Supporting Information

In Situ Synthesis of Cu/Ni Alloy Nanoparticles Embedded in Thin Polymer Layers

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Experimental

Materials

Pyromellitic dianhydride oxydianiline (PMDA-ODA) type polyimide films (50 μm-thick Kapton 200H, Toray-Du Pont Co. Ltd) were used as matrix polymer for composite films in this study. Potassium hydroxide (KOH), nitric acid (HNO_3) copper chloride ($CuCl_2$), nickel chloride ($NiCl_2$), were purchased from Wako Chemical Co. (Japan) and used as received.

Synthesis of nanocomposite films

The films were cleaned ultrasonically prior to use in ethanol at room temperature for 5 min. The polyimide films were initially treated with 5 M KOH aqueous solution at 50 °C for 5 min, followed by through rinsing with copious amount of distilled water. The modified films were then immersed into an aqueous solution containing $CuCl_2$ and $NiCl_2$ at different concentration (total concentration: 100 mM) at room temperature for 30 min. After rinsing with distilled water, the films were dried under a nitrogen stream and stored under ambient conditions. The ion-doped films were subsequently annealed in a quartz tube under a hydrogen gas flow at a rate of 10 °C min^{-1} up to 400 °C for 30 min.

Characterization

The amount of doped metallic ions was 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% HNO_3 at room temperature for 1 h. The

microstructure of the composite films were observed with a transmission electron microscope (TEM; JEOL JEM-1400) operated at 120 kV. The samples for TEM observations were prepared by ultra sectioning into ca. 100 nm-thick slices using a conventional microtome technique (Ultracut R, Leica). FMR signals were obtained using a X-band (9.5 GHz) electron-spin-resonance spectrometer (JEOL JES-FA100).

Supporting Data

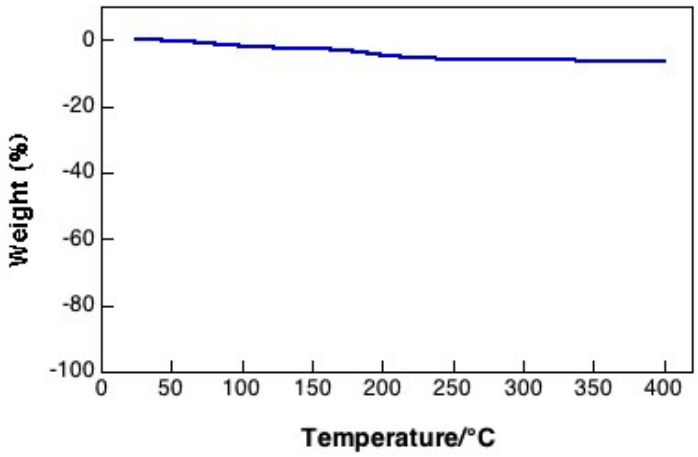

Figure S1. TG-curve of polyimide film obtained after hydrolysis using 5 M KOH aqueous solution at 50 °C for 5 min. Weight loss was slightly observed only due to re-imidization reaction that release water molecules around 150 -220 °C, the amount of which corresponds to 5% weight loss.

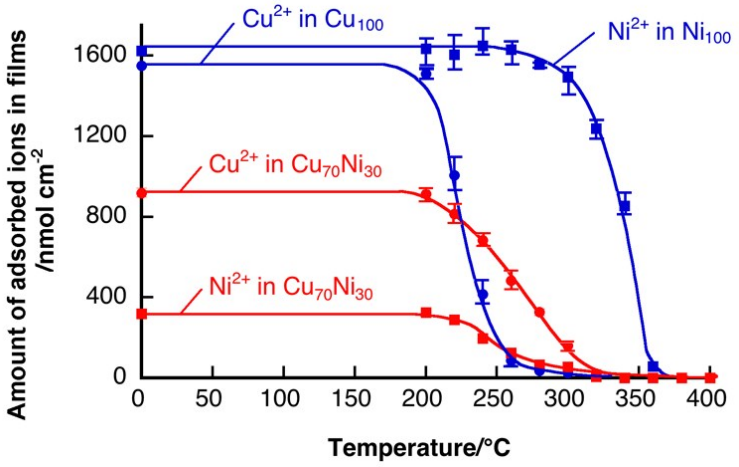

Figure S2. Plots of the amount of unreduced Cu and Ni ions in the films as a function of temperature for the samples with the composition of Cu_{100}, $Cu_{70}Ni_{30}$ and Ni_{100}.

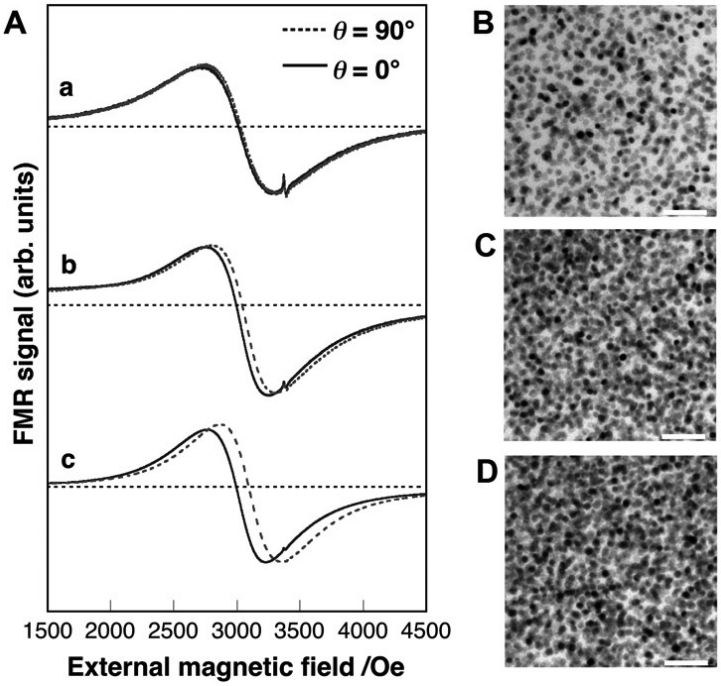

Figure S3. (A) FMR signals of alloy nanoparticles (Cu70Ni30) in the films obtained after annealing at 400 °C for (a) 5, (b) 150 and (c) 400 min. The values of $\theta = 0°$ and $\theta = 90°$ were assigned to the external magnetic field in the directions parallel and perpendicular to the film surface, respectively. Angular dependence of the FMR signals indicates strong magnetic

interaction between alloy nanoparticles. (B-D) Cross-sectional TEM images of alloy nanoparticles (images B-D correspond to those for the samples shown in signals a-c, respectively), demonstrating decreased interparticle distance among nanoparticles upon longer annealing time. Scale bar: 50 nm.