Supporting Information

Vertically-aligned Carbon Nanotubes Infiltrated with Temperature-responsive Polymers: Smart Nanocomposite Films for Self-Cleaning and Controlled Release

Wei Chen,[a] Liangti Qu,[a] Dongwook Chang,[a] Liming Dai,[a,]* Sabyasachi Ganguli[b] and Ajit Roy[b]

[a] *Department of Chemical and Materials Engineering, University of Dayton, Dayton, OH 4546, USA*

[b] *Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH 45433, USA*

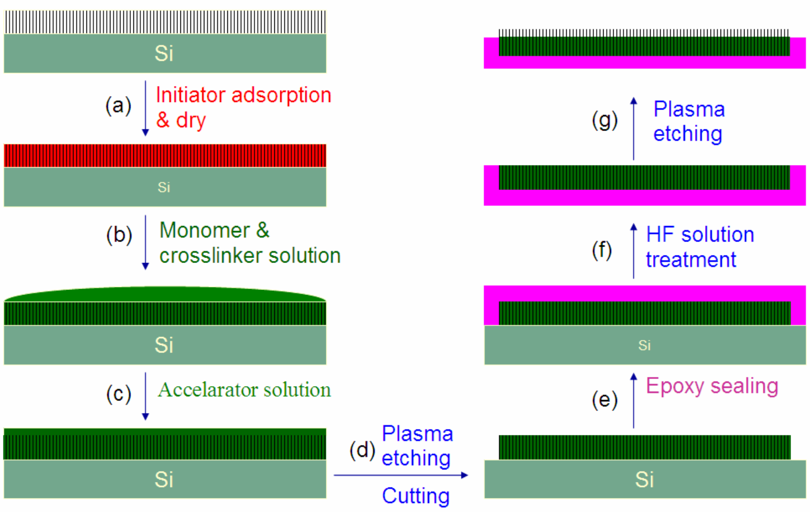
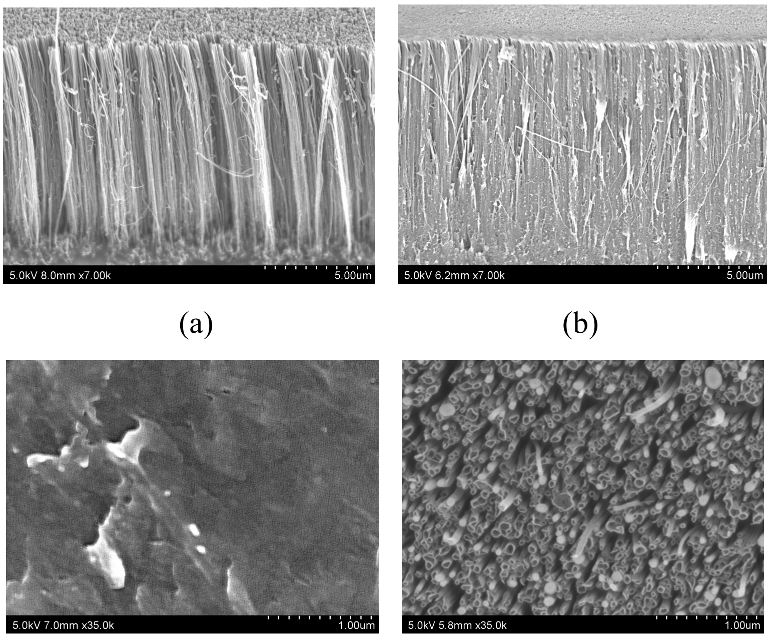


Figure 1. Schematic illustration of the procedure for fabricating the smart PNIPAAm/VA-MWNT nanocomposite films.

A. Composite Sample Preparation

Figure 1 shows schematically the procedure used to prepare the PNIPAAm/VA-MWNT nanocomposite film. To start with, we synthesized the VA-MWNT array by pyrolyzing iron (II) phthalocyanine (FePc) onto a silicon wafer in a tube furnace at 800 – 1100 ºC under a mixture gas flow of Ar and H_2, according to our published method.[1] The resultant VA-MWNT array supported by the Si wafer (Figures 1a & S1a) was then dipped into an aqueous solution of 10 wt% free radical polymerization initiator of potassium persulfate (Sigma-Aldrich),[2] followed by air-drying at room temperature (20 °C, Figure 1a). Thereafter, droplets of an aqueous solution of 10 wt% N-isopropyl acrylamide (NIPAAm) monomer (Sigma-Aldrich, purified by recrystalization) and 1 wt% N, N'-methylenebisacrylamide crosslinker (BIS, Sigma-Aldrich) were deposited onto the top surface of the VA-MWNT array to form a homogenous liquid film (Figure 1b). The free radical polymerization of NIPAAm was then initiated by adding a droplet of 5 wt% N, N, N', N'-tetramethylethylenediamine (TEMED) accelerator (Sigma-Aldrich) into the liquid film over the VA-MWNT array at room temperature (Figure 1c & S1b, c).

Upon completion of the polymerization for about 1 hour, the Si-wafer-supported VA-MWNT array was thoroughly rinsed with deionized water at room temperature to remove all the unreacted monomers, initiators, crosslinkers, and free polymer chains. Selective water-plasma-etching[3,4] (800 mTorr of water pressure, 30 W) of PNIPAAm was then used to expose the nanotube tips on the top surface of the PNIPAAm/VA-MWNT nanocomposite film to ensure a good contact with an epoxy sealant layer (Figures 1d & e), which was used for confining the PNIPAAm chains to expand/collapse along the nanotube length direction. The epoxy resin (Epon 862/Cure W, 100:26 by weight) was cast onto the plasma-etched PNIPAAm/VA-MWNT composite film over the whole Si wafer and cured in an oven at 80 ºC overnight (Figure 1e). Thereafter, the epoxy-sealed PNIPAAm/VA-MWNT nanocomposite film was removed from the Si wafer in an aqueous solution of HF (10 wt%)[1] and inverted (Figure 1f). Finally, the infiltrated PNIPAAm chains at the top surface of the PNIPAAm/VA-MWNT nanocomposite film were preferentially removed by the water-plasma etching to expose the VA-MWNTs (Figures 1g & S1d). As a reference, a similar VA-MWNT film infiltrated with the temperature-insensitive epoxy resin was also prepared.



