Supporting Information

Fabrication of Shape-Controlled Reduced Graphene Oxide Nanorings by Au@Pt Nanoring Lithography

Ho Young Jang,[a] Hee-Jeong Jang, [b] Dae Keun Park[b] and Wan Soo Yun[b] and Sungho Park [a,b]

[a] *Department of Energy Science, Sungkyunkwan University, Suwon, 440-746, South Korea.*

[b] *Department of Chemistry, Sungkyunkwan University, Suwon, 440-746, South Korea.*

AUTHOR INFORMATION

Corresponding Author

*E-mail: S. Park, spark72@skku.edu; W. Yun, ysyun87@skku.edu.

Experimental Section

Preparation of reduced graphene oxide

Graphite oxide was synthesized from graphite (SP-1 BayCarbon) by Hummer's method. Specifically, 0.5 g of graphite, 0.5 g of $NaNO_3$ and 23 ml of H_2SO_4 were stirred together in an ice bath. After that, 40 ml of water was added, and the solution was stirred for 30 min while the temperature was close to 90°C. Finally, 100 ml of water was added, followed by the slow addition of 3 ml of H_2O_2 (30%), and the color of the solution changed from brown to yellow. The solution was centrifuged with 100 ml of water at 1000 rpm for 2 min. This is repeated until all visible particles are removed (about 3-5 times) from the precipitates. Then, 1mg/ml of graphene oxide powder was redispersed in DI water by ultrasonication for 30 min. Next, after three centrifugation steps at 4000 rpm for 40 min, the supernatant was separated with residual insoluble small GO particles. The GO solution (40 ml) and 160 ml of H_2O were mixed and heated to the boiling point. Then, 10 µl of $N_2H_4 \cdot H_2O$ (Hydrazine monohydrate 35 %, FW=50.06, d=1.032, Aldrich) and 50 µl of HNH_3OH (pH=10.03) were added to the boiling GO solution followed by stirring for 12 hours. During the reduction process, the yellow-brown solution gradually became black.

Synthesis of rim-preferentially grown Au@Pt nanoplates

Au nanoprisms and nanohexagonal were prepared from 5-nm sphere seeds by the three-step seed-mediated method as reported previously.[1-4] Au nanodisks[4] were synthesized by further procedures with Au triangular nanoplates. All of the gold nanoplate solutions were optically normalized to the same concentration. In the presence of iodide ions (50 µM), 20 mL of 0.05 M CTAB, 5 mL of re-dispersed gold nanoplates, 340 µL of 0.1 M NaOH, and 54 µL of 2 mM aqueous $AgNO_3$ solution were added to a vial. Next, 426 µL of 10 mM ascorbic acid was added to the mixture. After gentle shaking, the mixed solution was heated to 70 ℃ and kept in an oven in order to deposit Ag layers onto the Au nanoplates. After one hour, 540 µL of a 2 mM aqueous H_2PtCl_6 solution was added to the heated mixture for the galvanic replacement reaction, and the mixture was kept at 70 ℃ for approximately 3 hours. Then, the as-synthesized product was concentrated by centrifugation at 4000 rpm for 40 minutes. The supernatant from the centrifugation was removed in order to reduce residual ions and CTAB, and distilled water was added.

Fabrication of RGO nanoring array film

Next, 25 ml of an aqueous reduced graphene oxide was filled to a Teflon cell (inner dimension, 8.0 X 4.0 X 1.7 cm), and 10 ml of hexane was added to the top of the colloid solution to form the water/hexane interface. Subsequently, 100 µl of 0.1 mM 3-mercaptopropyltrimethoxysilane (MPTMS) was added to the hexane layer in the case of the Au@Pt nanodisk film. Ethanol (6 mL) was then added drop-wise to the surface of the water/hexane layers (0.5 ml/min, using a mechanical syringe pump, KDS101 from KD Scientific Inc.), which leads to RGO sheets trapped at the interface. The RGO films were then transferred onto clean SiO_2 wafers. Then, Au@Pt nanoplates were transferred to RGO coated substrates using the same method. In order to etch the uncovered RGO area and make Au@Pt nanoplates rearrange to nanorings, O_2 plasma treatment (Diener Electronic Zepto) was conducted for 20 s with 40 W power in 0.4 mbar condition. After treatment, Au/Pt alloy nanoring films on the RGO-coated substrate were dipped into aqua regia (caution, it is very toxic.) for 3 hours and were then washed several times with DI water.

Characterization of graphene nanoring films

FE-SEM (JEOL 7600F) was used to observe the shape and structure of Au@Pt nanoplates and graphene nanorings. Raman spectra and images were recorded on a WITEC alpha300 with a 532-nm excitation wavelength. The extinction spectra were collected on a Scinco S-3100 UV-vis spectrophotometer. AFM (Park systems NX 10) was used to analyze z-axis profiles of the reduced graphene oxide sheets and graphene nanoring structures. The spectra of X-ray photoelectron spectroscopy (XPS) were obtained using an ESCA2000-VG (Microtech) with a monochromatic Al Kα (1486.6 eV) radiation source at a chamber pressure of 1.0 X 10^{-10}

mbar. The electrical measurements were performed using an HG Agilent 4156A under ambient conditions.

