Template-Free Synthesis of Large Anisotropic Gold Nanostructures on Reduced Graphene Oxide

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Supporting Information

Experimental section

Materials: Natural graphite flakes (300-mesh in size) were obtained from Qingdao Haida Graphite Co. Ltd (Shandong, China). 98% H_2SO_4, 30% H_2O_2, potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), 36%-37% HCl, 98% hydrazine monohydrate (N_2H_4 64-65%) and gold chloride ($AuCl_3$, 99.9%) were purchased from Sigma-Aldrich (Milwaukee, WI). Absolute Ethanol was purchased from Fisher. All the reagents were used as received. Fused quartz slides were purchased from Jiangsu Jinghe Optical Instrument Factory (Jiangsu, China). Ultrapure deionized water (18.2 MΩ • cm) (D.I. water) from a Milli-Q System (Millipore, Billerica, MA) was used in all experiments.

Synthesis of Graphene Oxide (GO): The GO sheets were synthesized by a modified Hummers' method.[1] The as-prepared GO sheets were sorted by size via a two-step centrifugation. Firstly, the GO solution was centrifuged at 10,000 g to remove the impurities and small sheets. Then the precipitant was re-dispersed in D.I. water and centrifuged at 1,000 rpm. The supernatant was carefully extracted. The GO sheets produced were 15-20 μm in size.

Deposition and Reduction of GO Thin Films: GO solution was sprayed onto fused quartz slides with an air brush. The quartz substrates were pre-treated with Piranha solution at 120 ^{o}C for 45 min, followed by rising with D.I. water and blowing to dry with N_2. The cleaned substrates were heated to 130 ^{o}C on a hot plate, and 6 ml of 0.2 mg/mL GO solution was sprayed on them. Heating the substrate above the boiling point of the carrier liquid prevents liquid buildup on the substrate during solution spraying, which improves the uniformity of the GO films.

The as-prepared GO thin films were reduced by three methods. (1) Low-reduction: The GO thin films were placed in a glass container with 100 μl of hydrazine (not in direct contact with the GO films). The container was sealed and heated to 100 ^{o}C overnight. (2) Medium-reduction: The GO thin films on quartz plates were transferred into a furnace and annealed at 1000 ^{o}C for 2 h, under the protection of forming gas (20% H_2 in Ar at 500 sccm). (3) High-reduction: These samples were loaded into a quartz tube, and forming gas (20% H_2 in Ar at 500 sccm) was introduced to the tube to purge undesired moisture and oxygen. The quartz tube was then heated to 1000 ^{o}C, followed by introducing absolute ethanol vapor into the tube using the forming gas as carrier, with bubbling of the forming gas through ethanol maintained at 0 ^{o}C (total flow rate decreased to 100 sccm while bubbling).

Synthesis of Gold Nanostructures: After reduction, the RGO thin films on quartz substrates were immersed into 10 mM $AuCl_3$ solution (25 °C) for 90 min, rinsed, and blown dry with N_2. For semicircular AuNPLs, the substrates were immersed in 10 mM $AuCl_3$ solution at 80 °C for 40min. Then the samples were put in an oven at 80 °C for 1 h before further characterization.

Characterization: Atomic force microscopy (AFM) was conducted using a MFP 3D microscope (Asylum Research, Santa Barbara, CA) in ac mode. Scanning electron microscopy (SEM) was performed using JEOL JSM-6700F and LEO 1550 Gemini field-emission scanning electron microanalyzer at an accelerating voltage of 5 kV. Analysis of particle composition was carried out using X-ray energy dispersive spectroscopy (EDS) with an accelerating voltage of 15kV. Transmission electron microscopy (TEM) was performed on a JEOL JEM-2010 high-resolution transmission electron microscope with an accelerating voltage of 200 kV. The AuNWs were scraped from the fused quartz substrates and dispersed in ethanol, and then dropped onto a 1000-mesh Ni TEM grid. X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Advance, equipped with a Cu Kα photon source (40 kV, 20 mA, λ=0.15406 nm) scanned at the rate of 1.0^{o} min^{-1} over the range of $35\text{-}100^{o}$ (2θ). Raman spectra were recorded with a WITec CRM200 confocal Raman microscopy system with 488 nm excitation and an air cooled charge coupled device (CCD) as the detector (WITec Instruments Corp, Germany).

