

## Supporting Information

# Functional Nanocomposites with Perfect Nanoblending between Water-Soluble Polymers and Hydrophobic Inorganic Nanoparticles: Applications to Electric-Stimuli-Responsive Films

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### Experimental Details

#### Synthesis of OA-TiO<sub>2</sub> NPs

In a 30 mL Teflon-lined stainless-steel autoclave, *tert*-butylamine (Aldrich, 0.1 mL) was dissolved in 10 mL of deionized water. Titanium(IV) *n*-propoxide (Aldrich, 0.5 mmol) and oleic acid (Aldrich, 1 mL) were then dissolved in toluene (Aldrich, 10 mL). This solution was transferred to the autoclave without any stirring. The autoclave was heated to 180 °C and maintained at this temperature for 12 h. The product was purified three times using methanol and centrifugation. The purified TiO<sub>2</sub> nanoparticles were dispersed in toluene.

#### Synthesis of OA-Fe<sub>3</sub>O<sub>4</sub> NPs

OA-stabilized Fe<sub>3</sub>O<sub>4</sub> NPs with a diameter of approximately 7 nm were synthesized as follows. Fe(acac)<sub>3</sub> (Aldrich, 2 mmol), 1,2-hexadecanediol (Aldrich, 10 mmol), OA (Aldrich, 5 mmol), oleylamine (Aldrich, 6 mmol), and benzyl ether (Aldrich, 20 mL) were mixed and stirred under a flow of nitrogen. The mixture was heated to 200 °C for 2 h and heated to reflux (approximately 300 °C) for 1 h under a blanket of nitrogen. The black-colored mixture was cooled to room temperature by removing the heat source. Ethanol (40 mL) was added to the mixture under ambient conditions, and a black material was precipitated and separated via centrifugation. The black product was dissolved in hexane in the presence of OA (0.05 mL) and oleylamine (0.05 mL). Centrifugation (6000 rpm, 10 min) was applied to remove any

undispersed residue. A black-brown hexane dispersion of 8 nm Fe<sub>3</sub>O<sub>4</sub> nanoparticles was produced.

### **Synthesis of OA-Ag NPs**

OA-stabilized Ag nanoparticles were synthesized as follows. Silver trifluoroacetate (Aldrich, 0.4 g), OA (Aldrich, 3.5 mL), and isoamyl ether (Aldrich, 30 mL) were mixed in a 250 mL three-neck flask under argon. The flask was heated to 160 °C and maintained at this temperature for 30 min. The flask was then cooled to room temperature by removing the heat source. The purification process was performed four times using excess ethanol as a poor solvent and centrifugation. The precipitated Ag nanoparticles were dispersed in toluene.

### **Synthesis of OA-Pt NPs**

OA-stabilized Pt nanoparticles were synthesized as follows. Pt(acac)<sub>2</sub> (Aldrich, 0.2 g), OA (Aldrich, 2 mL), oleylamine (Aldrich, 2 mL), and 1-octadecene (Aldrich, 20 mL) were mixed in a 250 mL three-neck flask under argon. The flask was heated to 120 °C and maintained at this temperature for 30 min. A solution of Fe(CO)<sub>5</sub> in hexane (0.1 mL, prepared by adding Fe(CO)<sub>5</sub> (Aldrich) in 1 mL of hexane) was rapidly injected into the flask. The flask was then heated to 200 °C and maintained at this temperature for 1 h. After the completion of the reaction, the purification process was performed five times using excess isopropanol as a poor solvent and centrifugation. The precipitated Pt nanoparticles were dispersed in toluene.

### **UV-vis Spectroscopy**

UV-vis spectra of dendrimer/hydrophobic NP multilayers on quartz glass were collected using a Perkin Elmer Lambda 35 UV-vis spectrometer.

