Interfacial interaction induced mesostructural changes in nanocylinders

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Experimental Details

Preparation and modification of porous alumina membrane (PAM). The PAM membranes were electrochemically fabricated using high purity (99.999%, Aldrich) Al foils in 0.3 M oxalic acid (97%, Cica-Reagent) by two-step anodization [1]. The first anodization was carried out at 40 V d.c. for 12 h at 15–17 °C. After complete removal of the first generated porous alumina film, the second anodization was lasted for 6 h and then the as-grown PAMs were electrochemically detached from back Al foils at 45 V d.c. at 10 °C in the mixture solution of ethanol (99.9%, Burdick & Jackson) and perchloric acid (60%, DC Chemical) (1:1 v/v). To adjust cylinder diameter, the PAMs were dipped in 10 wt.% H_3PO_4 (85%, Showa) solution for 10–30 min at ambient temperature, which resulted in the different cylinder diameters of 50 ± 3 and 83 ± 2 nm (Fig. S1). To prepare PAM with a smaller pore diameter, the second anodization was carried out in 0.3 M sulfuric acid (97%, Matsunoen Chemical) at 25 V d.c. for 6 h at 10 °C, which enables 34 ± 2 nm PAM after \sim 5 min pore widening process. The resulting as-made PAM membranes showed good water wettability with a contact angle of 6–26° (Fig. S2A).

For hydrophobic nanocylindrical environment, the as-made PAMs were chemically modified by treating with a chemical, 10 wt.% octadecyltrichlorosilane (90%, Aldrich) in toluene, through refluxing for 12 h, and then the resulting membranes were rinsed in successive volumes of toluene, ethanol, and deionized water. The resulting surface-modified PAMs have hydrophobic surface with a water contact angle of 104– 111° (Fig. S2B).

Fig. S1 Fabricated porous alumina membranes of different pore diameters of (A) 34 ± 2 , (B) 50 ± 3 , and (C) 83 \pm 2 nm with a pore density of \sim 1x10¹⁰/cm².

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Fig. S2 Water contact angle of (A) the as-made PAM and (B) the octadecyltrichlorosilane modified PAM.

Loading mesostructured silica into the PAM nanocylinders. The lyotropic mixture solution consisted of the silica source of tetraethylorthosilicate (TEOS, 98%, Sigma-Aldrich), poly(ethylene oxide)-b poly(propylene oxide)-b-poly(ethylene oxide) block copolymer (Pluronic F127, $EO_{106}PO_{70}EO_{106}$, 97%, Sigma), nitric acid (60%, Matsunoen chemicals), and ethanol was used in this study. The molar ratio of the precursor solution was 10 TEOS: 0.08 Pluronic F127: 0.1 HNO3: 50 ethanol. The PAM membranes with different pore diameters and different surface properties were dipped into the lyotropic precursor solution and kept for 48 h at room temperature to completely fill the nanocylinders with precursor solution. The lyotropic mixture infiltrated composite PAM membranes were taken out and allowed to gellation at 70 °C for 24 h, which were further calcined at 450 °C for 2 h. For the scanning and transmission electron microscope imaging, the mesoporous silica infiltrated PAM membranes were treated with 1 M HCl aqueous solution overnightly to remove the PAM host and then purified with deionized water repeatedly.

Fabrication of porous gold (Au) nanofibers. The composite PAM membranes including mesoporous silica were used as templates for electrochemical Au deposition. Thin Pt film was back-coated on the composite membrane using a sputter (Hitachi, E1030) in order to use as a working electrode. The deposition was carried out in the aqueous electrolyte including 0.02 M KAu(CN)₂ (98%, Aldrich) and 0.25 M Na₂CO₃ (99%, Cica-Reagent) under a constant current mode (2.0 mA/cm^2) in a two electrode system. The Au deposited composite membranes were treated with 10 wt. % HF (*Caution: toxic chemical*) to dissolve the composite templates consisted of silica and alumina. The resulting gold products were purified by applying repetitive suspension-centrifugation cycles to remove residual chemical species.

Characterizations. The resulting nanomaterials were imaged using a field-emission scanning electron microscope (FESEM, SU-70, Hitachi) equipped with an energy dispersive X-ray spectroscopy (EDX) system for elemental analysis. SEM imaging was typically operated at 1.5 keV in charge reduced mode for the porous silica insulating materials and at 5 keV for the gold nanomaterials. Transmission electron microscope (TEM) images were measured using a microscope (JEM-2100F, JEOL) operating at 200 keV. Surface property was measured using a contact angle analyzer (Phoenix 300, SEO, Korea).

Fig. S3 EDX spectra of the electrochemically-grown gold replicas using the mesoporous silica infiltrated composite PAM templates which are originating from the (A) as-made and (B) hydrophobic PAMs. The gold samples were dispersed on silicon wafers before analysis.

References

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