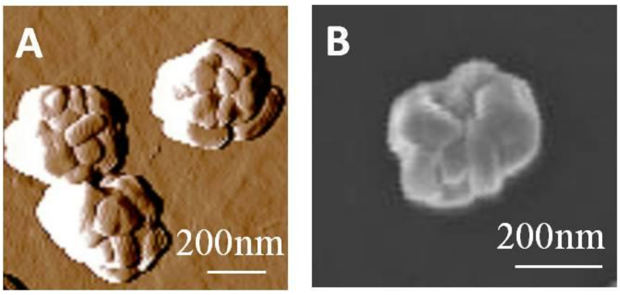


Fig. S1. AFM (A) and SEM (B) images of AuNPs formed on slightly-reduced GO thin films. The appearance of the particles as aggregates of nanorods is manifest.

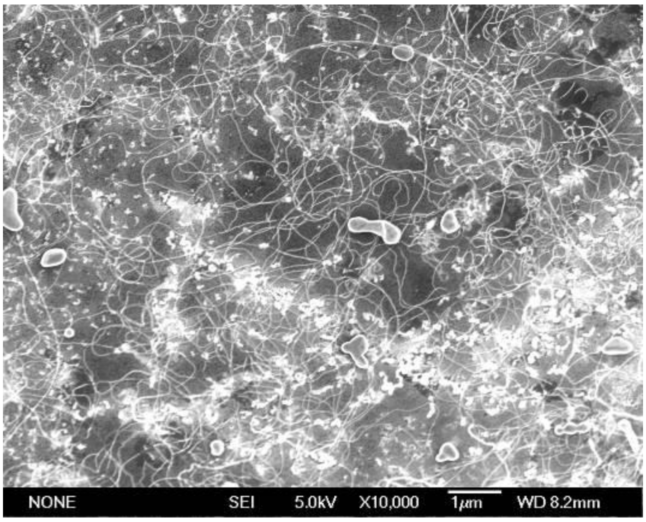


Fig. S2. SEM images of AuNWs in low magnification.

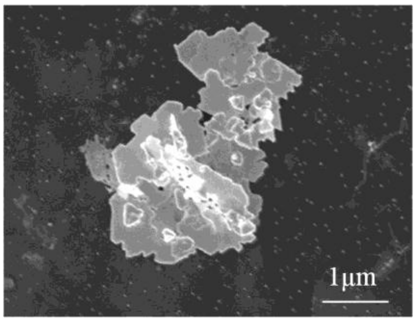


Fig. S3. Irregular-shaped AuNPLs together with low areal density small AuNPs formed on highly-reduced GO film (10 mM $AuCl_3$, 90 min, 25 ^oC).

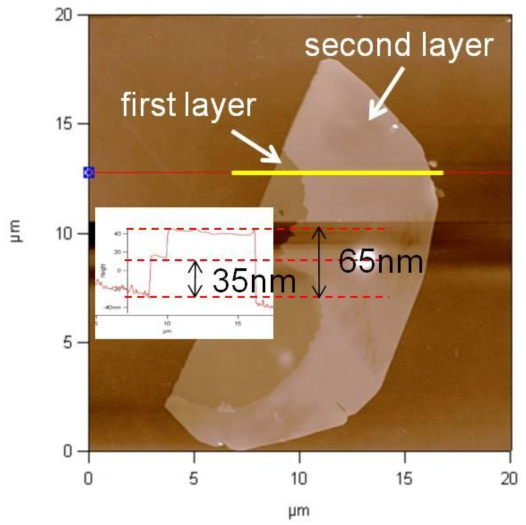


Fig. S4. AFM image of an Au nanoplate in an intermediate stage of formation with a complete first stacking layer and a partially formed second stacking layer. The inset shows the height along the yellow highlighted section. Each layer is about 30 nm thick.