### **Quartz Crystal Microgravimetry (QCM) Measurements**

A QCM device (QCM200, SRS) was used to examine the mass of the material deposited after each adsorption step. The resonance frequency of the QCM electrodes was approximately 5 MHz. The adsorbed mass of dendrimer and hydrophobic NPs,  $\Delta m$ , was calculated from the change in QCM frequency,  $\Delta F$ , using the Sauerbrey equation:

$$\Delta F(\text{Hz}) = -\frac{2F_0^2}{A\sqrt{\rho_q\mu_q}} \cdot \Delta m$$

where  $F_0$  (~5 MHz) is the fundamental resonance frequency of the crystal,  $A$  is the electrode area, and  $\rho_q$ , (~2.65 g·cm<sup>-2</sup>) and  $\mu_q$  (~2.95 × 10<sup>11</sup> g·cm<sup>-2</sup>·s<sup>-2</sup>) are the shear modulus and

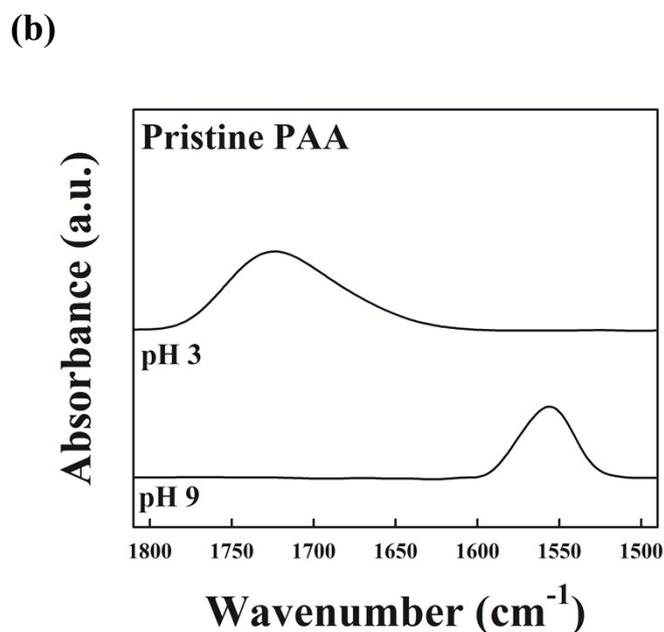
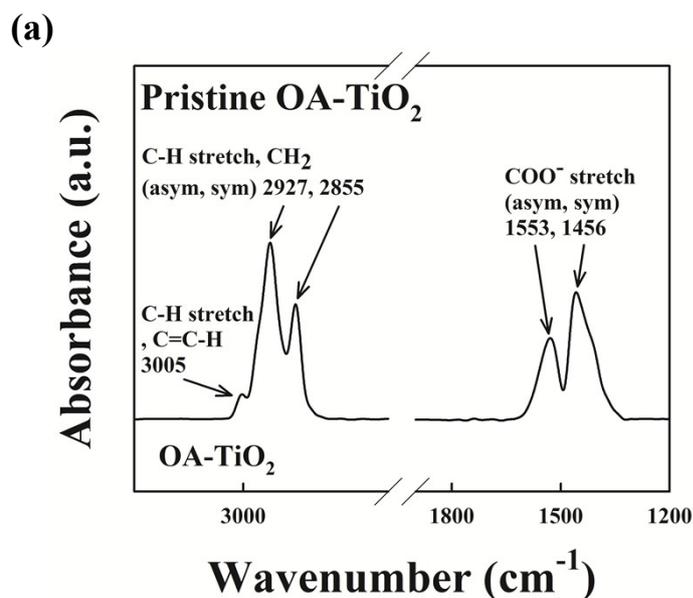
density of quartz, respectively. This equation can be simplified as

