Electrically bistable Ag nanocrystal-embedded metal-organic framework microneedles

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Supporting Information

Experimental

1) Chemicals and Materials

Silver nitrate ($AgNO_3$, product no. 209139, 100 g) and PVP (MW ≈ 29 kDa) were obtained from Aldrich (USA). 1,5-Pentanediol (product no. 76892, 250 mL, Aldrich) was used as the polyol. Melamine (product no. M2659, 5g) and cyanuric acid (product no. 185809, 25 g) were purchased form Aldrich (USA). All these chemicals were used without further purification. The ethanol (product no. 459844, 1L) and deionized (DI) water (product AH 365-4, 4L) used in the reaction were products of Aldrich (USA) and SK Chemicals (Republic of Korea), respectively.

2) Synthesis of MOF particles

In a typical synthesis, 3.0 mL of a 94 mM $AgNO_3$ solution (solvent: 1,5-pentanediol), 3.0 mL of a solution of PVP (solvent: 1,5-pentanediol) at a concentration of 147 mM of the PVP repeating unit, 1.5 mL of a 10.3 mM melamine solution (solvent: 1,5-pentanediol), and 4.5 mL of 1,5-pentanediol were mixed in a vial and heated at 160 °C with magnetic stirring. The

growth process of the resulting MOFs was examined at different stages of the reaction by conducting a series of reactions under identical conditions but stopping these reactions at different time points. The final product was collected by centrifugation and washed with DI water three times to remove most of the PVP. During the washing process, the suspension was centrifuged at 14,000 rpm for 10 min. Finally, the precipitate was re-dispersed in DI water for further use.

3) Characterization

The sizes and morphologies of the synthesized particles were obtained by using a field-emission scanning electron microscope (FE-SEM, Sirion, FEI) operating at an accelerating voltage of 10 kV, and a field-emission transmission electron microscope (FE-TEM, JEM-3011 HR, JEOL). The TEM (or SEM) sample was prepared by placing a drop of the final product (suspended in DI water) on a carbon-coated copper grid (or silicon wafer), and the sample was dried in a fume hood. The infrared (IR) spectrum was acquired by using a Fourier transform infrared (FT-IR) microscope (IFS66V/S & HYPERION 3000, BrukerOptiks). The elemental composition was obtained by using two kinds of element analyzers: EA1110-FISONS, ThermoQuest Italia S.P.A for carbon, nitrogen, and hydrogen; and FlashEA 1112, Thermo Finnigan for oxygen. X-ray diffraction (XRD) was recorded using a Philips 1820 diffractometer.