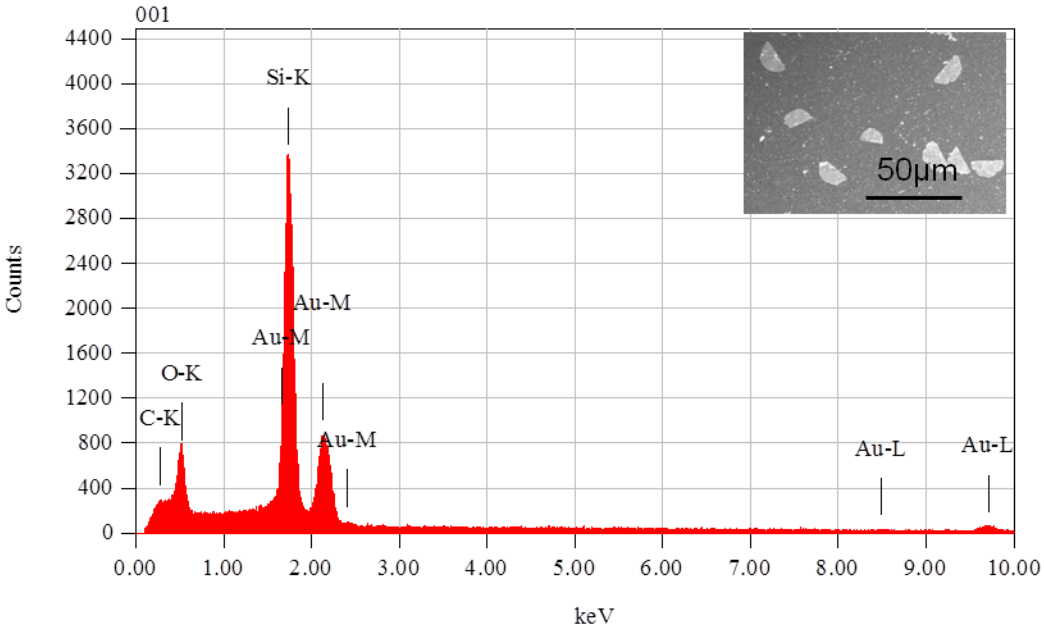


Fig. S5. EDS spectrum of semicircular AuNPLs on highly-reduced GO surface. The inset is a low-magnification SEM image of semicircular AuNPLs.

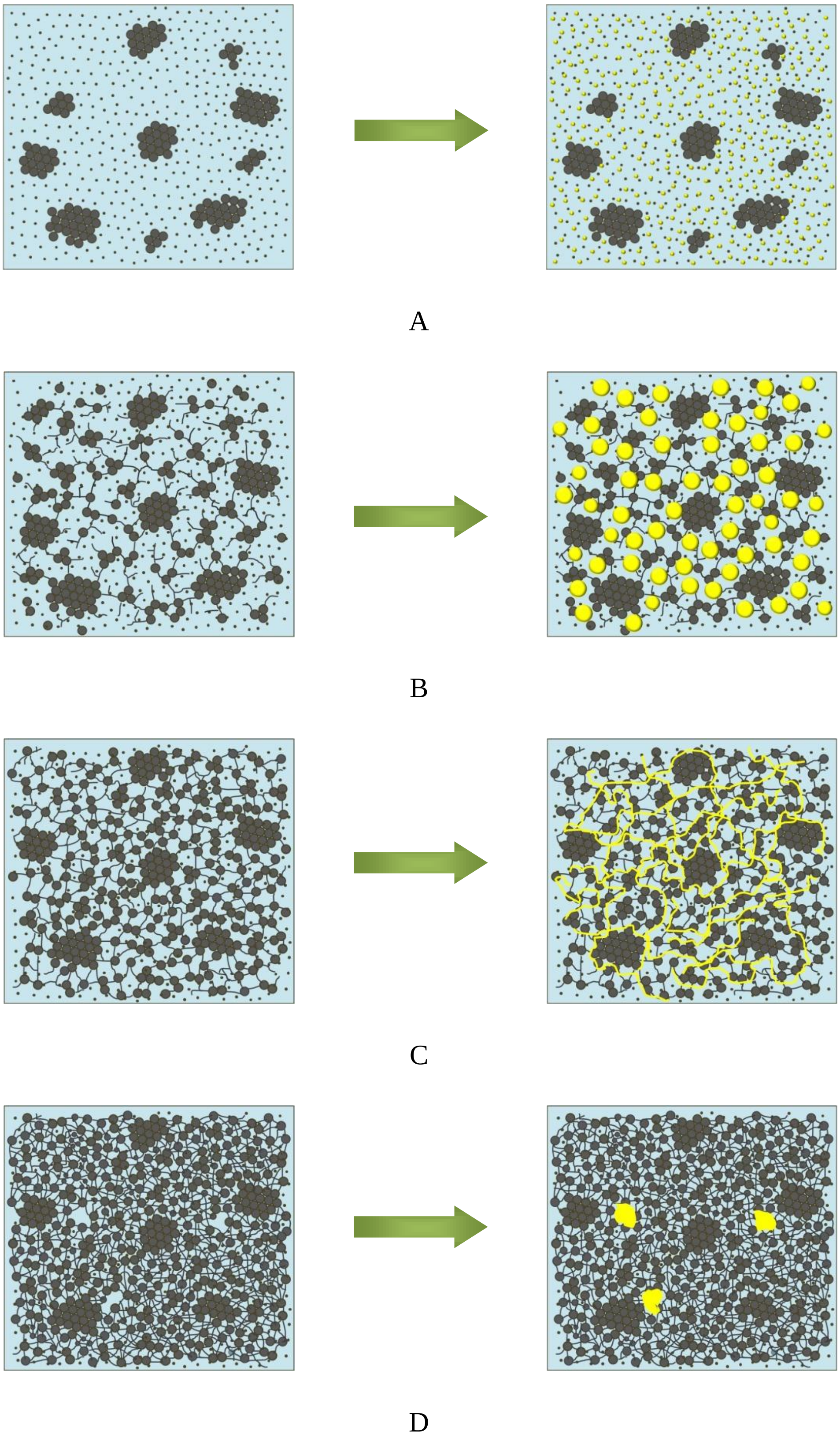
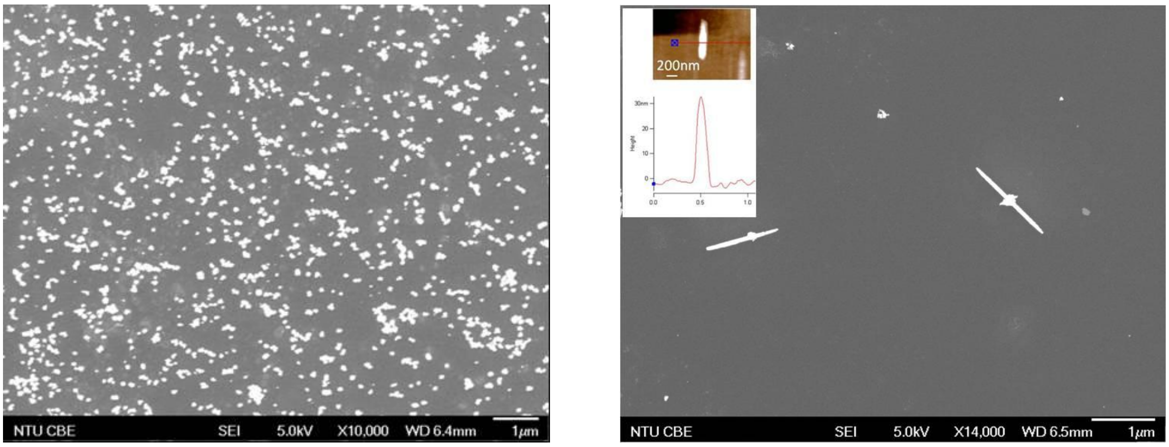


