

Functionalized Carbon Nanotube as pH Sensor Based on Surface-Enhanced Raman Scattering

Supporting Information Available: experimental details for fabrication of SWNT involved SERS-active substrate supplementary figures.

Preparation of Ag-coated Au particles (bimetallic particles). The 15-nm-size gold colloid was prepared by the citrate reduction method and used as seed. Gold seed solution (5 mL) was mixed with 3 mL of 10^{-2} M citrate acid and the final volume was made up to 50 mL. The solution was magnetically stirred and heated to 100 °C. Then 0.5 mL of 10^{-2} M AgNO₃ was added dropwise. The solution color changed from pink to deep yellow after reacting for 20 min. Finally, the colloidal solution was left in the ambient condition to cool it down to a room temperature. The Ag-coated Au colloid was stable for over 6 months.

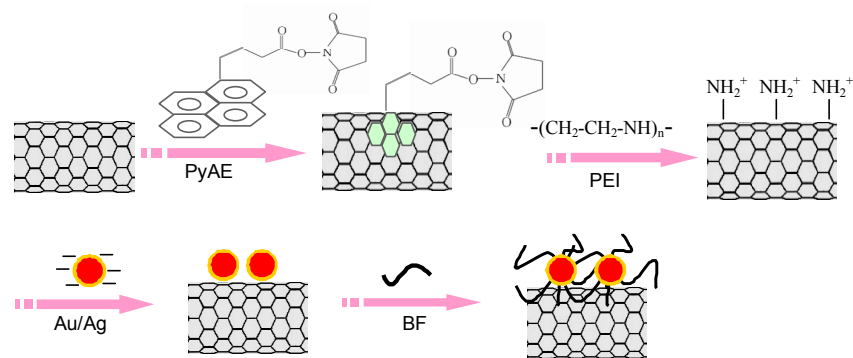
Amino-functionalized CNTs. Purified MCNTs (1 mg; SES research, 900-1201) were submerged for 1 hour in a 5 mM solution of 1-pyrenebutanoic acid succinimidyl ester in dry DMF, resulting in the binding of the pyrene residue to the sidewalls of the CNTs. The succinimidyl ester groups then served as anchoring points for poly(ethyleneimine) to obtain amino-functionalized CNTs. The mixture solution was centrifuged and rinsed with pure water to remove free molecules.

Fabrication of bimetallic nanoparticles loaded CNTs (SERS-active substrates). Amino-functionalized CNTs (0.1 mg) were dispersed in 10 mL of pure water and sonicated for 15 min. Then, 1 mL of bimetallic colloid was added dropwise followed by sonication for another 5 min. After

centrifugation at 15000 rpm and thorough rinsing with pure water, it was redispersed in water for further experiments.

Biotin-Fluorescein adsorption on SERS-active substrates (SERS-based pH sensor). Bimetallic-nanoparticle-loaded CNTs were diluted into solutions with a final Au concentration of 10^{-5} M. Biotin-fluorescein was added to a concentration of 10^{-6} M and the mixture was left to stand for 1 hour. After centrifugation and thorough washing with pure water to remove free biotin-fluorescein molecules, the SERS-based pH sensors were obtained. Biotin-fluorescein adsorption on Au colloid and Ag-coated Au bimetallic colloid was achieved in the same way at the same concentration.

SERS spectra of biotin-fluorescein molecules adsorbed on CNT with immobilized bimetallic nanoparticles. The samples were deposited onto a cover glass substrate and dried under vacuum. Before acquiring Raman spectra at each pH, the sample was immersed in PBS, with the pH adjusted to the desired value, for 10 min. The pH of the buffer was adjusted to an accuracy of 0.01 pH units. Raman spectra were then recorded while the entire substrate was immersed in ambient buffer solution, using a LabRam HR-800 Raman microscope (Horiba, Japan) with 514.32-nm excitation and 40 μ W power at the sample. Scans were collected from a single carbon nanotube at each pH value.



Scheme S1. Scheme for preparing pH sensor of biotin-fluorescein-attached SERS-active CNT.