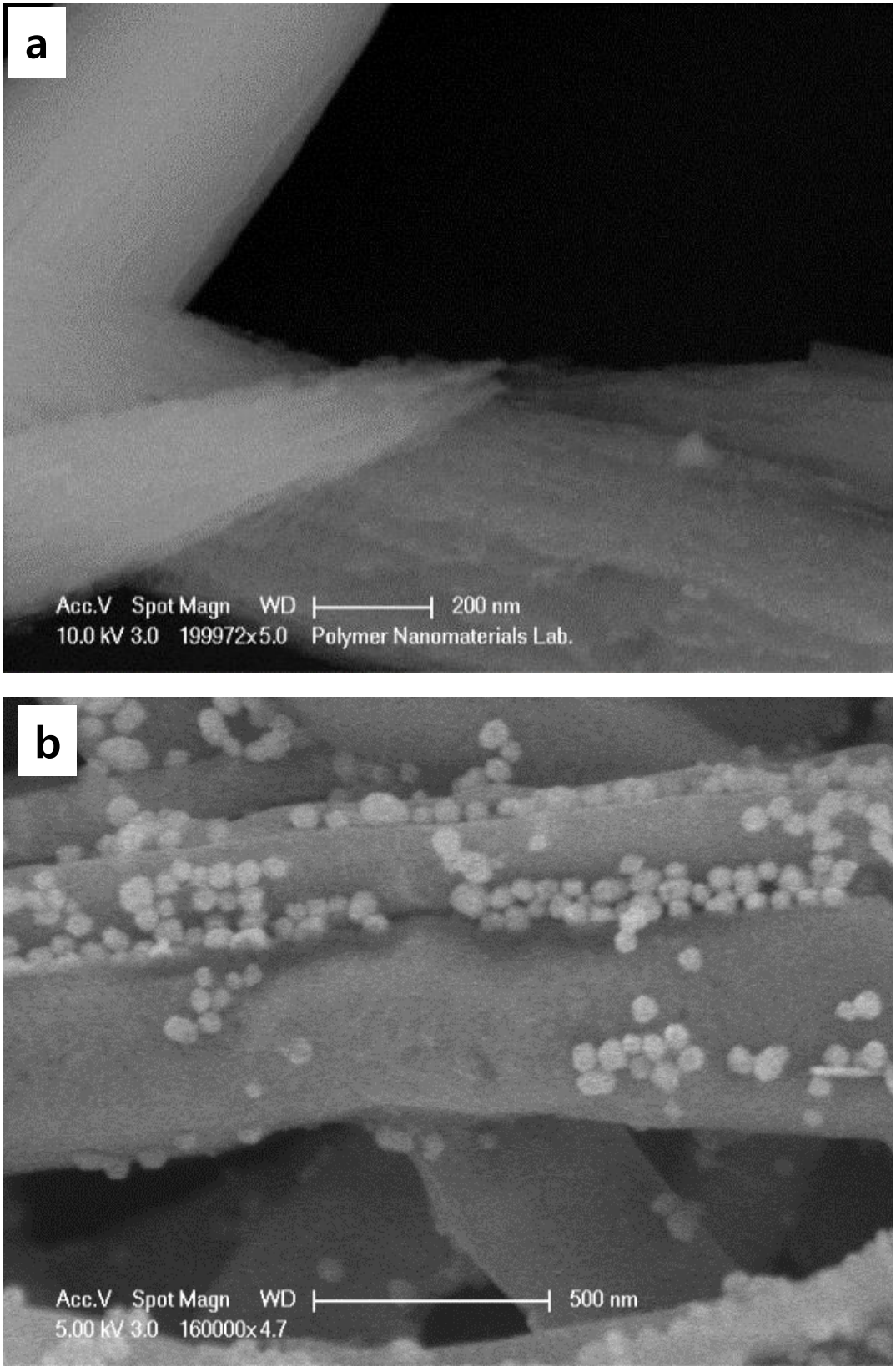

Fig. S1. Magnified SEM images of MOF microneedles embedded with Ag nanocrystals at reaction times of (a) t = 5 min and (b) t = 30 min.

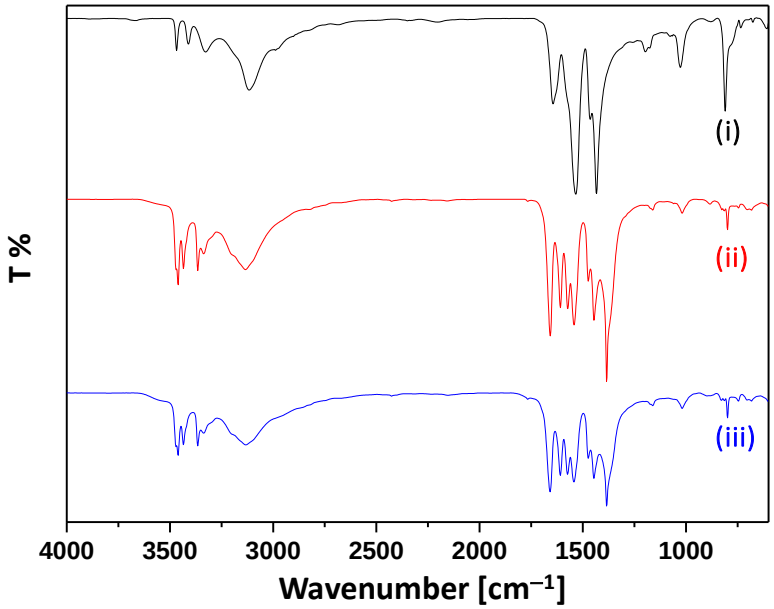

Fig. S2. FTIR spectra (for a wide range of wavenumbers) of (i) pure melamine and (ii, iii) the expected Ag nanocrystal-embedded MOF product at reaction times of (ii) 5 min and (iii) 10 min.