Fig. S6. Schematic drawing of -sp^2 domains (dark areas) and -sp^3 domains (blue areas) on GO and RGO surface (left) and the gold nanostructures formed after AuCl$_3$ treatment at room temperature (right). (A) GO: -sp^2 domains are isolated by the large quantity of -sp^3 carbon atoms. A lot of small AuNPs are evenly formed on the GO surface, as demonstrated in Fig. 1a; (B) Slightly-reduced GO: After HZ reduction, the original and newly reduced -sp^2 domains connect to each other. The remained fewer -sp^3 sites (active sites for Au^{3+} reduction) and larger -sp^2 domains (the areas which donate electrons) result in fewer and larger AuNPs, as shown in Fig. 1b; (C) Moderately-reduced GO: After H_2/Ar reduction, most -sp^3 carbons are reduced to -sp^2 sites. The network of -sp^2 domain is well formed, leaving some small areas and pathways of -sp^3 carbons. Au nucleus firstly form on the -sp^3 sites, and then prefer to grow along the edge of the nearby -sp^2 domains and pathways, which provide electrons for the crystal growth. Thus AuNWs are formed, as demonstrated in Fig. 1c; (D) Highly-reduced GO: After EtH_2 reduction, very few -sp^3 sites remain and they are far from each other, surrounded by the network of -sp^2 domains. At room temperature, only a few AuNPLs are formed, shown in Figure 1d. And at higher temperature (80^{o}C), well-defined semicircular-shaped AuNPLs (as shown in Fig. 1e) are formed due to the change of diffusion and dynamics.



A B

Fig. S7. SEM images of nanostructures formed on lower temperatures with H_2/Ar reduction method: (A) AuNPs formed on 600°C H_2/Ar reduced GO film and (B) Au nanorods formed on 800°C H_2/Ar reduced GO film. Inset of (B) is the AFM image of an Au nanorod.

References

1. X. C. Dong, C. Y. Su, W. J. Zhang, J. W. Zhao, Q. D. Ling, W. Huang, P. Chen and L. J. Li, *Phys. Chem. Chem. Phys.*, 2010, **12**, 2164.