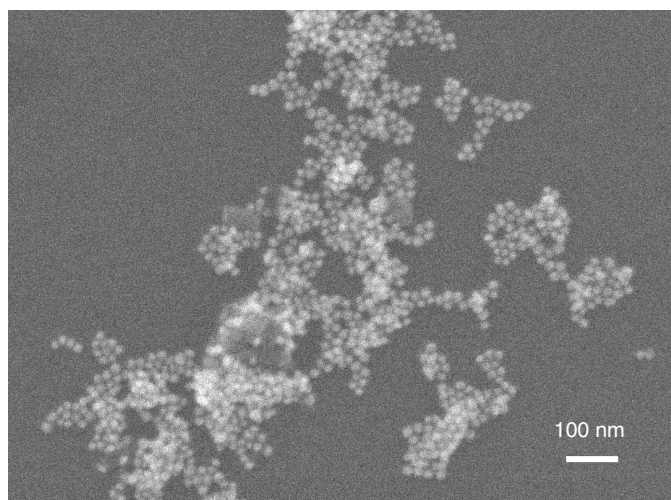


Figure S2. SEM image of silver-coated gold (Au/Ag) nanoparticles.

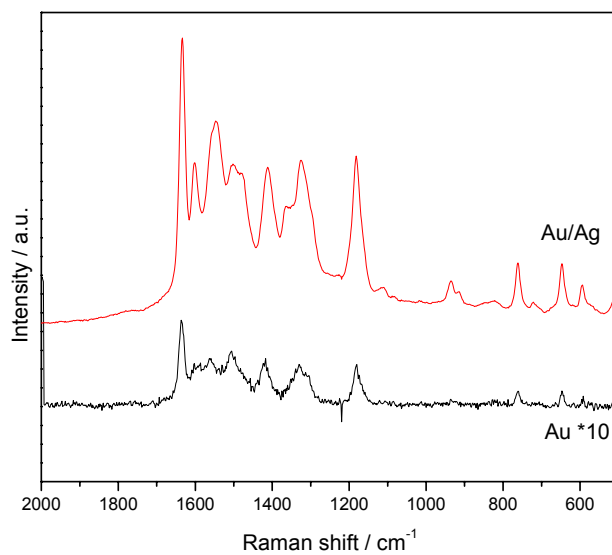
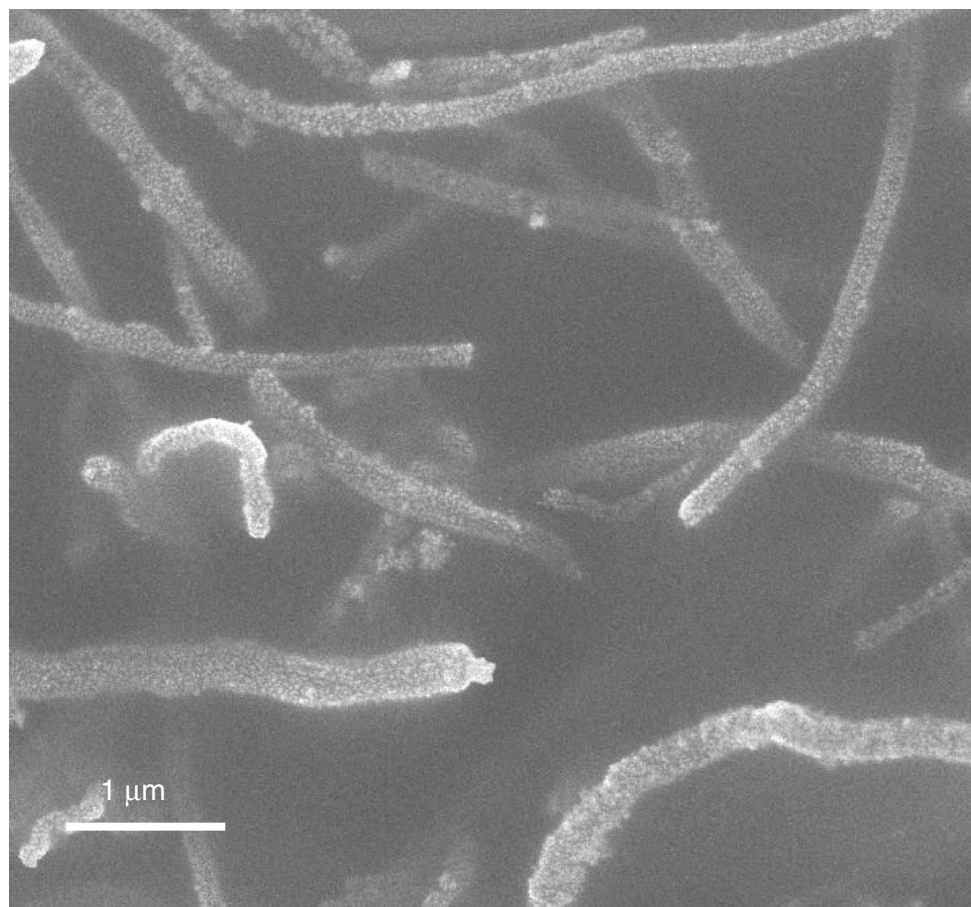


