Electronic Supplementary Information

Composite Free-Standing Films of Polydopamine/Polyethyleneimine Grown at the Air/Water Interface

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Experimental Section

Materials: Dopamine hydrochloride and Titanium bis(ammonium lactato) dihydroxide (TiBALDH) solution (50 wt% in H2O) were purchased from Sigma. Tetramethyl orthosilicate (TMOS), polyethyleneimine (PEI, Mw=600) and silver nitrate were procured from Aladdin Reagent Co. Ltd.. Other reagents such as tris(hydroxymethyl) aminomethane were obtained from Sinopharm Chemical Reagent Co. Ltd.. All reagents were used as received without further treatment.

Fabrication of free-standing film: Dopamine hydrochloride and PEI were dissolved in 10 mL tris-buffer solution (50 mM, pH=8.5) with different dopamine/PEI ratio (4:1, 2:1, 1:1, 1:2 and 1:4), and the concentration of dopamine is fixed to 2 mg/mL. Then the solution was kept at 25 °C in water for 6 to 30 hrs. After reaction, the light brown films were transferred to and kept in deionized water before further metallization or mineralization.

Fabrication of organic-inorganic hybrid films: All free-standing film used as templates were formed with dopamine/PEI ratio of 2:1 for 12 hrs. Ag-metallized films were fabricated by immersing afore-mentioned film into 100 mM $AgNO_3$ solution at room temperature for 12 hrs. The hydroxyapatite-coated films were obtained after mineralization of PDA/PEI composite film in mSBF solution (NaCl 141 mM, KCl 4 mM, $MgSO_4$ 0.5 mM, $MgCl_2$ 1.0 mM, $NaHCO_3$ 4.2 mM, $CaCl_2$ 5.0 mM and KH_2PO_4 2.0 mM). Silica and titania hybrid films were prepared by sol-gel method. The sol solution was prepared as following steps. 0.15 mL TMOS was added to 5 mL HCl solution (1 mM) with stirring for 20 min. Then the silicic acid was mixed with 5 ml phosphate buffer solution (0.1 M, pH=6.0). The precursor solution for titania coating was simply prepared by adding 0.12 mL TiBALDH solution to 10 mL ammonium hydroxide solution (100 mM). The films were transferred to the precursor solution and aged for 12 hrs. All samples were washed by deionized water and then transferred to PET substrates for further characterization.

Characterization: The surface morphologies were observed by field emission scanning electron microscopy (FE-SEM, Hitachi, S4800) and scanning probe microscopy (SPM, VEECO, Multimodel). UV absorption spectra was detected by ultraviolet spectrophotometer (Shimadzu, UV 2450) from 800 to 200 nm (the films were attached on the wall of cuvette). Surface elements components were characterized by X-ray photoelectron spectrometer (XPS, PerkinElmer). The contact angles were measured by contact angle system (MAIST Vision Inspection & Measurement Co. Ltd., DropMeter A-200).

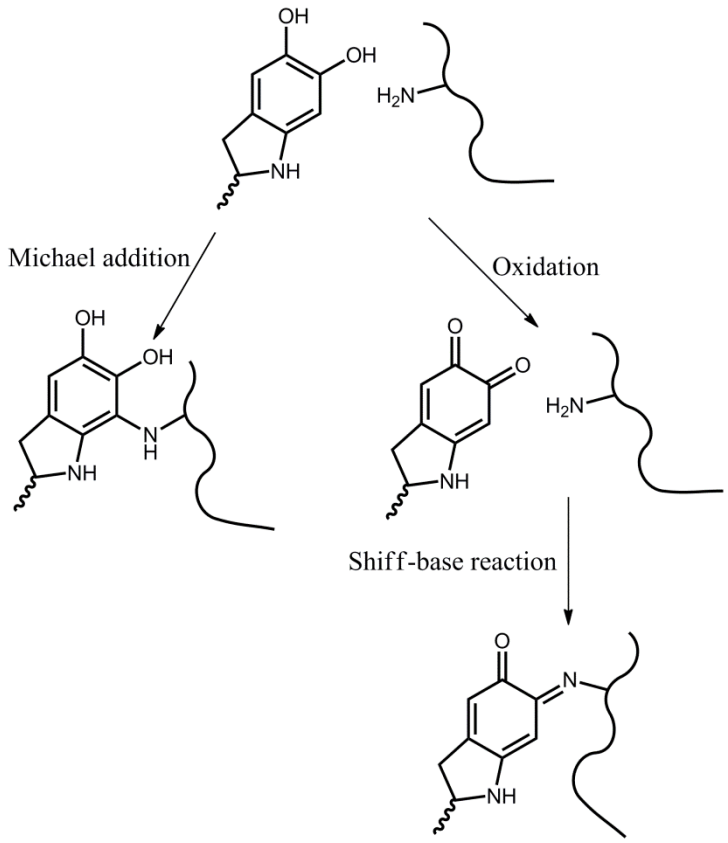

Figure S1. Possible oxidation and cross-link reactions between PDA and PEI.

