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Binding of an Anti-Fullerene IgG Monoclonal Antibody to Single Wall Carbon Nanotubes

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Single wall carbon nanotubes (SWNTs)[1] are a remarkable new class of nanometer diameter metallic and semiconducting wires that carry current as π electrons propagating on their graphitic surface. They are physically robust, exhibit great tensile strength, do not oxidize or have surface states under ambient conditions, and show high conductivity.[2] They are easily grown in lengths of tens of microns and can be precisely positioned and manipulated when attached to AFM tips.[3] Their remarkable electrical properties suggest they might be components of some future nanoscale electronics. We now report observation of specific binding of a biomolecule to SWNTs.

To preserve electrical conductivity in biologically derivatized SWNT wires, the sp^2 graphitic sidewall structure should be minimally perturbed in a specific yet noncovalent contact. A recent inventive approach to this problem involved adsorption of the pyrene moiety of the aqueous bifunctional small molecule: 1-pyrenebutanoic acid succinimidyl ester. Subsequently, the surface-immobilized esters were reacted with several proteins rich in surface amines.[4] Previous experiments on multiwall tubes have demonstrated physical adsorption of metallothionein and streptavidin proteins.[5,6]

We now show that a monoclonal antibody specific for C_{60} fullerenes[7,8] recognizes and binds specifically to SWNTs. The sequences of the light and heavy chains of this IgG antibody were determined recently, and using X-ray crystallography of its Fab' fragment, it was found that the binding cavity was formed by clustering of hydrophobic amino acids.[8] An induced fit mechanism participated in the binding of fullerenes, thus suggesting that SWNTs might also be recognized.

The immunochemical reaction between SWNTs and the C_{60} antibody was first demonstrated in an ELISA,[9] a procedure in which a known ligand of anti-fullerene and a presumptive one compete for binding to an anti-fullerene antibody that is adsorbed to the surface of a plastic well. The presumptive ligand, in this case, was a colloidal suspension of SNWT. Nonspecific binding was eliminated by the presence of a detergent (0.05% Tween 20). Competition was seen at very high dilutions of the SWNT colloidal suspension. A quantitative measure of binding coefficient will require detailed study as a function of available SWNT surface area, structural type, and extent of SWNT aggregation into ropes.

C_{60} Antibodies on SWNTs were directly imaged by atomic force microscopy. SWNT ropes on mica were initially imaged, the surface was then exposed to antibody solution, and finally, the same SWNT was imaged again in air. This sequence distinguishes any preexisting surface particles from bound antibodies. Three drops of aqueous SWNT suspension (0.064 mg/mL in Triton 100X surfactant, from Tubes@Rice) were spun onto a freshly cleaved mica surface. The sample was imaged by tapping mode AFM in air, as shown in Figure 1a. One drop of fullerene-specific antibody (0.00125 mg/mL in 10 mM phosphate buffer, 150 mM NaCl, pH 7.3) was then deposited onto the surface. Liquid was removed by glass pipet after 8 min, and the sample was dried in air. The sample was then washed with 60 drops of water while spinning, to remove weakly bound, physisorbed antibody layers. The same SWNT was then imaged in Figure 1b. A significant number of objects are adsorbed on the nanotube, in previously clean regions, and on the mica substrate. A higher resolution perspective surface plot in Figure 1c shows antibodies on the nanotube and on mica. The mica antibody images are similar in height, width, and dimpled appearance to those previously reported for monoclonal mouse IgG1 on mica.[10] A before and after control experiment with a non-fullerene-specific monoclonal antibody, H413 (specific for aldosterone receptor[11]), yielded antibody aggregates on the mica but left the nanotube clean.

In a separate experiment, we mixed an aqueous SWNT suspension with an anti-fullerene antibody solution and then imaged the SWNTs on mica. One drop of antibody solution (0.25 mg/mL) was mixed with 5 mL of SWNT suspension (0.064 mg/ml) and cooled at 5 °C for 2 h. Three drops of this mixture were spun on a freshly cleaved HOPG surface