Figure S3. SERS spectra of BF with gold and silver-coated gold colloids.



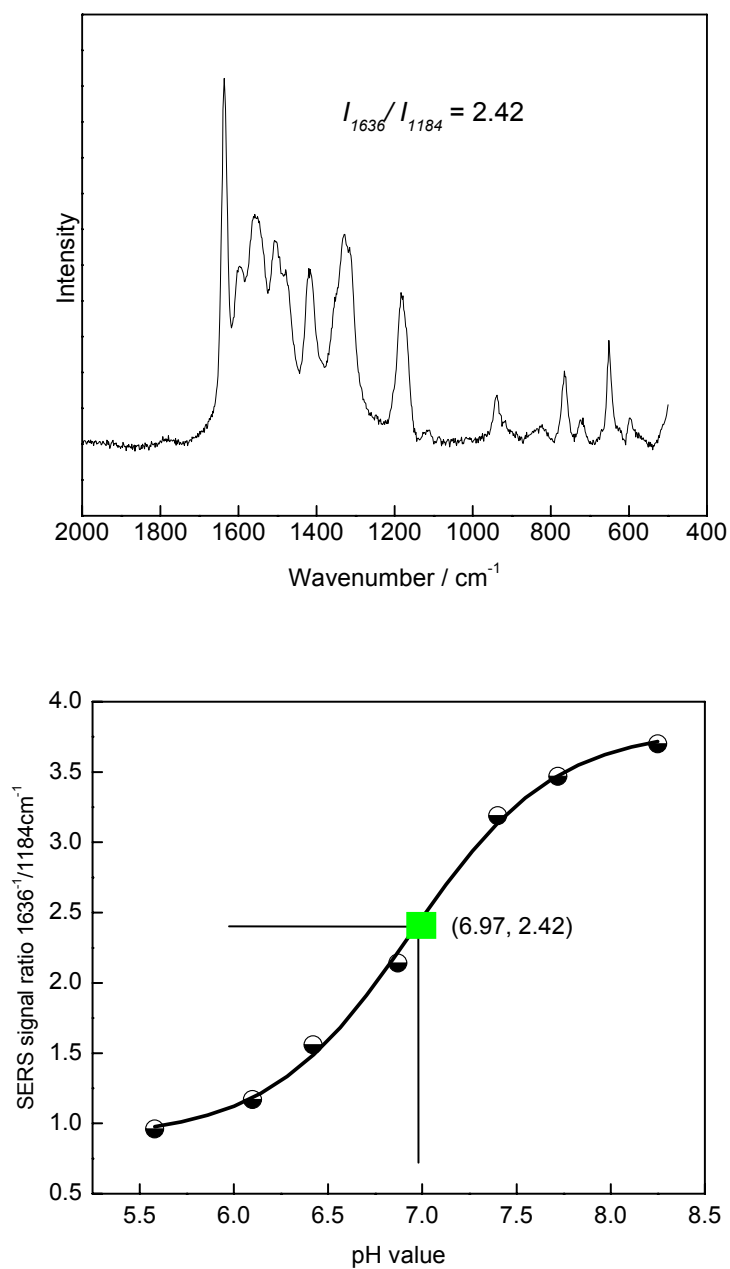


Figure S5. SERS response of BF on a single metal functionalized CNT in ultrapure deionized water (resistivity of 18.2 M Ω at 25°C). The signal ratio of the 1636 cm⁻¹ to the 1184 cm⁻¹ band was 2.42, which corresponds to a pH of 6.97 on the fitted line of the characteristic pH response.