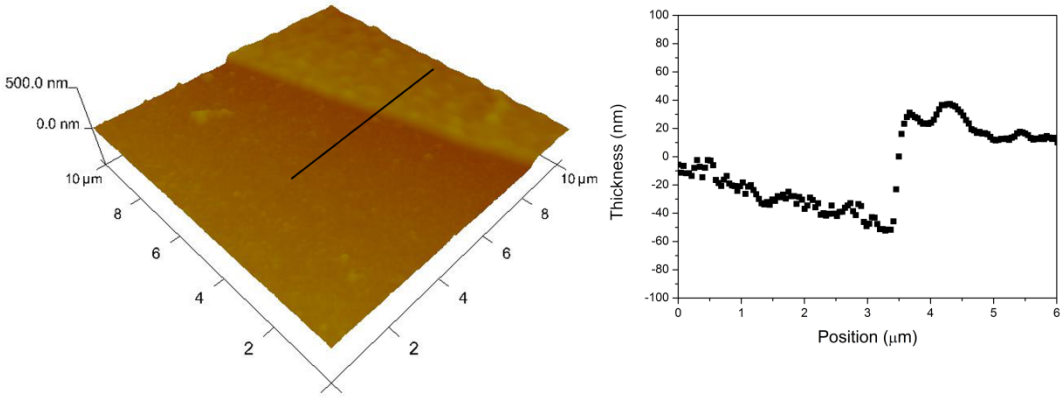

Fig. S2 AFM image of a free-standing film from PEI/dopamine=1:1 for 12 h.

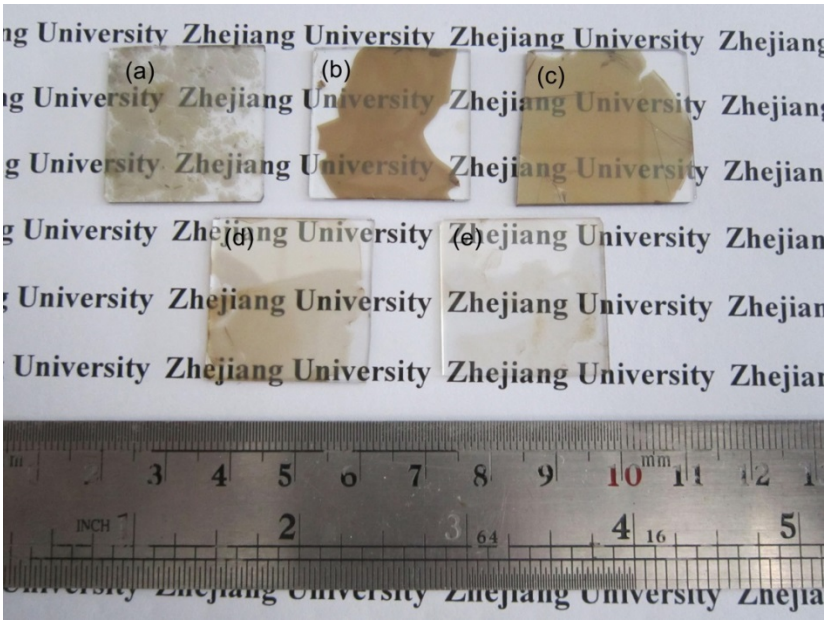

Fig. S3 Free-standing films fabricated with different PEI/dopamine ratios after 12 hrs. (a) dopamine, (b) PEI/dopamine=1:4, (c) PEI/dopamine=1:2, (d) PEI/dopamine=1:1, (e) PEI/dopamine=1:2. The concentration of dopamine was fixed at 2 mg/mL.

