Research Letter

Surface Adsorption and Replacement of Acid-Oxidized Single-Walled Carbon Nanotubes and Poly(vinyl pyrrolidone) Chains

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Quartz crystal microbalance (QCM) was used to investigate the adsorption of acid-oxidized single-walled carbon nanotubes (Ox-SWNTs) and poly(vinyl pyrrolidone), PVP. It was found for the first time that Ox-SWNTs adsorbed onto the QCM electrode can be effectively replaced by PVP chains in an aqueous solution. This replacement process was also investigated by atomic force miscroscopic (AFM) imaging, which shows good agreement with the QCM measurements. This study provides powerful tools for fundamental investigation of polymer-nanotube interactions and for controlled design/fabrication of functional polymer-nanotube surfaces for potential applications.

Carbon nanotubes have been demonstrated to possess excellent electronic [1], mechanical [2], and thermal [3] properties attractive for a large variety of potential applications. Examples include their uses as reinforcement fillers in nanocomposite materials and nanoscale building blocks in electronic, photonic, and biomedical devices. With no exception for carbon nanotubes, however, it is very rare that a material with desirable bulk properties also possesses the surface characteristics required for certain specific applications (e.g., strong interface with polymers in nanocomposites, good interfacial properties in colloid systems, and strong biocompatibility for nanotube sensors). Therefore, surface modification becomes essential to render carbon nanotubes dispersible in nanocomposites and to exhibit good bulk and surface properties for biomedical applications. In this context, both chemical and physical approaches have been used for surface modification of carbon nanotubes. Chemical modification of carbon nanotubes with functional molecules [4], including polymer chains [5–9], has been demonstrated to significantly improve their self-assembling properties and compatibility with other material systems. However, these modifications have been shown to alter the nanotube structure, and hence its properties. To conserve the nanotube structure,

physical modification has been used to functionalize carbon nanotube surfaces through the noncovalent adsorption of surfactants [10–13], biomacromolecules [14, 15], or synthetic polymers [16–24]. In particular, it has been demonstrated that many high molecular weight polymers (e.g., poly(vinyl pyrrolidone), PVP; poly-*m*-phenylenevinylene, PmPV) can wrap around the surface of single-walled carbon nanotubes (SWNTs) via hydrophobic-hydrophilic [22–24] and/or π-π interactions [25]. Similar to the chemical modification, wrapping carbon nanotubes with appropriate polymer chains could also significantly reduce the intertube van der Waals force thereby enhancing nanotube solubility. Unlike chemical modification, however, the noncovalent (physical) adsorption has advantages in largely retaining the pristine structure and properties of the modified carbon nanotubes.

It is well known that polymer adsorption is a dynamic process, in which adsorbed polymer chains on a particular surface can be desorbed or replaced by other absorbing species that have a greater affinity to the surface [26–29]. The adsorption and desorption processes are important to many fundamental studies and practical applications, including the use of adsorbed polymer chains for stabilization

of colloidal particles, controlled release of drugs, and mimicking cell membranes. As far as we are aware, the possibility for surface replacement between carbon nanotubes and polymers has yet been recognized, though carbon nanotubes, having the large number of well-defined carbon-carbon single and double bonds in their molecular structure, are polymeric in essence. Using quartz crystal microbalance (QCM) and atomic force microscopy (AFM), we found that acid-oxidized single-walled carbon nanotubes (Ox-SWNTs) preadsorbed onto a QCM electrode can be readily replaced by poly(vinyl pyrrolidone), PVP, chains in an aqueous solution. Here, we report our QCM and AFM results from the first study on the surface replacement between carbon nanotubes and polymer chains.