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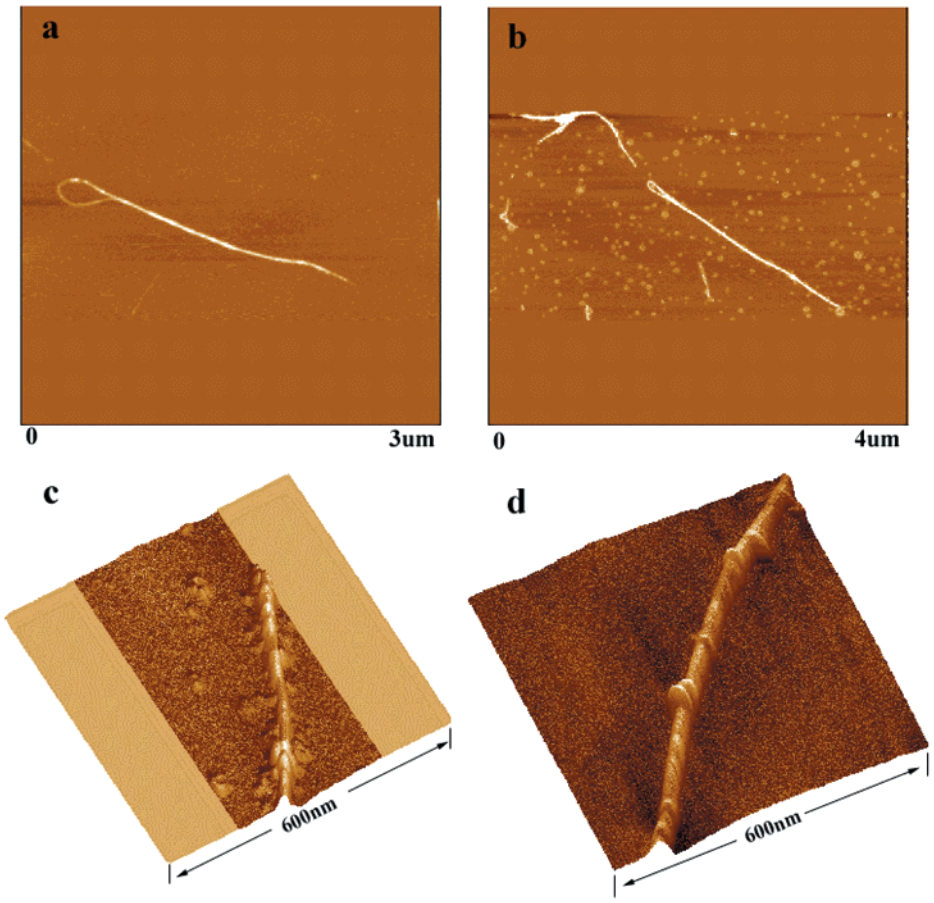

Figure 1. (a) Tapping mode AFM height image (Digital Instruments NanoscopeIII) of SWNT on mica in air, data height range 15 nm. The SWNT ropes were obtained from Tubes at Rice Co. (b) Height image of the same nanotube after exposure to fullerene-specific antibody for 8 min and washed with water, data range 15 nm. The tube shape has changed somewhat. (c) Higher resolution surface plot of the tube in (b), data range 15 nm. (d) Surface plot of height image of SWNTs with fullerene-specific antibody on highly ordered pyrolytic graphite (HOPG), data range 20 nm.

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(Highly Ordered Pyrolytic Graphite) and imaged without washing. Figure 1d shows many SWNT-adsorbed antibody images similar to those in Figure 1c.

We conclude that this monoclonal IgG C_{60}-specific antibody specifically binds to aqueous carbon SWNT ropes. SWNTs have a curved, hydrophobic, π-electron-rich graphitic surface[2] analogous to that of C_{60} itself; the hydrophobic binding site of the antibody is sufficiently flexible to recognize both. Our work bridges two disparate disciplines: electrical nanotechnology and monoclonal immunology.[12] A combination of the extensively developed methods of both fields can have practical consequences. For example, the antibody-coated SWNTs can be used as probes of cell or membrane function. An SWNT rope has a diameter of roughly 10 nm, far smaller than present metallic or glass capillary intracellular probes. They should be capable of insertion into and withdrawal from specific regions of some cells, hopefully with minimal disturbance of cell or membrane function. The anti-fullerene antibody on the surfaces of carbon nanotubes can be covalently decorated with probes of cell function, e.g., redox or luminescent probes (e.g., for Ca^{2+}). After insertion, the probe molecule(s) can be optically excited or electrically addressed via the conducting SWNT wire. Unlike most semiconductors and metals, SWNTs do not form insulating surface oxides at room temperature. There is direct electrical contact with the antibody, as would occur at a Au electrode; indeed, recent experiments have demonstrated that nanotube electrical properties change with reversible adsorption of molecular species[13,14]

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