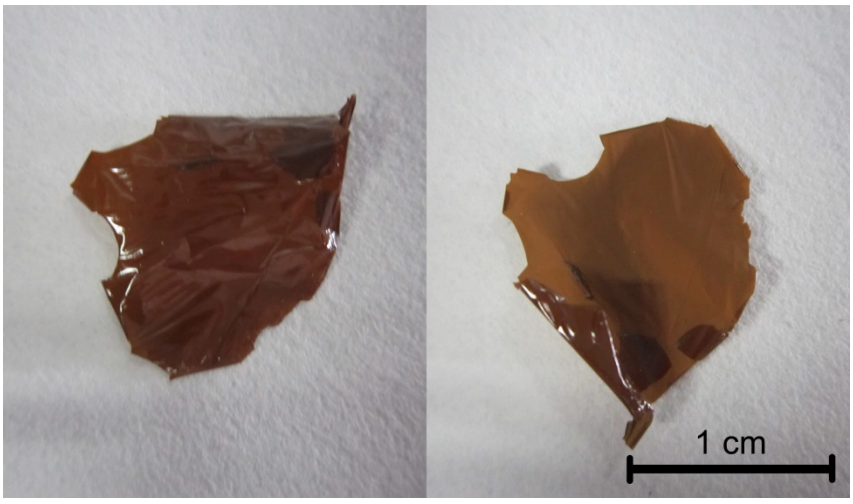

Fig. S4 Photographs of PDA/PEI papers after 3 d reaction.

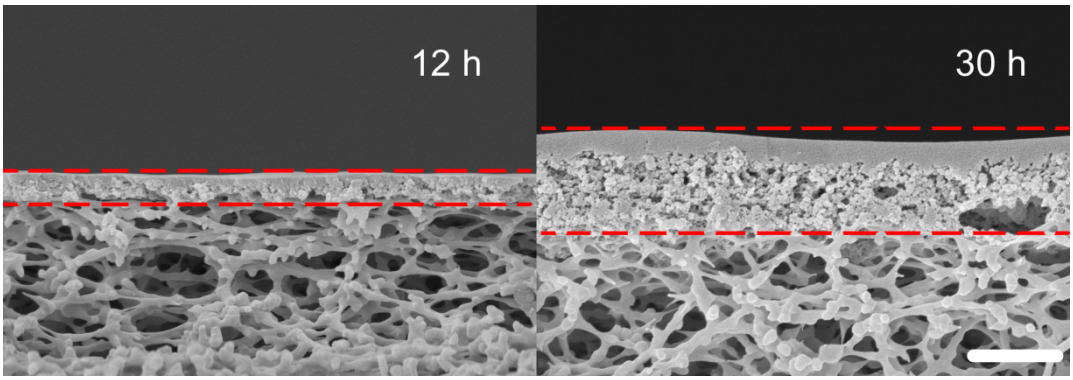

Fig. S5 FESEM images of the free-standing film cross-sections for different reaction times. The scale bar is 1 μm.

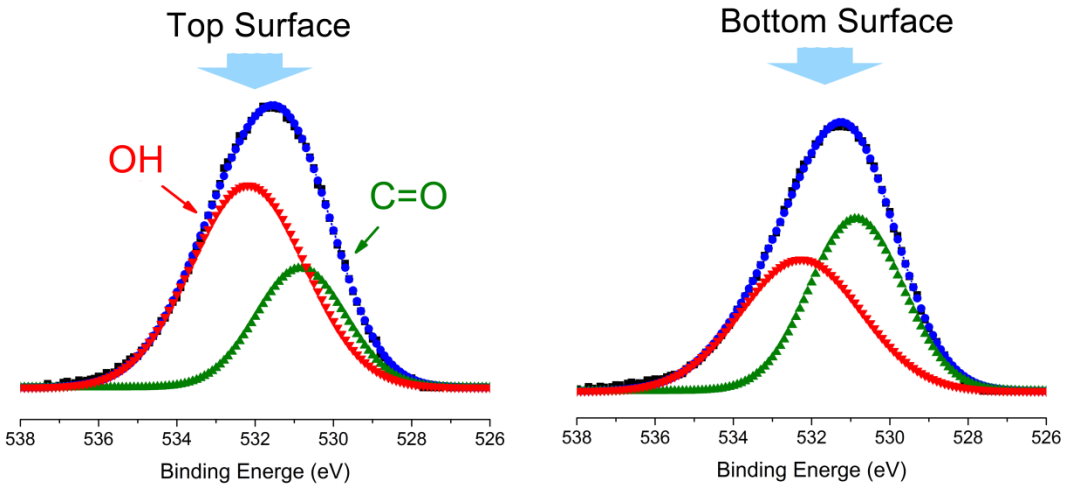

Fig. S6 Narrow XPS scan spectra for the two film surfaces of the free-standing film.