In a typical experiment, 1 mg HiPCo SWNTs (from Tubes@Rice) were oxidized in 8 mL concentrated H_2SO_4/HNO_3 (3/1 w/w) solution under ultrasonication (Branson 2510R, 100 W at 42 KHz) for 1 hour [30, 31], followed by filtration through a Teflon filter of 1-μm pores and redispersed in pure (deionized) water to produce an aqueous dispersion of 2 mg/L Ox-SWNTs for subsequent investigation. A platinum-coated AT-cut QCM crystal (9 MHz) of 5 mm in diameter was used as the electrode for the QCM measurements (QCM 922, Princeton Applied Research). Prior to the QCM measurements, the platinum electrode was cleaned electrochemically by scanning 300 cycles between 0 and 1.5 V versus Ag/AgCl electrode in an aqueous solution of 0.5 M H_2SO_4 until a constant frequency was obtained, then repeatedly washed with pure water. The QCM electrode thus cleaned was then transferred into a clean glass cell containing 20 mL pure water, with and without Ox-SWNT and/or PVP, for the frequency/mass measurements. We adopted the well-known Sauerbray equation $\Delta f = -2\Delta m f^2/A(\mu\rho_q)^{0.5} = -C_f \Delta m$, using a value of 0.903 Hz/ng for the integrated QCM sensitivity, C_f, to calculate the "apparent adsorption mass" from the measured frequencies (± 5 Hz) [32–35]. QCM results were further verified with AFM imaging. For each of the QCM measurements, AFM imaging (AFM, Digital Instrument NanoScope III) with an SiN tip under tapping mode was performed on a corresponding mica sheet sputter-coated with a thin platinum layer (Denton Vaccum, Desk IV; 40 mA for 5 minutes, *ca.* 20 nm) after having been placed in the same glass cell under the same conditions as for the QCM measurement, followed by rinsing three times with pure water and air dried.

Figure 1(a) shows a time-dependence of the increased mass for adsorption of Ox-SWNTs onto the surface of a QCM platinum electrode. As can be seen, each addition of the 1 mL Ox-SWNT dispersion (2 mg/L) (Figure 1(a)a–d) led to a significant increase in the adsorption mass. The corresponding AFM images given in Figure 2 also show a successive increase in the surface coverage of the adsorbed carbon nanotubes. At the initial adsorption stage (Figures 1(a)a and 2(a)), the platinum surface was only partially covered by the adsorbed Ox-SWNTs. The observed partial surface coverage can be attributed to the low concentration of Ox-SWNTs in the dispersion coupled with a relatively slow adsorption kinetics. Upon the second and third additions of the Ox-SWNT dispersion, much more dramatic increases
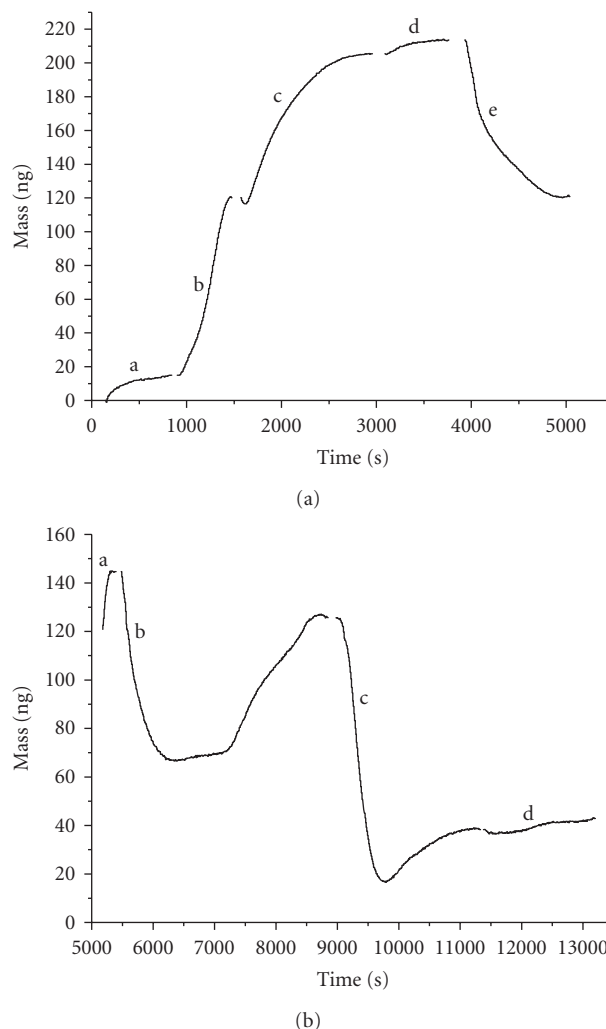