$$\Delta F \text{ (Hz)} = - 56.6 \times \Delta m_A,$$

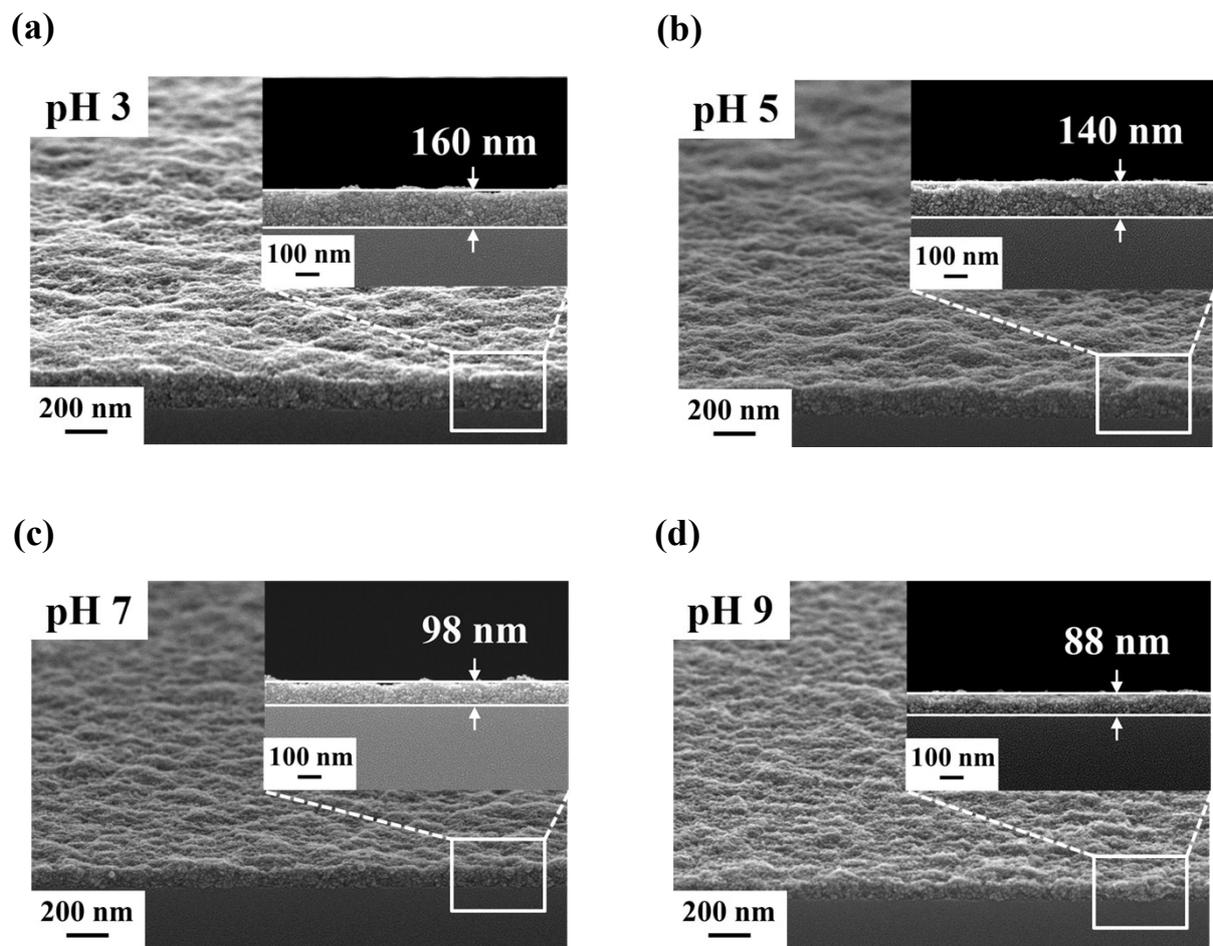
where  $\Delta m_A$  is the mass change per quartz crystal unit area in  $\mu\text{g}\cdot\text{cm}^{-2}$ .

### **Fourier Transform Infrared Spectroscopy**

Vibrational spectra were measured by FTIR spectroscopy (iS10 FT-IR, Thermo Fisher) in ATR modes. The sample chamber was purged with  $\text{N}_2$  gas for 2 h to eliminate water and  $\text{CO}_2$  prior to the FTIR measurements. An ATR-FTIR spectrum for the (water-soluble polymer/hydrophobic NP)<sub>n</sub> film deposited onto an Au-coated substrate was obtained from 300 scans. The acquired raw data were plotted after baseline correction, and the spectrum was smoothed using spectrum analysis software (OMNIC, Nicolet).



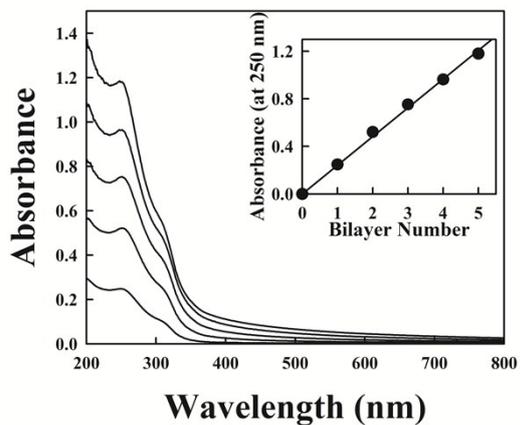
**Figure S1.** (a) FTIR spectra of pristine OA-TiO<sub>2</sub> NPs. The observed C–H stretching (2855, 2927 cm<sup>-1</sup>) and COO<sup>-</sup> stretching (1553 and 1456 cm<sup>-1</sup>) peaks originate from long aliphatic chains and the COO<sup>-</sup> groups of the OA ligands bound to the TiO<sub>2</sub> NPs, respectively. (b) FTIR spectra of pristine PAA. C=O stretching (1725 cm<sup>-1</sup>) and COO<sup>-</sup> stretching (1553 cm<sup>-1</sup>) peaks originate from the uncharged carboxylic acid group (-COOH) at pH 3 and the charged carboxylic acid group (-COO<sup>-</sup>) at pH 9.