Figures

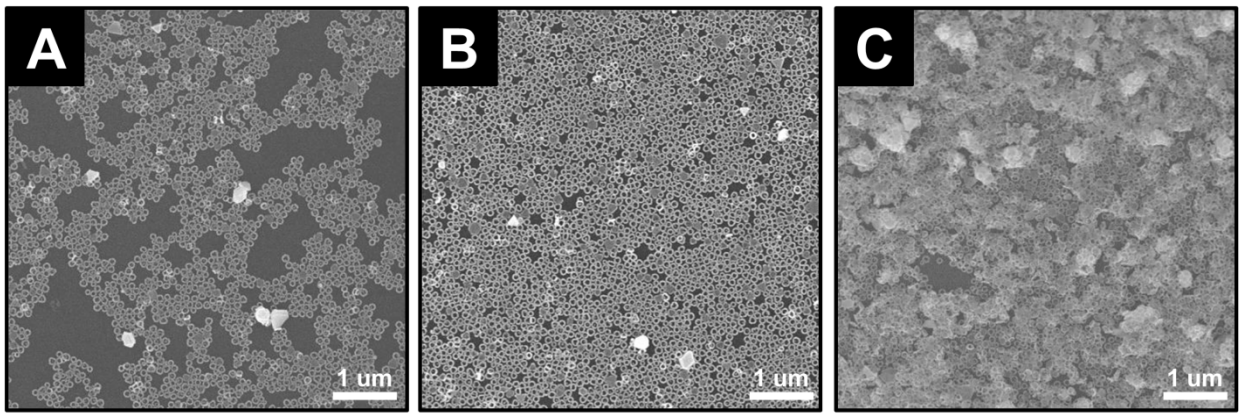

Figure S1 SEM images of Au/Pt alloy nanoring arrays on SiO_2 substrates with different MPTMS concentration. (A) 0.01 mM, (B) 0.1 mM and (C) 1 mM concentration.

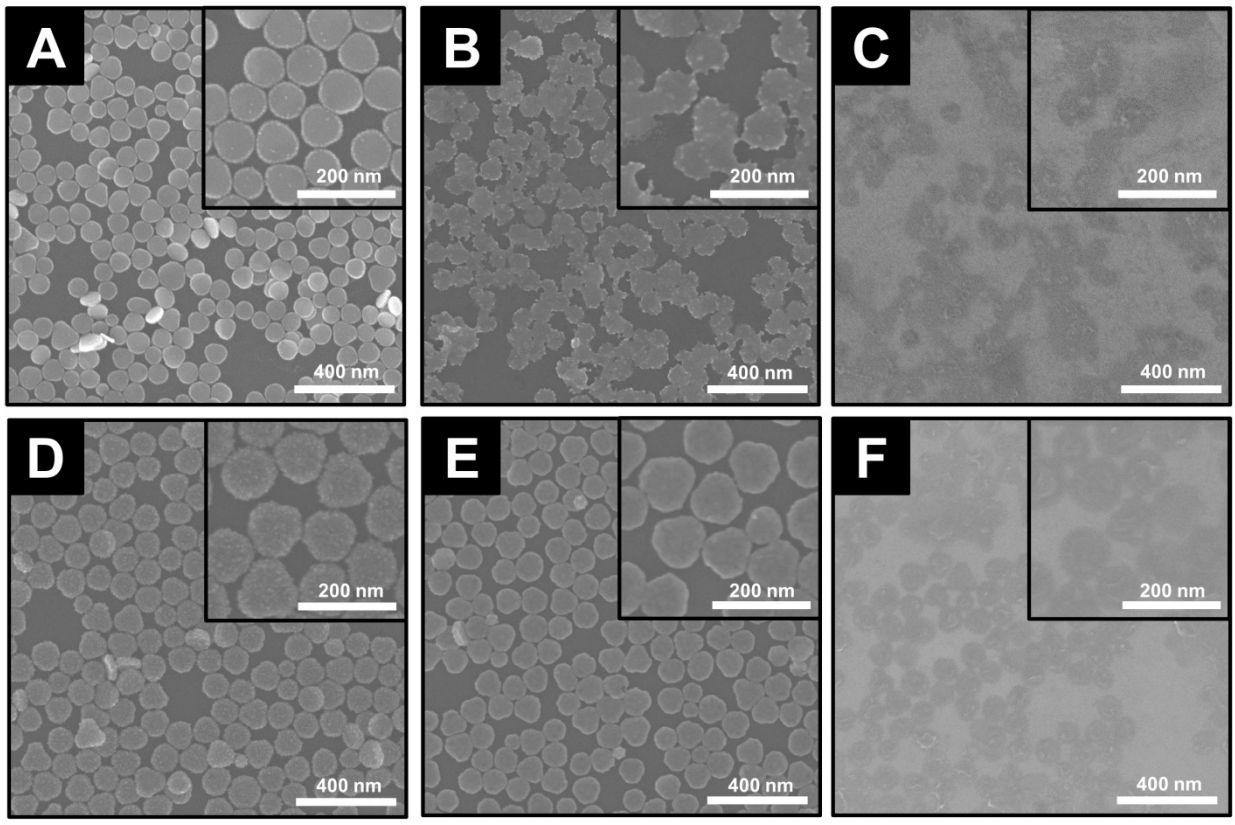

Figure S2 SEM images of fabrication process for RGO nanoring structures with various Pt thickness of Au@Pt nanodisks in cases of thin Pt frame (A-C) and Thick Pt frame (D-F).

References

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