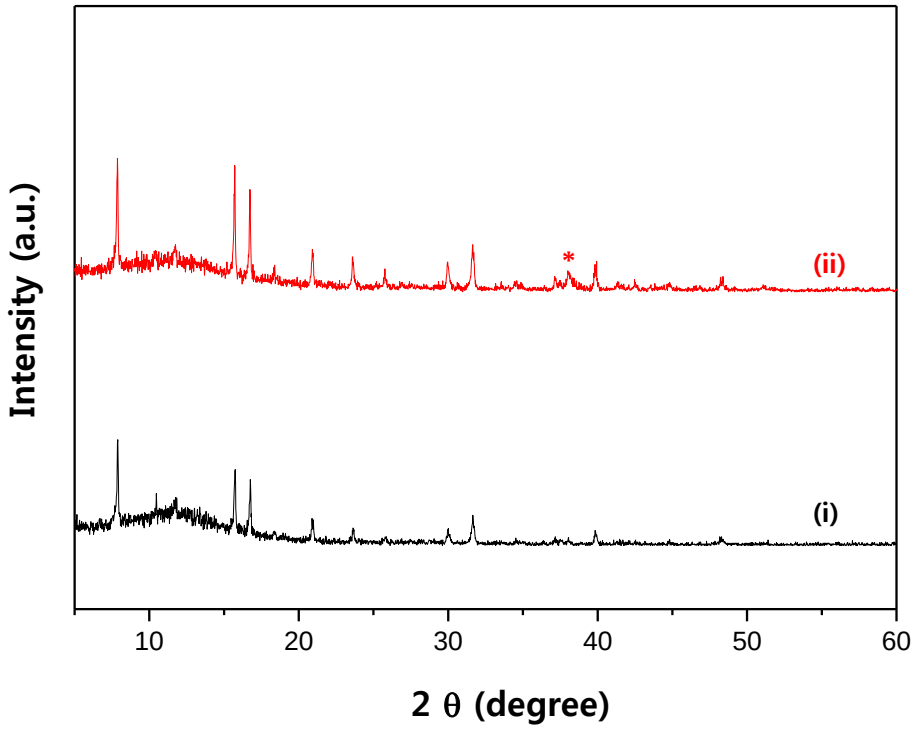

Fig. S3. PXRD patterns of MOF microneedles embedded with Ag nanocrystals at reaction times of (i) t = 5 min and (ii) t = 15 min.

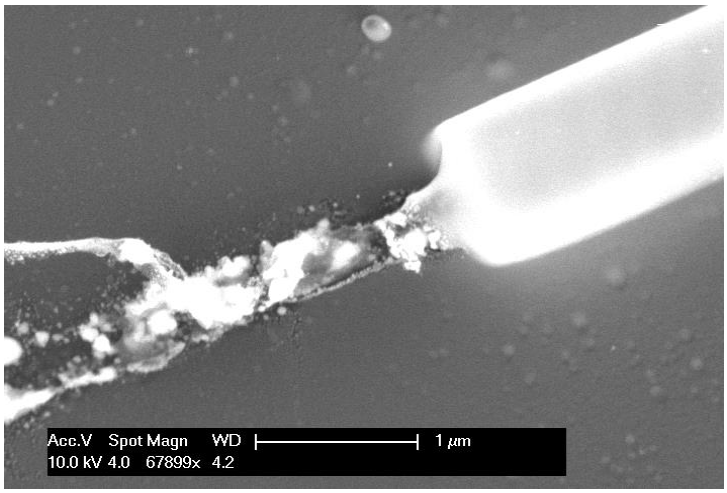

Fig. S4. SEM image of the microneedle when it was broken apart after applying a bias voltage of over ~ 50 V.