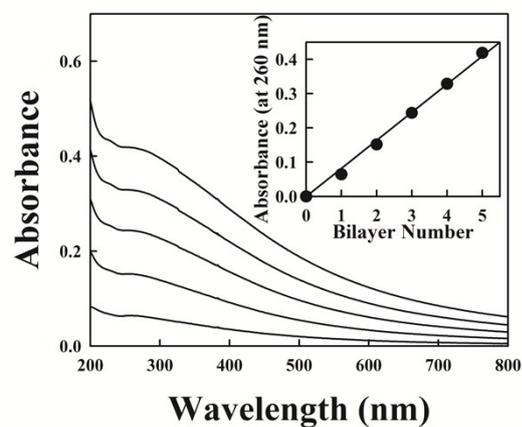
**Figure S2.** Tilted and cross-sectional FE-SEM images of  $(\text{PAA/OA-TiO}_2 \text{ NP})_{10}$  multilayers as a function of the pH of the PAA solution.



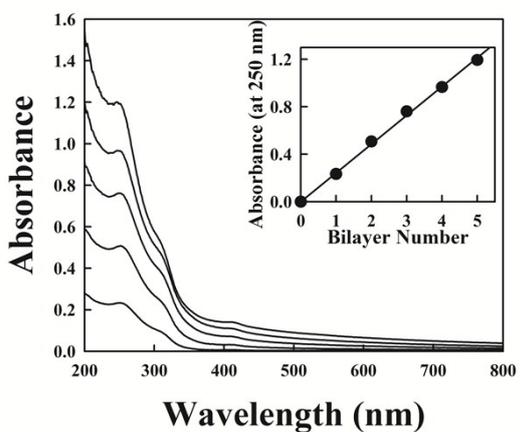
(a)



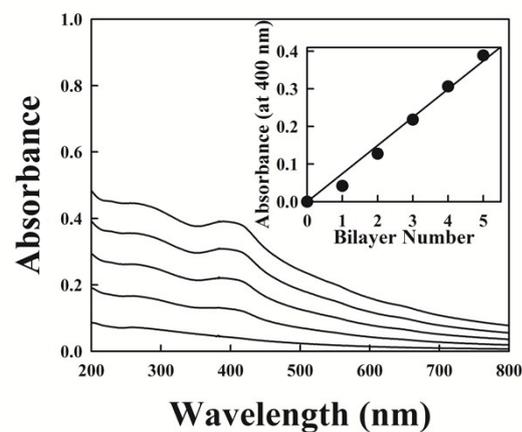
(b)



