

Supplementary Information

In Situ Synthesis and Microstructural Tuning of Metal/Polymer Nanocomposite Thin Films on Glass Substrates by Using Highly Cross-Linked Polymer Matrices with Tailorable Ion Exchange Capabilities

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Experimental

Materials

Poly (methacrylic acid) (PMAA), styrene, 4-chloromethylstyrene (CMS), α -chloro-*p*-xylene (CX), 2,2'-azobisisobutyronitrile (AIBN), and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) were purchased from Aldrich. Copper chloride (CuCl₂), nickel chloride (NiCl₂), sodium carbonate (NaCO₃) toluene, dimethylformamide (DMF), tetrahydrofuran (THF), hexane, dimethyl sulfoxide (DMSO), and 3-aminopropyltriethoxysilane (APTMS) were purchased from Wako Chemical Co. (Japan) and used as received.

Synthesis of polymer precursors

PMAA (1g) were dissolved in DMF (30 mL), and CMS, CX, and DBU were added in the solution to bind carboxyl and vinyl groups into PMAA backbone. The final concentration of the DMF solution is shown in Table S1. The DMF solution was heated at 40 °C for 3 hours under nitrogen atmosphere. After reaction, the DMF solution was dropwisely added into distilled water under vigorous stirring, and the precipitates were filtered to obtain white powders. The powders were then dissolved in THF, and the solution was dropwisely added into hexane under vigorous stirring. The obtained powders were filtered and dried under ambient.

Table S1. Concentration of reaction solution for the synthesis of PMAA precursors with controlled amount of carboxylic acid and vinyl groups.

Sample	fraction of residual carboxylic acid groups	PMAA	CMS	CX	DBU
1	30%	1 g	0.355 g (2.33mmol)	0.814 g (5.79mmol)	1.237 g (8.12mmol)
2	40%			0.651 g (4.63mmol)	1.042 g (6.84mmol)
3	50%			0.488 g (3.47mmol)	0.868 g (5.70mmol)

Surface modification of glass substrates

Glass substrates (1×2 cm²) were first treated with 5M KOH aqueous solution at 50°C for 5 min. To modify substrates with amino functional groups, the substrates were immersed into toluene solution of ATPMS (1%) for 60 min, and rinsed with toluene and ethanol under ultrasonication for 10 min. The modified substrates were then immersed into DMF solution of 4-vinyl-benzoyl chloride (50 mM) with pyridine (50 mM) at 50 °C for 5 hours to obtain glass substrates modified with vinyl functional groups.

Synthesis of composite thin films

The precursor polymers with carboxyl and vinyl groups were dissolved into DMF (15% solution) containing AIBN (100 μM). The precursor thin films (200 nm thickness) were prepared by spin coating of the solution onto the modified substrates (1000 RPM). The precursor films were then irradiated with ultraviolet light using 250 W UV ramp (SP7, Ushio Co. Ltd.) for 15 min to initiate photoinduced cross-linking between the vinyl groups introduced in the precursors and between the vinyl groups in the precursors and the substrate surface. In order to fabricate composite film patterns, quartz photomask with Ti micropatterns was used for UV irradiation.

The cross-linked polymer thin films on glass substrates were treated with 200 mM aqueous solution of NaCO₃ for 20 min. Copper and Ni ions were introduced into the films by treatment of the films with 200 mM aqueous CuCl₂ and NiCl₂ solution for 20 min. The ion-doped films were then annealed at 250 °C (for Cu) and 330 °C (for Ni) for 30 min under hydrogen flow to reduce the doped ions to metals.

Characterization

The amount of doped metallic ions were quantified using inductively coupled plasma atomic emission spectroscopy (ICP-AES; SPS8700, Seiko Instruments). The doped copper and nickel ions were extracted from the films by immersing in 10% HNO₃ at room temperature for 1 h. Changes in the chemical structure of the films upon chemical treatment and annealing was characterized using a Fourier transform infrared (FTIR) spectrometer (FT/IR 615R, Japan Spectroscopic Co.) equipped with an attenuated total reflection (ATR) attachment. The microstructure of the composite films were observed with a transmission electron microscope (TEM; JEOL JEM-1400) operated at 120 kV. The TEM samples were prepared by directly depositing the films on carbon coated copper grids placed on glass substrate. UV-VIS absorption spectra of samples were measured using JASCO V-550 spectrophotometer. FMR signals were obtained using a X-band (9.5 GHz) electron-spin-resonance spectrometer (JEOL JES-FA100).

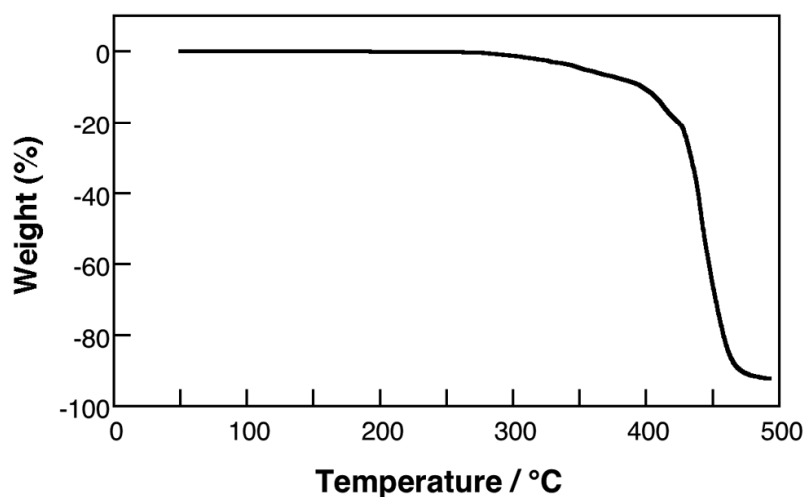


Figure S1 TG curve of the polymer matrix obtained after photoinduced cross-linking reaction.