Table S1 Atom ratios from the XPS data for the two surfaces of the free-standing flim.

	C	O	N	N/O
Top surface	71.3	17.8	10.9	0.612
Bottom surface	69.9	16.2	14.0	0.864

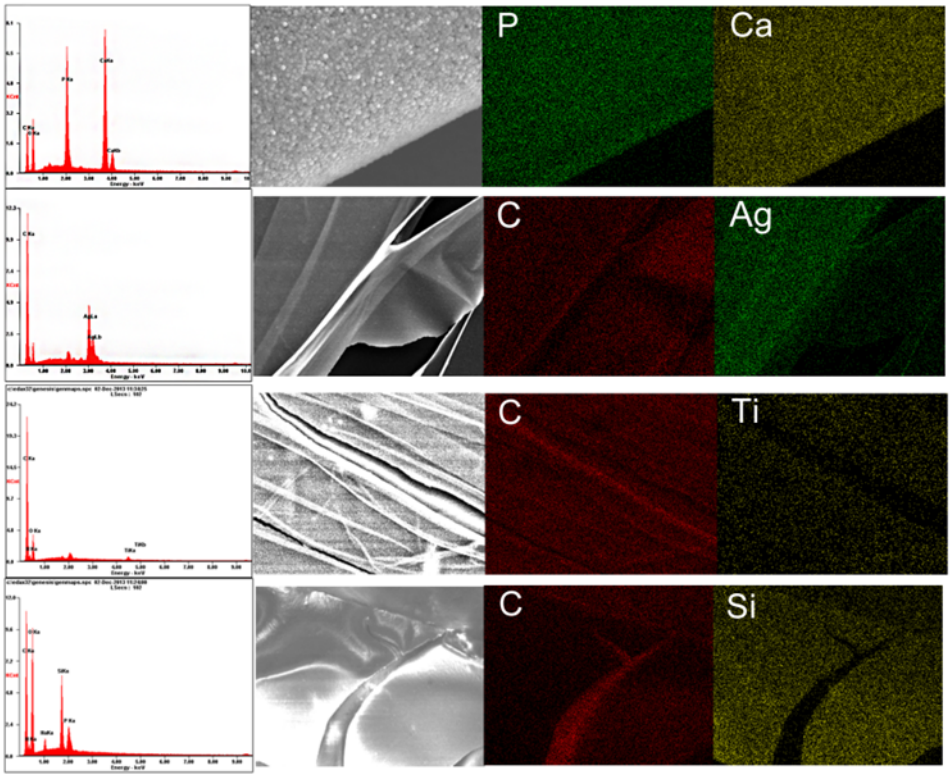

Fig. S7 Energy dispersive X-ray spectra (EDX) of the silver, hydroxyapatite, titania and silica films.

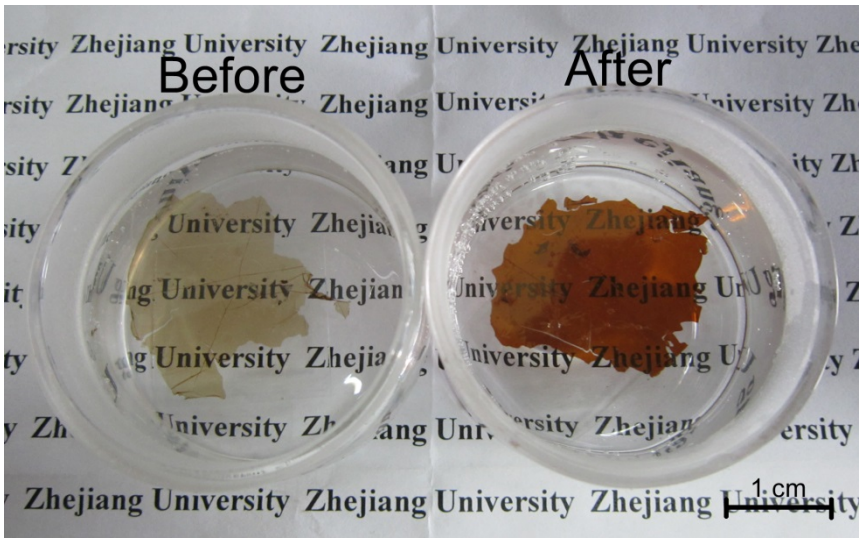

Fig. S8 Free-standing films before and after reacted in silver nitrate solution for 12 hrs.