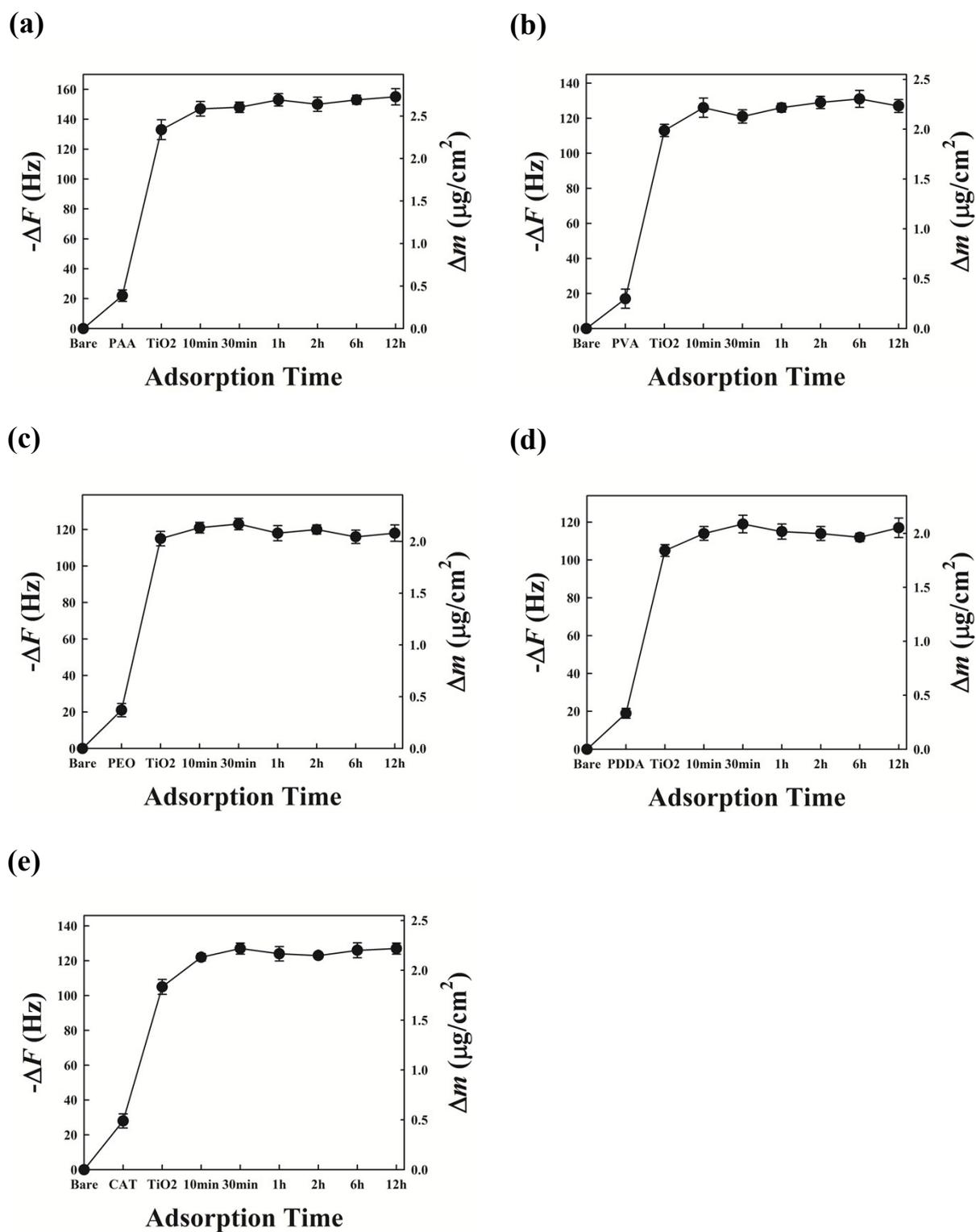
(c)



