

Electronic Supplementary Information

Nanospring Electrochemical Lithography (NEL): Noble Metal Nanohelices

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Materials and experimental methods

Materials

Commercial anodic aluminum oxide templates (AAO; diameter \approx 13 mm, pore size \approx 250 nm, thickness \approx 60 μ m) were purchased from Whatman® International. An Au plating solution (Orotemp 24 RTU) was purchased from Technic Inc. Palladium chloride (PdCl₂), copper chloride (CuCl₂), potassium iodide (KI), and thiophenol (99 %) were obtained from Sigma-Aldrich. Hydrochloric acid (HCl, 35 %) was obtained from Samchun. Hydrogen hexachloroplatinate (IV) hydrate (H₂PtCl₆·*n*H₂O, 99 %) was obtained from

Kojima. Iodine (I_2) was purchased from Duksan. Nitric acid (HNO_3 , 60 %) was supplied by Daejung. Absolute ethanol was purchased from Fisher. All aqueous solutions were prepared with deionized water (Millipore, $> 18.2 M\Omega$) with the exception of thiophenol, which was prepared by dissolving absolute ethanol. A carbon bar was employed as a working electrode.

Instruments

Electrochemical deposition was performed using Autolab® equipment with a three-electrochemical system. The counter electrode and reference electrode were Pt mesh and an Ag/AgCl electrode, respectively. Field-emission scanning electron microscopy (FESEM, model JEOL 7600F) was used to observe the structures of all samples. Transmission electron microscopy (TEM, model JEM 2100F) and energy dispersive X-ray spectroscopy (EDS) were conducted to examine the elemental composition of the samples. Confocal Raman spectroscopy (WiTec alpha 300R) was used to obtain optical images and measure the SERS spectra by using a He-Ne laser at 632.8 nm.

Preparation of conducting layer and pre-deposition

A previous paper discussed the preparation of the conducting layer on a commercial AAO template and Au pre-deposition.¹ Briefly, Au nanoparticles were filtered on the bottom side of the AAO template to form a conducting layer. A home-made Teflon cell was assembled with the AAO template for electrochemical experiments. Then, an Au plating solution was used to prepare Au segments by electrodeposition at a potential of

-0.95 V (vs Ag/AgCl) for 2500 s within the AAO template in order to ensure a conductive interface between the Au particle film and the subsequently deposited metal.

Synthetic process of NEL

In a typical synthesis, all electrochemical methods were carried out at room temperature (24 °C). After casting a solution that contained precursors of 30 mM PdCl₂, 20 mM CuCl₂, and 0.1 M HCl into the Teflon cell and applying an electric potential of -0.1 V (vs Ag/AgCl) for 500 s, Pd/Cu nanorods were prepared on the bottom Au segment within the AAO template.² For this process, N₂ gas was bubbled into the precursor solutions during electrochemical deposition in order to diffuse metal ions homogenously in the solution. To etch the Cu section of the Pd/Cu nanorods, a Cu etching solution (containing 300 mM CuCl₂ and 0.1 M HCl) was added to the Teflon cell. The etchant was kept at 50 °C for approximately 30 min, leading to vertically-aligned Pd nanosprings on the Au segment. Next, electrochemical cyclic voltammetry was combined with the Au plating solution and used to reduce the Au ions on the Pd nanosprings within the AAO membrane. The CV potential range was taken from -0.2 V to -0.65 V at 40 mV/s. 25 deposition cycles were used to grow Au. In order to dissolve the Pd section of the Au/Pd composites, 30 % nitric acid was used. After selective Pd etching, an Au trimming process was performed by using a 100-fold diluted KI/I₂ solution, which consisted of 4 g of KI and 1 g of I₂ in 40 mL of deionized water, for 20 min.³ Finally, Au nanohelices were obtained on the Au substrate within the AAO template. The AAO template was completely removed by immersion in a 3 M NaOH solution for 20 min. The obtained Au

nanohelices can be dispersed in deionized water by sonication. To control the gap distance of Au nanohelices, the Pd nanospring templates are tailored by controlling the Pd²⁺ concentrations: 25 mM, 30 mM, and 35 mM with a Cu²⁺ concentration of 20 mM.

For the Pt nanohelices, a 10 mM aqueous H₂PtCl₆ solution was prepared (instead of the Au plating solution) to synthesize Pt/Pd composites. During the Pt trimming process, a 2-fold diluted KI/I₂ solution was used as the trimming solution. The etchant was kept at 70 °C for approximately 60 min.

SERS Measurements

Confocal Raman spectroscopy was used to measure the SERS performance. A He-Ne laser source (632.8 nm) was used for excitation during an exposure time of 30 s and measured five times. In order to measure the SERS performance, all of the samples were dropped on Si wafers and immersed in a solution of 0.1 M thiophenol in ethanol for 8 h.

