

## Application of Host–Guest Chemistry in Nanotube-Based Device Fabrication: Photochemically Controlled Immobilization of Azobenzene Nanotubes on Patterned $\alpha$ -CD Monolayer/Au Substrates via Molecular Recognition

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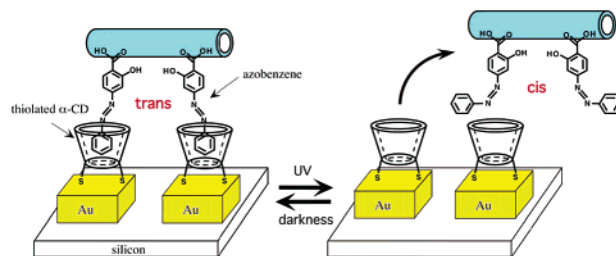
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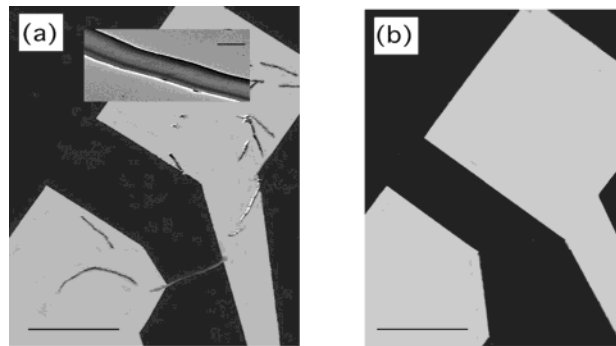
The design and fabrication of nanometer-sized functional materials have become a widely studied field in nanotechnology due to their potential use as building blocks in nanodevices.<sup>1</sup> Smart nanotubes, which can recognize specific complementary molecules, have become increasingly important to design nanodevices for electronics, optics, and sensor applications.<sup>2</sup> Recently, molecular recognitions were also applied to guide nanotubes onto desired locations.<sup>3</sup> Functionalized nanotubes, which recognize and selectively bind a well-defined region on complementary ligand-patterned substrates, can be used as building blocks to assemble three-dimensional nanoscale architectures by placing them at the uniquely defined positions. In addition to molecular recognition, it would also be useful to develop smart nanotubes with a switching function, which can control the nanotube attachment and detachment on electronic components by external stimuli such as photons, electric fields, and magnetic fields. Whereas the molecular recognition based on host–guest chemistry has not yet been explored extensively in the field of nanotube-based device fabrication, robust control of the host–guest complexation via light<sup>4</sup> or electric field<sup>5</sup> is advantageous for application to the switchable building block.

Cyclodextrins (CDs) and their derivatives have been known to form inclusion complexes with a number of complementary azo compounds via host–guest recognitions, and photoisomerizations of azo compounds control the inclusion and the exclusion due to the stability of host–guest complexes.<sup>6</sup> These machinelike switching motions have been applied to molecular shuttles, motors, and information storage in various matrixes.<sup>4,7,8</sup> If azobenzenes are incorporated onto nanotubes as switchable recognition components, nanotube-based photoactive switches can be fabricated on  $\alpha$ -CD/Au substrates. As a proof-of-principle, we demonstrate that azobenzene-coated nanotubes were immobilized onto  $\alpha$ -CD SAMs on a patterned Au substrate via host–guest recognition and the azobenzene nanotubes were detached via UV irradiation due to their photoisomerization to the cis conformation. The attachment–detachment of azobenzene nanotubes on the  $\alpha$ -CD SAMs was reversible as illustrated in Figure 1.