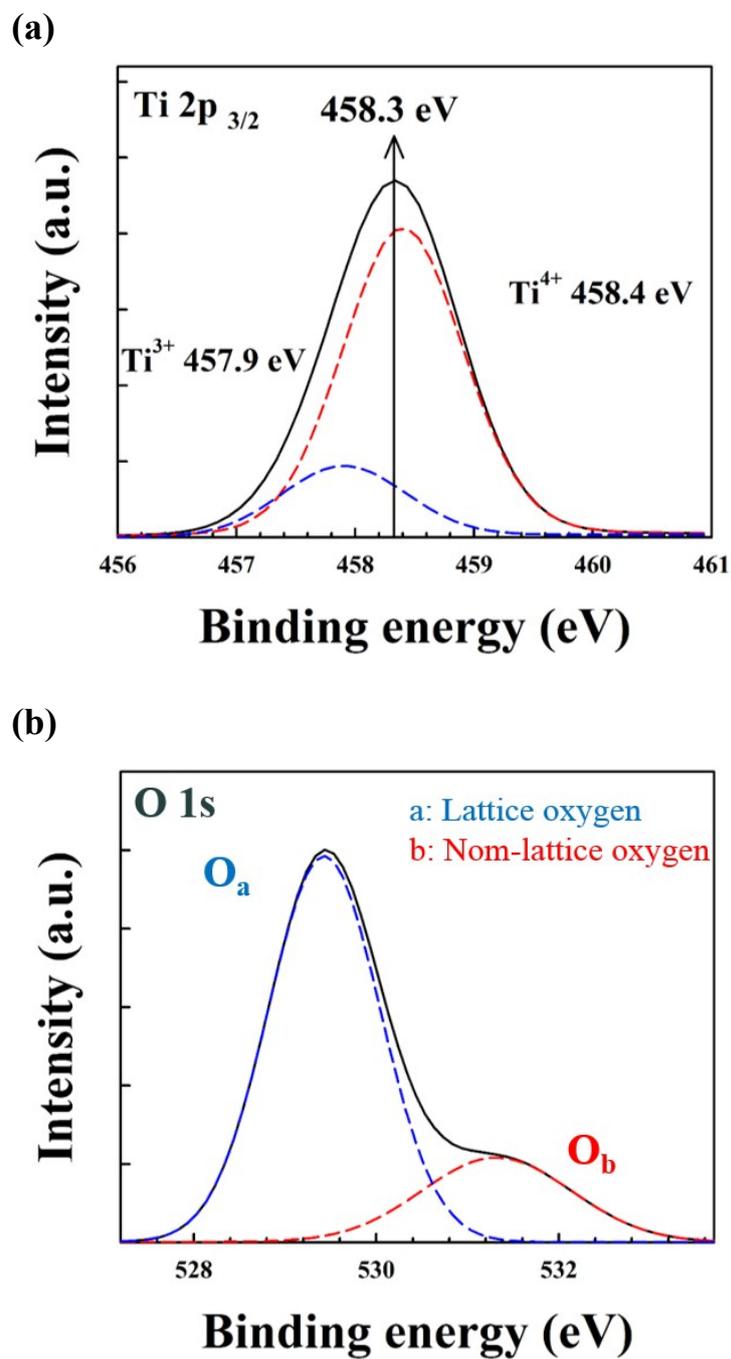
(d)



**Figure S4.** UV-vis spectra of (a) (ferritin/OA-TiO<sub>2</sub> NP)<sub>n</sub>, (b) (ferritin/OA-Pt NP)<sub>n</sub>, (c) (hemoglobin/OA-TiO<sub>2</sub> NP)<sub>n</sub>, and (d) (hemoglobin/OA-Pt NP)<sub>n</sub>.

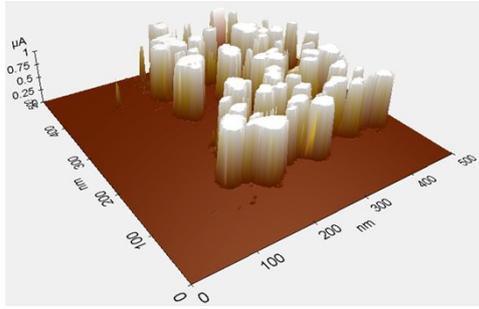


**Figure S5.** Stability test of the adsorbed OA-TiO<sub>2</sub> NPs during the deposition of (a) PAA, (b) PVA, (c) PEO, (d) PDDA and (e) CAT. In this case, the QCM frequency and mass changes were investigated with increasing the deposition time of polymers from 10 min to 12 h.

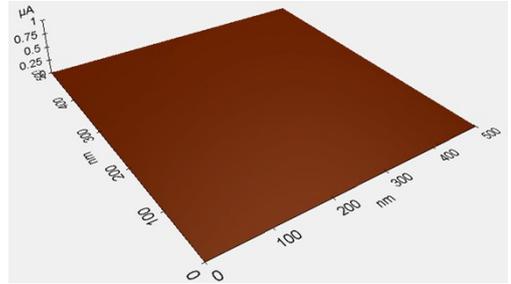


**Figure S6.** XPS spectra and deconvoluted (a) Ti 2p<sub>3/2</sub> and (d) O 1s spectra of PAA/OA-TiO<sub>2</sub> NP nanocomposite films.

