Supporting Information

Grafting polyelectrolytes to hydrocarbon surfaces by high-energy hydrogen induced cross-linking for making metallized polymer films

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Experimental details

Materials. All chemicals were purchased from Aldrich and used as received. PET films 100 μm thick were purchased from Transilwrap Inc (Canada), which were cleaned using ethanol before use. Poly (2-(methacryloyloxy)ethyl-trimethylammonium chloride) (PMETAC) was synthesized by solution polymerization of 2-(methacryloyloxy)ethyl-trimethylammonium chloride in water at 50 wt % concentration catalysed by 1 wt % potassium persulfate at 75 ^{o}C, which was collected by precipitation in acetone and dried in vacuum at 60 ^{o}C.

Fabrication of metallized PET. 5 mg/mL of PMETAC solution in ethanol was spin coated on the pre-cleaned PET film at 5000 rpm for 30 s. Subsequently, the samples were exposed to high-energy hydrogen neutrals with an extraction current of 10 mA at the pressure of 8×10^{-4} Torr to yield PMETAC grafted PET film (PMETAC-PET). Briefly, an electron-cyclotron-resonance microwave plasma (87.5 mT, 2.45 GHz) was set up to generate hydrogen plasma. The positive ions (H^+, H_2^+, and H_3^+) were then extracted through an applied potential of -100 V and accelerated before going into a drift zone full of molecular hydrogen, where binary collisions happened and generated various high-energy hydrogen projectiles. After repelling residual electrons and positive ions using two stages with potential of +100 V and -50 V, molecule hydrogen projectiles with proper kinetic energy that can break C-H bonds without affecting other bonds were obtained. The high-erergy hydrogen exposure time was fixed at 120 s, which is sufficient time to cross-link an organic film (*ACS Appl Mater Interfaces*, 2011, **3**, 1740). Next, the PMETAC grafted PET composite film was immersed in a 5 mM $(NH_4)_2PdCl_4$ aqueous solution for 15 min to immobilize $PdCl_4^{2-}$ by ion exchange. Finally, samples were immersed in a freshly prepared Cu ELD plating bath for 30 min at room temperature, resulting in the Cu coated PET. The plating bath contains a 1:1 mixture of freshly prepared solutions A and B. Solution A consists of 12 g/L NaOH, 13 g/L $CuSO_4\cdot5H_2O$, and 29 g/L potassium sodium tartrate. Solution B is 9.5 mL/L HCHO in water.

Measurements. Chemical composition information about the samples was obtained by X-ray photoelectron spectroscopy (XPS). The measurement was carried out using a Kratos Axis Ultra spectrometer using a monochromatic Al Kα radiation source. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. The morphology of Cu coated PET was investigated using a Hitachi S-4500 field emission scanning electro-microscope (FESEM) using a 5 kV accelerating voltage. Atomic force microscopy (AFM) was performed on Nanoscope V (Veeco, Inc.) in tapping mode to characterize the surface morphology of the modified PETs and thickness of PMETAC coatings and Cu films by scanning the edge of a scratch. Resistance measurements were carried out by a four-probe method using M 2400 Keithley Multimeter.