FIGURE 1: Apparent adsorption mass of (a) Ox-SWNT onto a platinum electrode by consecutively adding 1 mL Ox-SWNT dispersion (2 mg/L) four times (a, b, c, and d) into 20 mL water in a glass cell containing the cleaned QCM electrode, followed by thoroughly washing with pure water (e), and (b) the Ox-SWNT preadsorbed QCM platinum electrode (i.e., an electrode corresponding to the end of Figure 1(a)e) after having been thoroughly washed with pure water and reimmersed into 20 mL pure water in the glass cell, to which four 1 mL PVP solution (0.01 g/L) was added consecutively (a, b, c, and d).

in the absorption mass (Figure 1(a), b and c) and the nanotube surface coverage (Figures 2(b) and 2(c)) were observed for the QCM platinum electrode and the mica-supported platinum surface, respectively. It is worthwhile to note that the adsorbed Ox-SWNTs form some aggregate-like assemblies, leading to somewhat nonuniform distribution of the surface-adsorbed Ox-SWNTs (Figures 2(a)–2(d)). The observed surface-adsorbed nanotube aggregates may arise directly from Ox-SWNT bundles in an aqueous solution with limited dispersion. This scenario is consistent with our observation made on the Ox-SWNT preadsorbed surfaces being subjected to extensive water washing. Figure 1(a)e shows
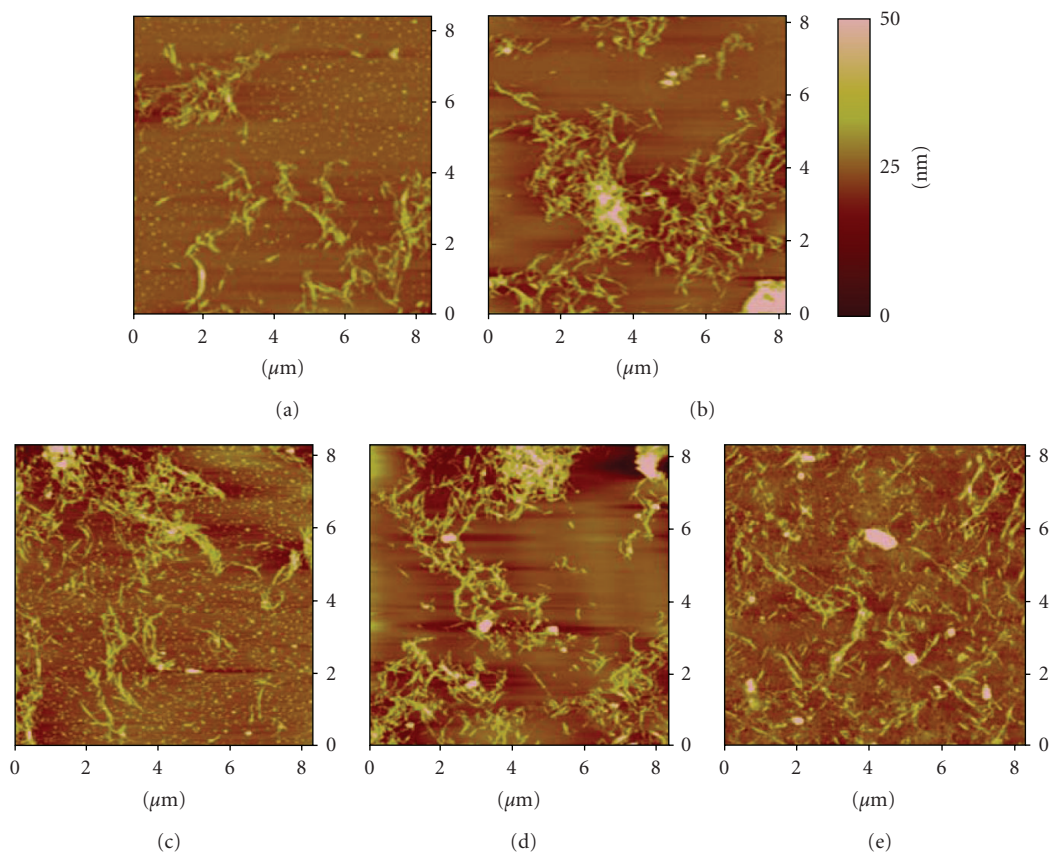
FIGURE 2: Surface coverage of Ox-SWNTs on a platinum sputter-coated mica substrate after consecutively adding 1 mL Ox-SWNT dispersion (2 mg/L) four times (Figures 2(a), 2(b), 2(c), and 2(d)) into 20 mL water in a glass cell containing the cleaned QCM electrode, followed by thoroughly washing with pure water (**Figure 2(e)**). The scanning ranges for all of the five images are $8.3\,\mu m \times 8.3\,\mu m$.
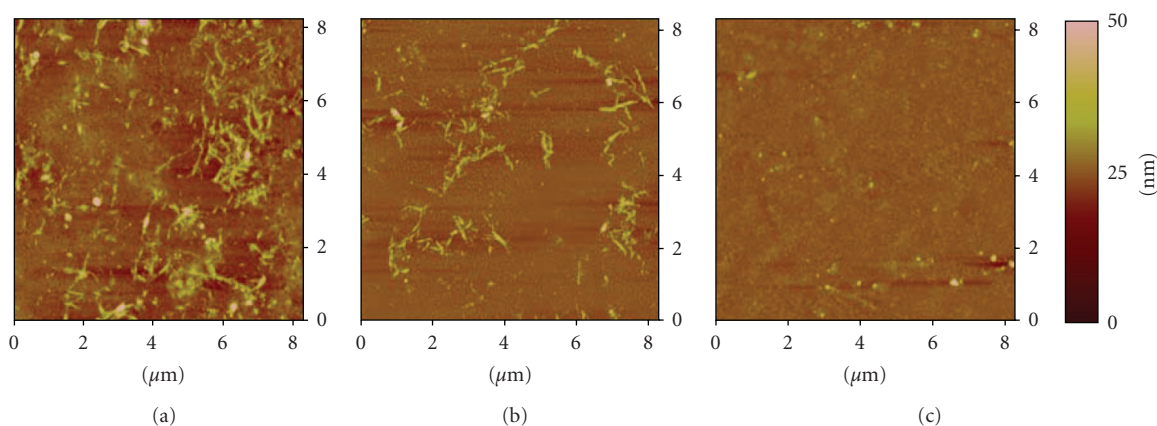