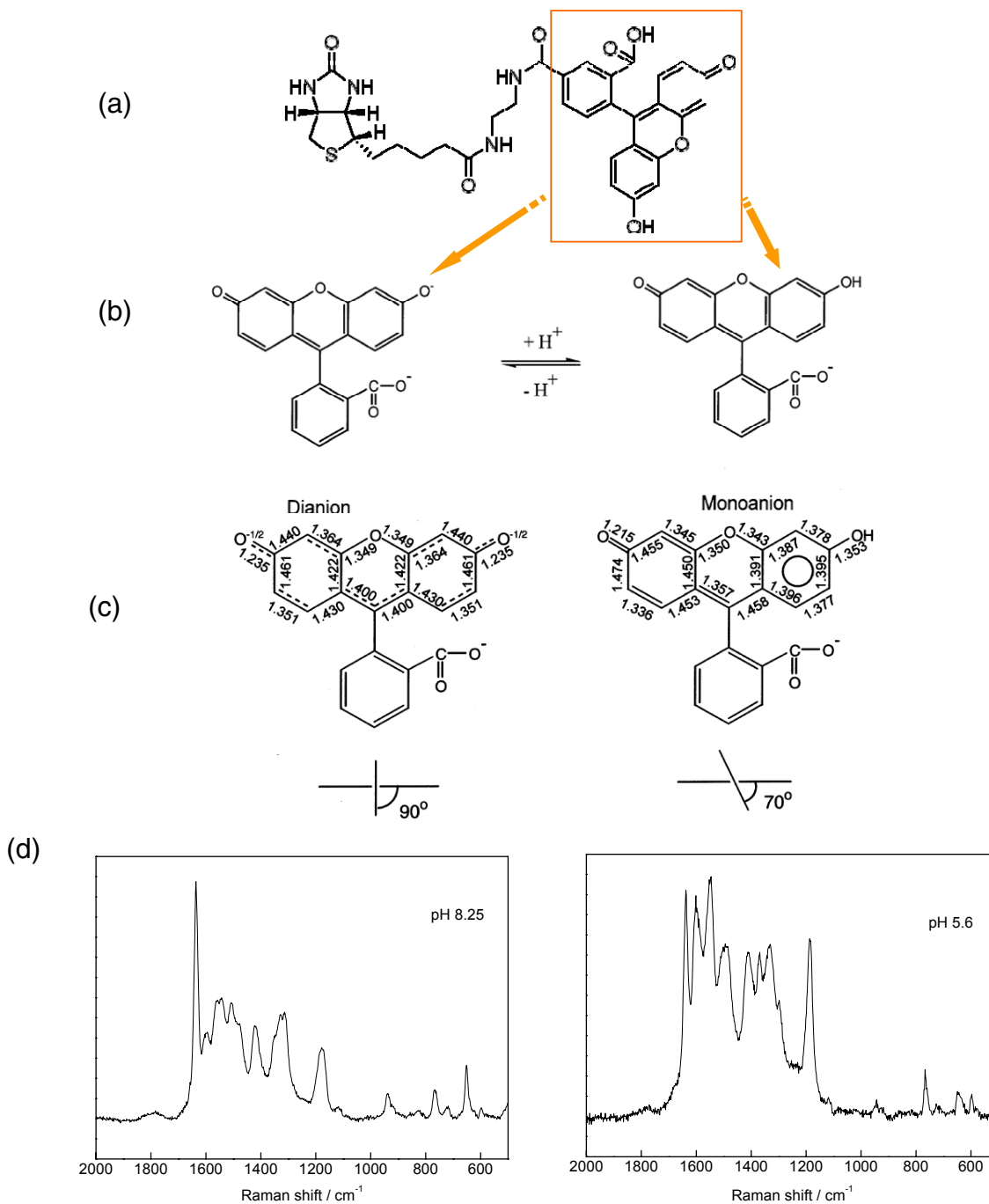


Figure S6. (a) Biotin-fluorescein. (b) Diagram of chemical changes of fluorescein dianion and monoanion forms during the protolytic reaction. The reaction is driven by changes in pH. (c) Geometries of fluorescein dianion and monoanion forms at the local energy minima obtained from the

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ab initio calculations^{7b}. The dotted line in the dianion structure denotes the presence of molecular orbitals, which are delocalized over the three-ring xanthene moiety. The angle shown below each structure is the angle between the plane of the xanthene moiety and the plane of the benzoate ring. (d) The Raman spectrum illustrates the dominant state of the molecule under the conditions described above.