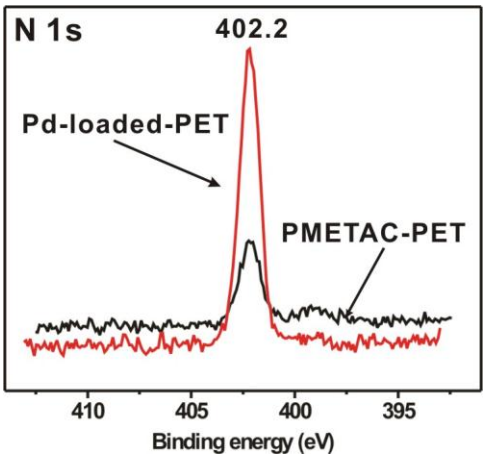

Fig.S1 XPS high resolution spectra of N 1s

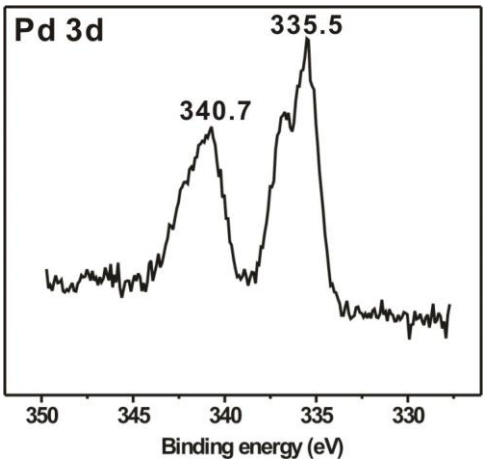

Fig.S2 XPS high resolution spectra of Pd 3d for Pd-loaded PET

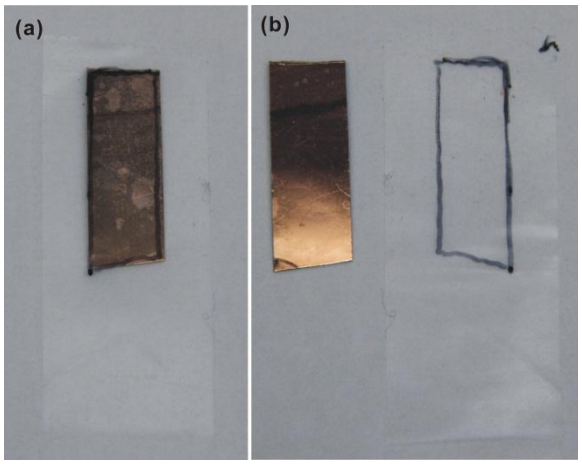

Fig.S3 Photos of Scotch tape test before (a) and after (b) peeling-off

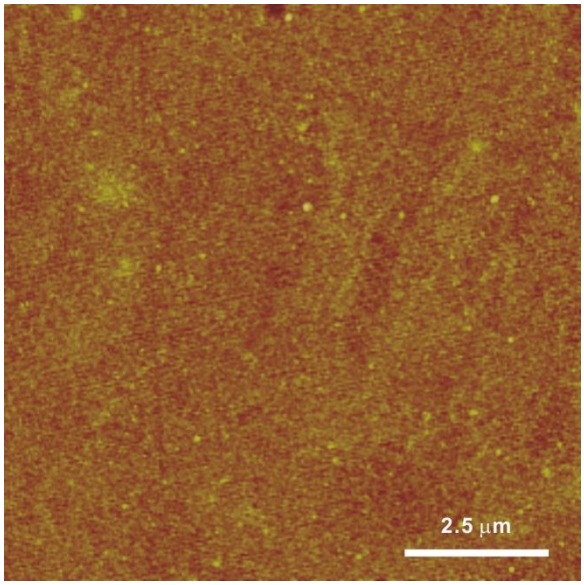

Fig.S4 AFM image of PMETAC-PET obtained by HHIC exposure on 42.7 nm-thick PMETAC coating. The Z-scale is 100 nm.

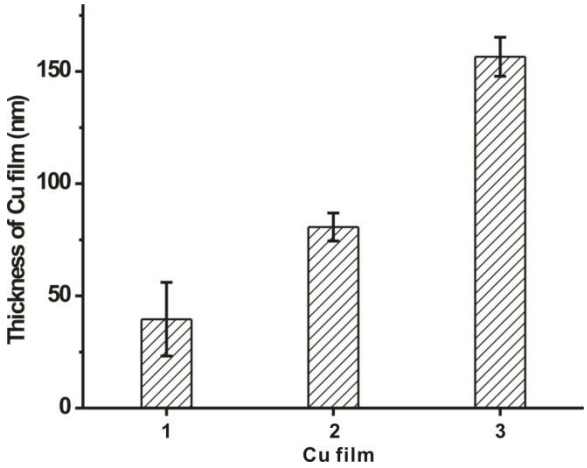

Fig.S5 Thickness of Cu films obtained at 10 min of ELD on PMETAC-PET surfaces based on PMETAC coating with initiate thickness of 9.9 nm, 26.8 nm, and 42.7 nm before HHIC exposure.

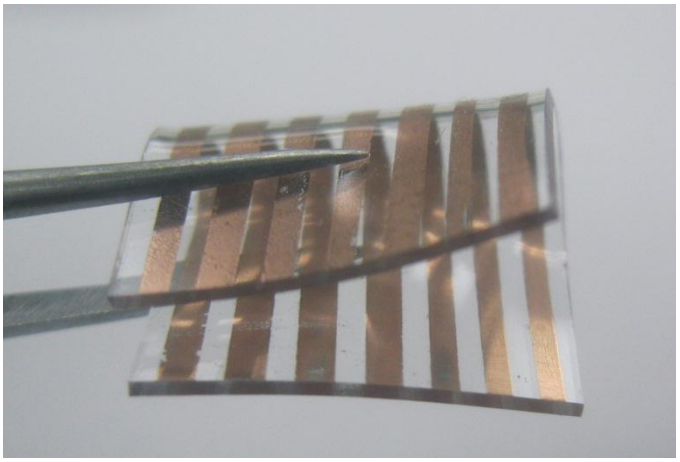

Fig.S6 Patterned Cu lines on PDMS film.