FIGURE 3: Surface coverage of Ox-SWNTs on a platinum sputter-coated mica substrate after consecutively adding 1 mL PVP aqueous solution (0.01 g/L) into 20 mL pure water in the glass cell containing the Ox-SWNT preadsorbed QCM platinum electrode (i.e., an electrode corresponding to the end of Figures 1(a)e and 2(e)). Note that the labels of (a), (b), and (c) in the AFM images correspond to the end of the labels of a, b, and c in **Figure 1(b)**, respectively. The scanning ranges for all of the three images are $8.3\,\mu m \times 8.3\,\mu m$.

a significant decrease in the absorption mass upon the replacement of the Ox-SWNT dispersion with pure water, followed by thoroughly washing the QCM electrode in the adsorption cell with pure water several times. The observed decrease in the adsorption mass is most probably due to a washing-induced dissociation of the overlaid Ox-SWNT aggregates into the solution, leading to an equilibrium state for the adsorbed Ox-SWNTs at the liquid/solid interface. The corresponding AFM image given in **Figure 2(e)** shows some rearrangement of the adsorbed nanotubes to generate a more

homogenous surface coverage for the adsorbed Ox-SWNTs. The overall limiting adsorption mass of Ox-SWNTs was measured to be about 130 ng for the QCM electrode of 5 mm in diameter (Figure 1(a)e). Since each bundle of the Ox-SWNTs is approximately 25 nm in diameter and 1 micron in length with a density of $1.40 \, g/cm^3$ [36], the above measured limiting adsorption mass gives a submonolayer surface coverage of about 10 SWNT bundles per μm^2 corresponding to approximately 25% surface coverage. This surface coverage value of the adsorbed Ox-SWNTs estimated from the QCM measurements corresponds well with the AFM image given in Figure 2(e).