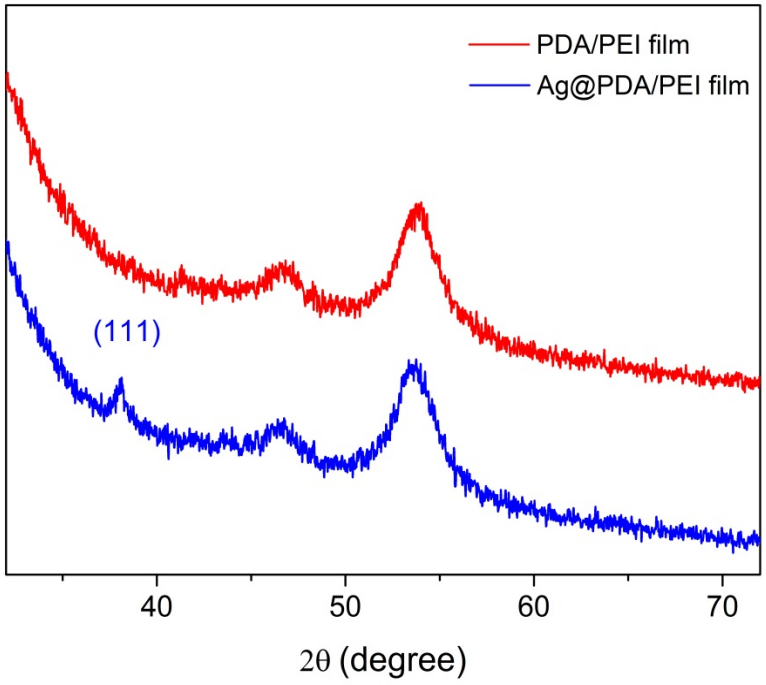

Fig. S9 XRD spectra of the free-standing film with and without Ag nanoparticle coating. The substrate is PET film.

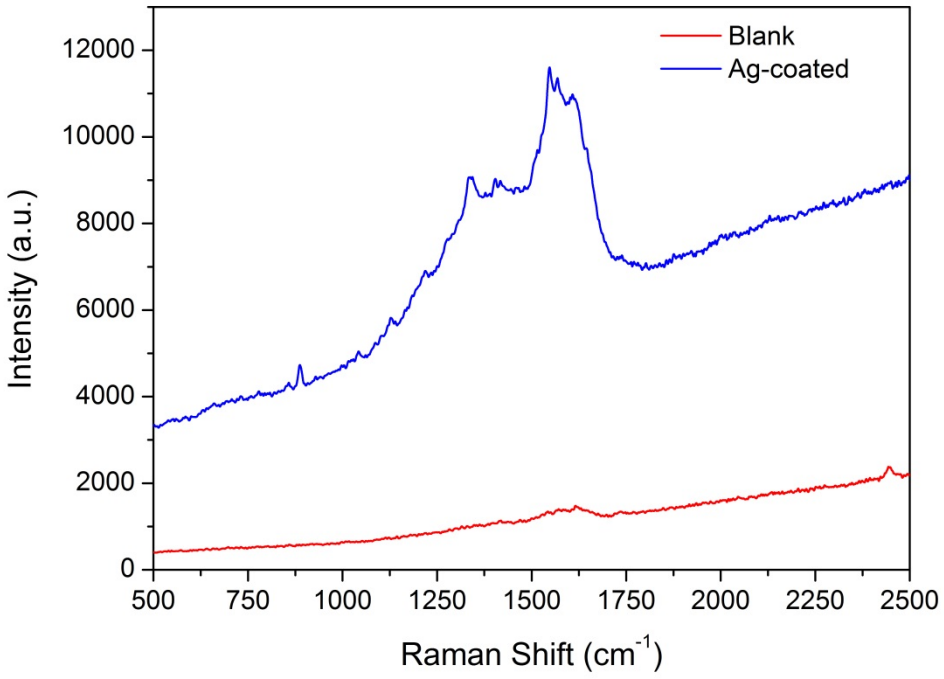

Fig. S10 Raman spectra of the free-standing film with and without Ag nanoparticles coating.