In this report, we used peptide nanotubes, self-assembled from peptide bolaamphiphile, as templates to fabricate azobenzene nanotubes (Figure 2a, inset).<sup>9,10</sup> This peptide nanotube incorporates amide sites to anchor decorating molecules such as proteins, nanocrystals, and porphyrins via hydrogen bonding.<sup>2b,11</sup> Hydroxy azobenzene carboxylic acid (HABA) in ethanol–water (1:1, v/v) solution was incubated into the peptide nanotube solution in the dark at 4 °C for 48 h to immobilize the HABA onto the nanotubes via hydrogen bonding between carboxylic acids of the HABAs and amides of the peptide nanotubes. The immobilization of azobenzenes on the nanotubes was confirmed by Raman microscopy (Supporting Information). The procedure to produce the HABA-coated nanotube is described in the Supporting Information. To



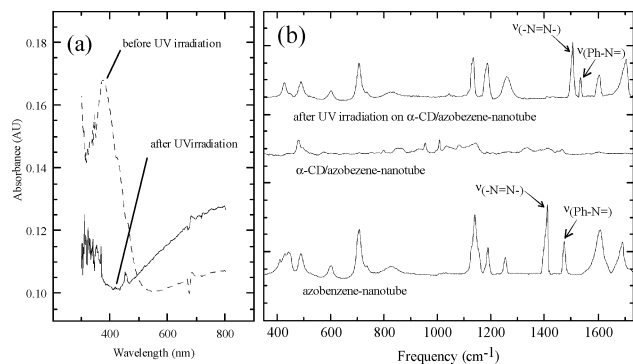
**Figure 1.** Schematic diagram of the azobenzene nanotube assembly on the complementary  $\alpha$ -CD/Au substrates via host–guest molecular recognition and light-induced nanotube detachment/attachment on the  $\alpha$ -CD surfaces.



**Figure 2.** SEM images of (a) the azobenzene nanotubes immobilized on the  $\alpha$ -CD/Au substrates, scale bar = 7  $\mu\text{m}$ ; (inset) TEM image of the single nanotube, scale bar = 70 nm; (b) the  $\alpha$ -CD/Au substrates after the removal of nanotubes via UV irradiation, scale bar = 9  $\mu\text{m}$ .

anchor the azobenzene nanotubes onto surfaces, thiolated  $\alpha$ -CD molecules were self-assembled on the photolithographically patterned Au substrates (Supporting Information).<sup>12</sup>

After the azobenzene nanotubes in the ethanol/water solution were incubated on the  $\alpha$ -CD/Au substrate for 48 h at 4 °C in the dark, the azobenzene nanotubes were immobilized on the  $\alpha$ -CD SAMs, as is shown in Figure 2a. The azobenzene nanotubes either were immobilized on the  $\alpha$ -CD SAM or bridged two regions of the  $\alpha$ -CD SAMs, and the attachment of the nanotubes on the  $\alpha$ -CD SAMs was maintained even after sonication. This result indicates that the azobenzene nanotubes recognized and attached onto the  $\alpha$ -CD SAMs via the host–guest interaction. When the azobenzene nanotubes on the  $\alpha$ -CD SAMs were irradiated by UV light (360 nm) in the stirred solution for 5 h, the azobenzene nanotubes were detached from the  $\alpha$ -CD SAMs, as is shown in Figure 2b. This observation suggests that the photoisomerization of azobenzenes on the nanotubes to the cis conformation destabilized the azobenzene– $\alpha$ -CD complexes, which resulted in the removal of the nanotubes from the surfaces. It should be noted that those azobenzene nanotubes reattached onto the  $\alpha$ -CD SAMs after the



**Figure 3.** (a) UV-vis spectra of the azobenzene nanotube/ $\alpha$ -CD solution before (upper trace) and after (bottom trace) UV irradiation. (b) Raman spectra of the azobenzene nanotubes (bottom trace), the azobenzene nanotubes in the  $\alpha$ -CD solution (middle trace), and the azobenzene nanotubes in the  $\alpha$ -CD solution after UV irradiation (upper trace).

solution was kept in the dark for 24 h. Therefore, the reversibility of the nanotube immobilization can be controlled by UV irradiation. Although less than 20% of nanotubes formed the bridge configuration between two  $\alpha$ -CD SAMs due to the aggregation, we are currently limiting the azobenzene immobilization at the ends of nanotubes<sup>13</sup> and shrinking the patterned Au areas to increase the number of nanotubes interconnecting multiple  $\alpha$ -CD SAMs/Au electrodes for electronics and sensor applications.