The surface rearrangement seen in Figure 2(e) indicates that there is only a finite affinity of the Ox-SWNTs to the platinum surface, and hence it is possible to replace the preadsorbed Ox-SWNTs by other absorbing species of a high affinity to the surface (e.g., polymers). To investigate the surface replacement between the Ox-SWNTs and polymers, we simply consecutively added a predetermined amount of an aqueous PVP solution (1 mL PVP, 0.01 g/L; M_w = 1 300 000; Sigma-Aldrich) into 20 mL pure water in the glass cell containing the thoroughly-washed QCM platinum electrode with preadsorbed Ox-SWNTs (i.e., the QCM electrode corresponding to the end of Figure 1(a)e). As can be seen in Figure 1(b), the first addition of the PVP solution caused a slight increase in the adsorption mass, attributable to PVP adsorption into the nanotube-free areas on the QCM platinum electrode and/or onto the preadsorbed nanotube surface. Subsequent additions of the PVP solution led to a tremendous decrease in the adsorption mass due to desorption of the preadsorbed nanotubes, which was followed by an increase in the adsorption mass through additional adsorption of PVP chains into the newly-generated free electrode surface from desorption of nanotubes. The successive desorption of the preadsorbed nanotubes and adsorption of PVP chains could eventually solubilize all the Ox-SWNTs into the solution (*vide infra*).

Further evidence for the replacement of the preadsorbed Ox-SWNTs by PVP chains comes from our AFM images recorded after each addition of the PVP solutions. As can be seen from Figures 3(a)–3(c), the surface coverage of Ox-SWNTs decreased significantly after each of the additions of the PVP solution and incubation for a certain period of time, leading to the disappearance of the majority of the adsorbed nanotubes (Figure 3(c)) and a limited adsorption mass of *ca.* 40 ng (Figure 1(b)d). Therefore, the value of 40 ng for the limited absorption mass indicated in Figure 1(b)d must arise predominantly from the absorbed PVP chains. Given that the PVP molecular weight and the QCM electrode diameter are 1 300 000 and 5 mm, respectively, the above value of the limited adsorption mass (i.e., 40 ng) corresponds to a monolayer coverage of PVP chains [37] on the QCM platinum surface.

Generally speaking, the surface adsorption arises from two opposing interactions; an attractive interaction with the surface favoring adsorption and an attractive interaction with solvent molecules preventing unlimited adsorption. Since adsorption of PVP chains on the Ox-SWNTs could enhance the nanotube solubility in water [22–24], the adsorbed Ox-SWNTs, especially those overlaid on the top of

the nanotube aggregates, can be removed from the surface into the liquid phase by adsorbed polymer chains. This was followed by subsequent absorption of PVP chains onto the newly-generated free surface of platinum.

In summary, we have used the combined quartz microbalance (QCM) and atomic force microscopy (AFM) to demonstrate the first surface replacement of preadsorbed acid-oxidized single-walled carbon nanotubes (Ox-SWNTs) by poly(vinyl pyrrolidone), PVP, chains. We found that carbon nanotubes preadsorbed onto a QCM platinum electrode can be effectively replaced by poly(vinyl pyrrolidone) chains from an aqueous solution. These results would not only open new frontiers for fundamental studies into polymer-nanotube interactions, but also provide powerful tools for the controlled design and fabrication of functional polymer-nanotube surfaces for potential applications, ranging from polymer/nanotube-related micro- or nanoelectronics to biomedical systems.

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