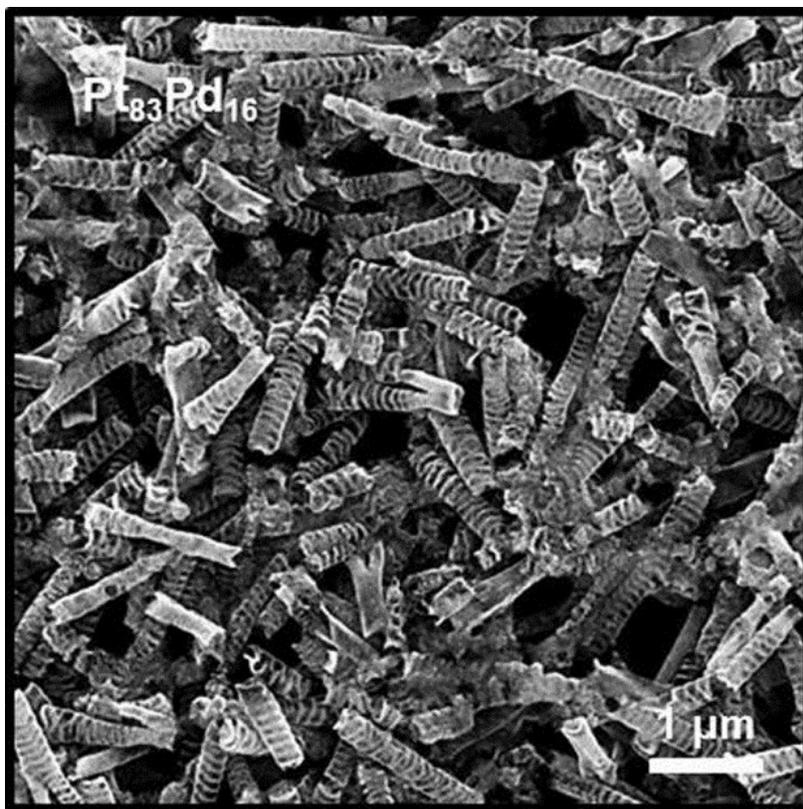


Fig. S1 SEM images of Pt nanohelices. EDS composition analysis showed 83% of Pt and 16 % of Pd.

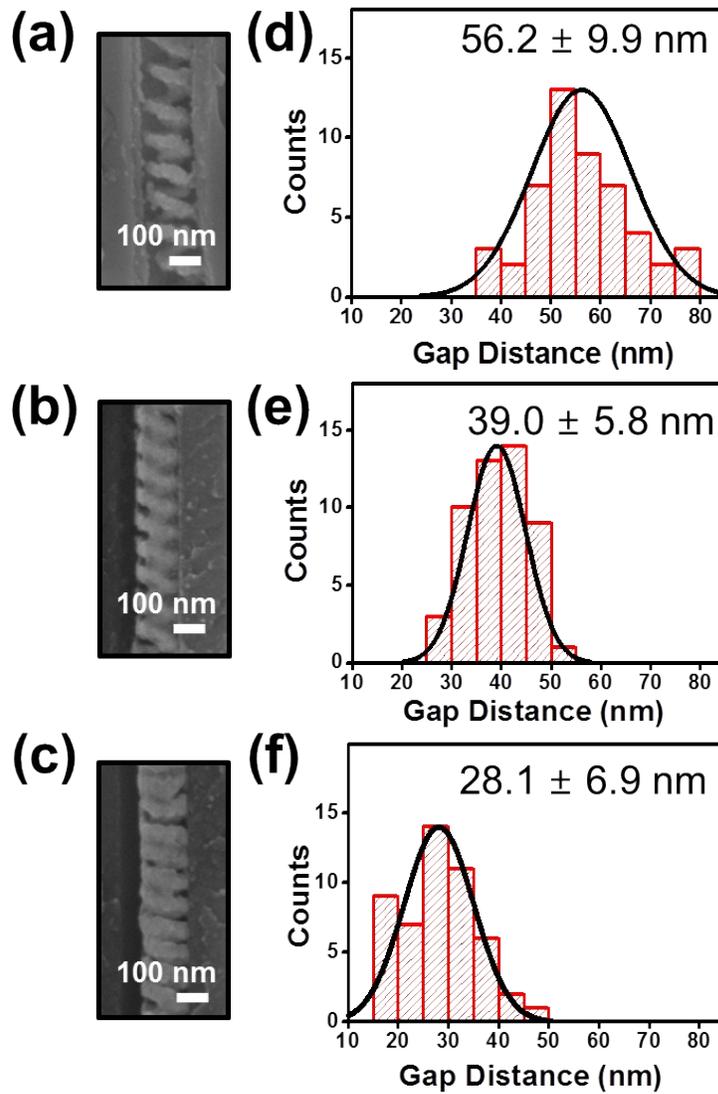


Fig. S2 SEM images of gap-controlled Au nanohelices. (a) wide-gap, (b) middle-gap (c) narrow-gap Au nanohelices. (a), (b), and (c) share the same scale bar in (c). Panel (d), (e) and (f) are the gap distributions of Au nanohelices in (a), (b), and (c), respectively.

References

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