(a) (b)

(c) (d)

Figure S1. SEM images of (a) the *as-synthesized* VA-MWNTs; (b) the PNIPAAm infiltrated VA-MWNT film; (c) a top-view of the as-prepared PNIPAAm/VA-MWNT film with the constituent aligned nanotubes fully coated by the polymer film; and (d) a top-view of the PNIPAAm/VA-MWNT film after the water-plasma etching.

B. Gold Nanoparticle Preparation

Deionized ultra filtered water from Fischer Scientific Co. was used for all preparation, and all glass wear was cleaned with aqua regia prior to use. $HAuCl_4 \cdot 3H_2O$ was purchased from Alfa Aesar. In a typical experiment, gold nanoparticles, which have diameters ranging from about 20 to 50 nm, were synthesized via a galvanic displacement reaction by adding 0.2 ml of 8.13×10^{-4} mol L^{-1} $HAuCl_4 \cdot 3H_2O$ solution to approximately 1.8 ml of an aqueous solution of sodium citrate (Fisher Scientific) at a predetermined concentration in a quartz cuvette at room temperature under the ambient condition.[5] UV-Vis spectra were measured using a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer. A typical optical absorption spectrum for the resultant gold nanoparticles is given in Figure S2, which clearly shows the surface plasmon resonance peak around 530 nm.

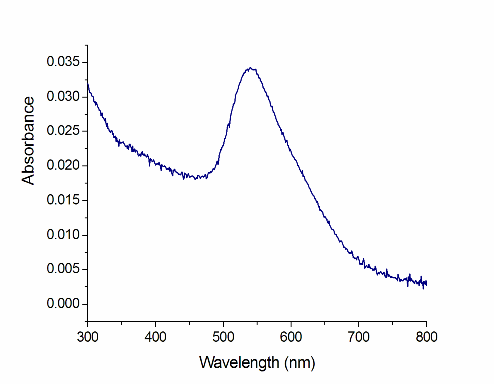
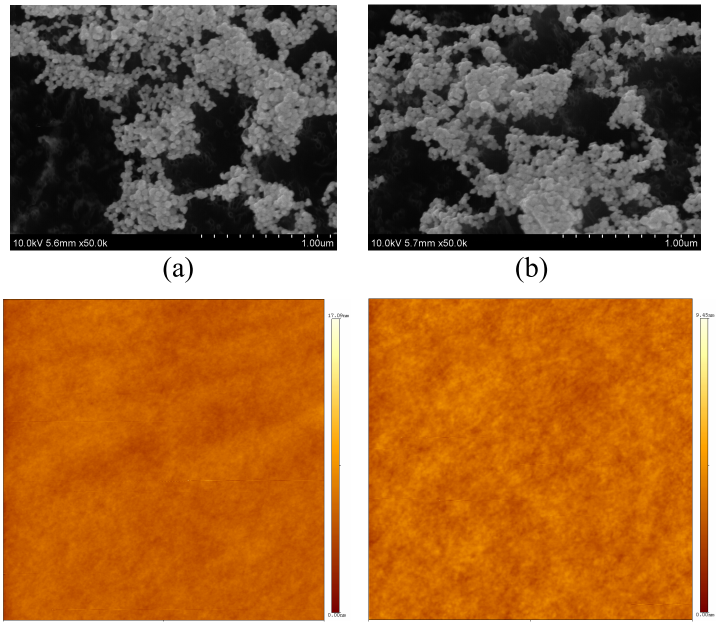


Figure S2. A typical UV-Vis spectrum of the *as-prepared* Au nanoparticles in water.

C. Self-cleaning Test for Reference Film

As a comparison to Figures 3a &b for the PNIPAAm/VA-MWNT nanocomposite film, we have also immersed the epoxy/VA-MWNT reference nanocomposite film into an aqueous solution of the gold nanoparticles at 50 ºC to allow for adsorption of the nanoparticles onto the nanotube top surface (Figure S3a).



(a) (b)

(c) (d)

Figure S3. SEM images of (a) the epoxy/VA-MWNT reference film after adsorbing gold nanoparticles on its top surface from the aqueous solution at 50 ºC and (b) as for (a) after being cooled down to 25 ºC. Note that the micrographs shown in (a) and (b) were not taken from the same spot due to technical difficulties. An aqueous PNIPAAm film at (c) ~50 ºC and (d) ~20 ºC. XY-scale: c, d) 5μm × 5μm, Z-scale: c) 17 nm; d) 10 nm.

By reducing the solution temperature down to or even below 25 ºC (< LCST ≈ 32 ºC), we found that almost all of the pre-adsorbed gold nanoparticles remained on the top surface of the epoxy/VA-MWNT nanocomposite film (Figure S3b). While a similar temperature change caused an aqueous PNIPAAm film to become only slightly rougher, if any, at about 25 ºC (Figure S3d) than 50 ºC (Figure S3c), the pure PNIPAAm film showed no obvious adsorption-desorption of gold nanoparticles during the temperature-change cycle. Therefore, it is the unique combination of the temperature-responsive PNIPAAm chains and the aligned carbon nanotube forest that makes the self-cleaning possible.

References

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