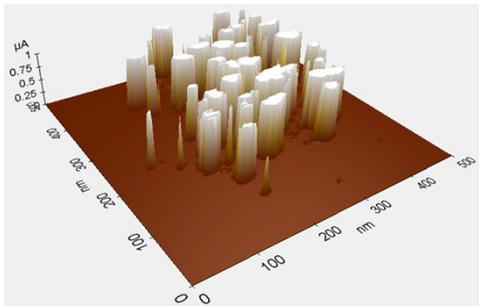
(a)



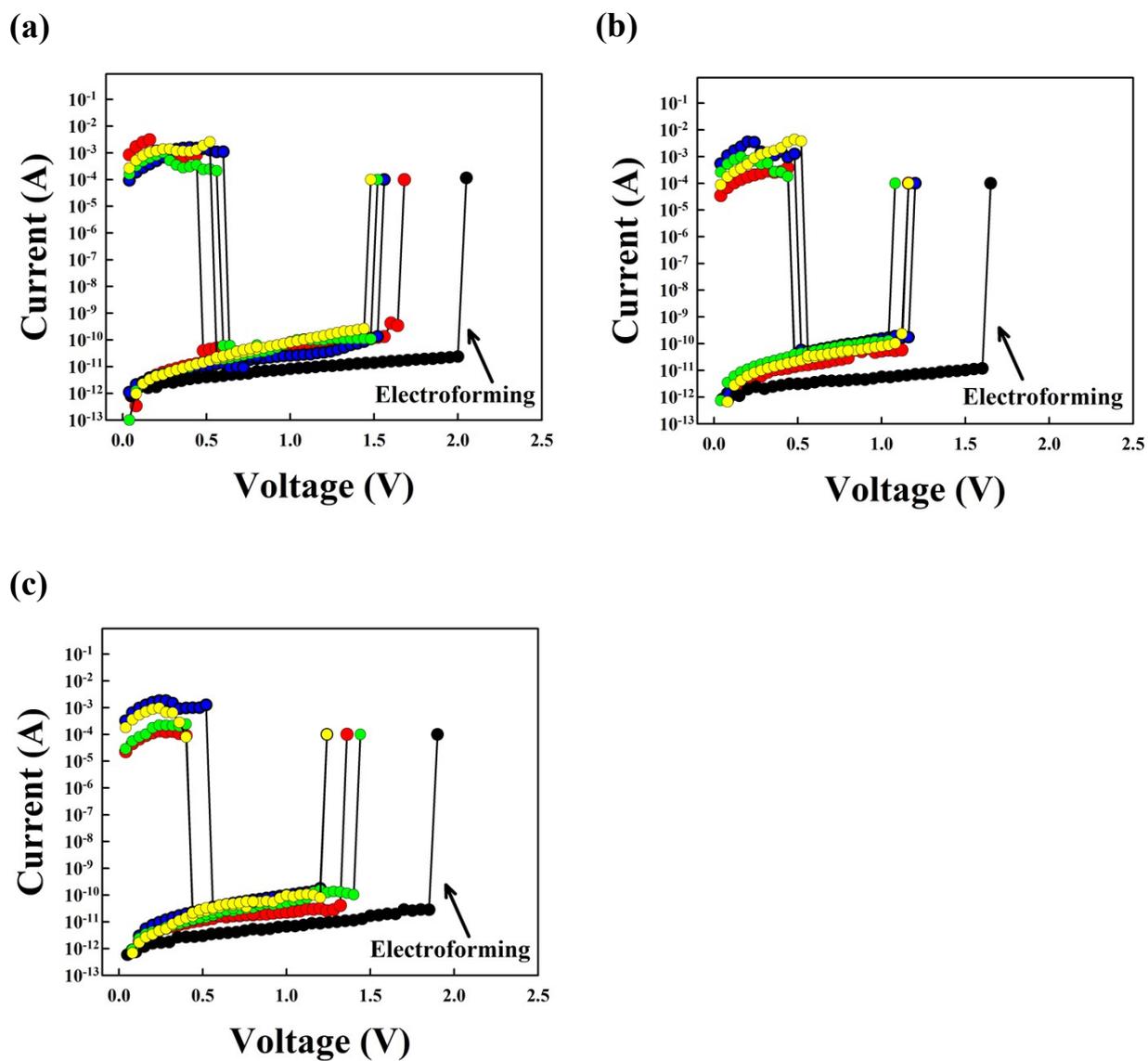
(b)



(c)



**Figure S7.** CS-AFM images of  $(\text{PAA/OA-TiO}_2 \text{ NP})_n$  multilayers after (a) electroforming at 3 V, (b)  $V_{\text{RESET}}$  at 1 V and (c)  $V_{\text{SET}}$  at 2 V, respectively.



**Figure S8.** *I-V* curves of the  $(\text{PAA/OA-TiO}_2 \text{ NP})_8$  device using Au, W, and Pt top electrodes instead of Ag electrode.