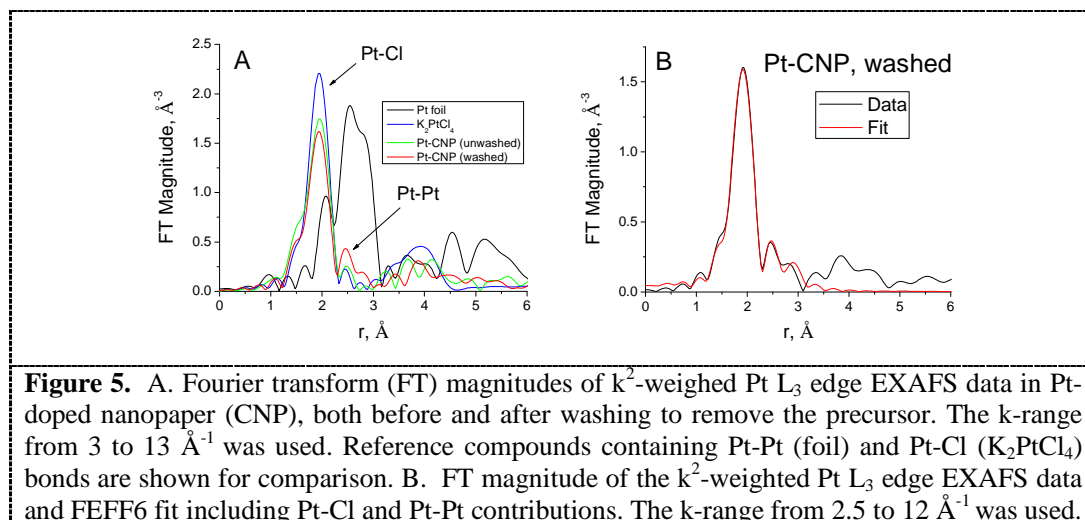


Figure 4. XANES data in the as-received and purified nanotubes measured at (a) Mo K-edge and (b) Co K-edge. The edge step ratio (Mo:Co) decreases after purification.

Pt L_3 EXAFS data were collected in the Pt-CNP samples before and after surfactant removal. Figure 5 a) demonstrates that a Pt-Pt peak is present in the Pt-CNP samples indicating the formation of metal Pt particles. The Pt-Pt peak intensity increases (and the Pt-Cl peak intensity decreases) after rinsing of the Pt-CNP sample, due to apparent removal of the Na_2PtCl_4 precursor. Quantitative data analysis was done by fitting FEFF6 theory of Pt-Cl and Pt-Pt contributions (calculated from the K_2PtCl_4 and bulk Pt structures, respectively), to the unknown Pt-CNP data (figure 5 b). Fitting variables included the coordination numbers, bond lengths and bond length disorder parameters of Pt-Cl and Pt-Pt pairs, as well as the correction to the photoelectron energy origin, ΔE_0 . The number of relevant independent points in the data was 9, and the total number of adjustable parameters was 7.

Using the best fit results for the Pt-CNP samples and standard compounds we obtained the average size of Pt nanoparticles as follows. The coordination number (CN) of Pt-Cl pairs in K_2PtCl_4 (which has the same structure as the precursor Na_2PtCl_4 used in Pt-CNP synthesis) is equal to 4. In Pt-CNP (after washing off the excess of the precursor) we obtained the CN of Pt-Cl pairs to be equal to 2.7 ± 0.3 which corresponds to the 67% molar fraction of the un-reduced precursor remaining in Pt-CNP sample after washing. The CN of Pt-Cl bonds in the Pt-CNP sample can be used to evaluate the average number of Pt atoms in the metal nanoparticles and the mean particle size in this heterogeneous sample [9,10]. The CN of Pt-Pt pairs (1.7 ± 1.2) obtained in the best fit is not uniquely related to the average particle diameter, even if one assumes that the distribution of sizes is reasonably uniform and the shape of the particles is known (for simplicity, we assume a 3D shape of truncated cuboctahedron). In order to evaluate the average diameter of Pt nanoparticles we need to know the CN of Pt-Pt pairs specific to the particles, not just the ensemble-average value (1.7 ± 1.2) that we obtained over the sample. Assuming that there is x per cent molar fraction of Na_2PtCl_4 and $(1-x)$ per cent molar fraction of Pt nanoparticles, we can find the modified coordination number N^* for the fraction of the sample contained in the nanoparticle phase only [10]: $N^* = N/(1-x)$. From the value of the modified coordination number (5.2 ± 3.6) we estimate the sizes of the Pt nanoparticles as ranging from 10 to 80 atoms per particle.



4. Summary and conclusions

The multi-technique characterization allowed us to optimize a purification method of single-walled carbon nanotubes. Future work will include the addition of static light scattering measurements to obtain the length of the SWNTs before and after purification, and the use of Fourier-transform infrared spectroscopy to verify nanotube functionalization. When this data is available we will optimize the sonication regime in order to purify the SWNTs with minimum damage. Pt deposition on the carbon nanotube nanopaper was done by the electroless method and resulted in the formation of metal particles, as confirmed by EXAFS. In the next stage of this work we will conduct cyclic voltammetry experiments, as well as *in situ* XANES and EXAFS measurements in order to assess the effectiveness of platinum-decorated self-supported SWNTs as electrocatalysts for hydrogen fuel cells.

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