To confirm that the attachment/detachment of azobenzene nanotubes on the  $\alpha$ -CD SAMs is controlled by the conformation change of azobenzenes on the nanotubes, UV-vis spectra and Raman spectra of the azobenzene nanotubes were analyzed in the  $\alpha$ -CD solution before and after UV irradiation. Figure 3a (upper trace) is a UV-vis spectrum of the azobenzene nanotube solution (250  $\mu$ L) mixed with 1.0 mM  $\alpha$ -CD in 500  $\mu$ L of DMSO/H<sub>2</sub>O (1:1, v/v) solution before UV irradiation. Appearance of a peak at 340 nm indicates that the  $\alpha$ -CD molecules bound the *trans*-azobenzenes on the nanotubes.<sup>14</sup> When this solution was irradiated by UV light for 3 h, the 340 nm peak in the UV-vis spectrum disappeared, as is shown in Figure 3a (bottom trace). This spectral change suggests that the azobenzenes were detached from the  $\alpha$ -CD molecules via the photoisomerization of azobenzenes to the *cis* form.<sup>14</sup> Further investigation of the conformation change was examined by Raman microscopy. When the azobenzenes were immobilized on the nanotubes, characteristic  $-\text{N}=\text{N}-$  and  $\text{Ph}-\text{N}=\text{N}$  peaks of the azobenzene in the *trans* conformation at 1406 and 1470  $\text{cm}^{-1}$  were observed in the Raman spectrum (bottom trace in Figure 3b).<sup>12</sup> When this nanotube solution was mixed with the  $\alpha$ -CD solution, the Raman spectrum of the resulting solution (middle trace in Figure 3b) agrees with the combined spectrum of the  $\alpha$ -CD and the azobenzene<sup>15</sup> (Supporting Information). This spectral change indicates that the  $\alpha$ -CD molecules were complexed with the azobenzenes on the nanotubes. When this  $\alpha$ -CD-azobenzene nanotube complex was irradiated by the UV light (360 nm) for 3 h, the resulting Raman spectrum (top trace in Figure 3b) was consistent with the azobenzene nanotube spectrum (bottom trace in Figure 3b) except for peaks at 1501 and 1531  $\text{cm}^{-1}$ . These peaks are assigned as the  $-\text{N}=\text{N}-$  and  $\text{Ph}-\text{N}=\text{N}$  vibrations of the *cis*-azobenzene, which were shifted from the 1406 and 1470  $\text{cm}^{-1}$  peaks of the *trans* form in Figure 3b (bottom trace).<sup>15</sup> Therefore, this spectral change means that the azobenzenes were isomerized to the *cis* form after UV irradiation and the  $\alpha$ -CD molecules were removed from the surfaces of the azobenzene nanotubes. It should

be noted that the conformation of azobenzenes on the nanotubes returned to the *trans* form after the nanotube solution was kept in the dark for 48 h at 4  $^{\circ}\text{C}$ , probed by Raman microscopy. These spectroscopic results support that the attachment/detachment of azobenzene nanotubes on the  $\alpha$ -CD SAMs was photochemically controlled by the conformations of azobenzenes on the nanotubes, as is illustrated in Figure 1.

In conclusion, this study demonstrates that the azobenzene nanotubes could recognize and attach onto well-defined regions of thiolated  $\alpha$ -CD SAMs via host-guest molecular recognition. The binding between the azobenzene nanotubes and the  $\alpha$ -CD SAMs was controlled by UV irradiation. Some of the nanotubes were capable of interconnecting two regions of  $\alpha$ -CD SAMs on the Au substrate. This smart building block may be applied to build photoactive nanometer-scale mechanical switches in electronics.

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**Supporting Information Available:** Procedures to form azobenzene nanotubes,  $\alpha$ -CD SAMs, azobenzene nanotube assembly on the  $\alpha$ -CD SAMs; Raman instrumentation; magnified Figure 3b and additional Raman spectra of the neat nanotube and the neat HABA (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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