Ultrasonication-assisted Synthesis of High Aspect Ratio Gold Nanowires on Graphene

Template and Investigation of Their Growth Mechanism

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Experimental

Chemicals and Materials. Multilayer graphene (AO-2) was purchased from Graphene Supermarket (Calverton, New York). Gold chloride hydrate (HAuCl₄ ·xH₂O, 99.999%) was purchased from Sigma-Aldrich, USA. The chemicals were used without any further purification.

Oxygen Plasma Treatment of Graphene Templates. Graphene multilayers (2.5 mg) was first dispersed in 10 mL deionized water (0.25 g/mL). The probe ultrasonication was utilized to improve the graphene dispersion with a vibra-cell VCX-130 with VC-50 mirco-tip (Sonics & Materials, Inc.) at 25% amplification (32.5 watts) for 60 seconds with the on and off frequencies of 1 Hz and 0.5 Hz, respectively. After that the graphene suspension was dropped on an ethanol cleaned aluminum foil. When the excessive water was evaporated, a thin graphene film was formed on the substrate. To make the plasma treatment effective, the thickness of the graphene film should well controlled. AtomfloTM plasma system (Surfx[®] Technologies LLC) was used to activate graphene surfaces. The system was powered at 150 W with the feeding rate of helium at 30 L/min and oxygen at 0.5 L/min, respectively. We considered the scanning from one end of the sample to the other as one scan. With the scan rate of 20 mm/s, a total of 45 scans was applied to the sample.

Ultrasonication of Plasma Activated Graphene Template with Gold Precursor. When the plasma treatment was completed, the graphene film was flushed with 10 mL deionized water from the substrate to a 40-mL glass vial. 0.5 mL gold precursor HAuCl₄ (2.85 mM) was then added to the vial with a pipette. The suspension was treated with a vibra-cell VCX-130 with VC-50 mirco-tip (Sonics & Materials, Inc.) at 25% amplification (32.5 watts) for a total time of 6 minutes with the on and off frequencies of 0.5 Hz and 0.1 Hz, respectively.

One-pot Synthesis of G/AuNWs Assembly. After ultrasonication, the glass vial was capped and maintained at 80 °C in the oven for the hydrothermal reduction. A series of experiments were carried out with different time steps, *t*. Control experiment was performed without using ultrasonication. The final products were collected by centrifuge, washed thoroughly with deionized water, and transferred to specific substrates for further characterizations.

Characterizations. Top view scanning electron microscopy (SEM) images of samples with different *t* and from the control experiment were obtained with FEI Nova NanoSEM 230. Diameter distributions of AuNWs were determined from more than 30 nanowires of different SEM images. The system was coupled with energy dispersive X-ray (SEM/EDX) detector (ThermoFisher Scientific), from which the 2-D spatial elemental mapping of G/AuNWs assembly were obtained. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were captured with FEI Titan S/TEM system at 300 keV. The X-ray diffraction (XRD) measurements were performed on a Jordan Valley D1 diffractometer using Cu K α 1 radiation. They were under double axis diffraction condition. The step size of the 2 $\theta - \omega$ scans was 0.04° and the count time was 3 s. Raman spectroscopy analysis was obtained with a Renishaw In-Via Raman system with the laser length of 633 nm and laser power of 1mW at objective lens magnification of 50x and a grating spacing of 1200 l/mm.



Figure S1. Raman spectra of as received graphene (black), plasma treated graphene (red) and plasma treated graphene/AuNWs (blue). Inset is the location of G peak, showing the doping activity with graphene oxidization.



Figure S2. Statistical analysis of AuNWs sizes obtained with and without ultrasound. (a) Diameter and (b) length distributions of AuNWs with ultrasound. (c) Diameter and (d) length distributions of AuNWs without ultrasound.



Figure S3. (a) A representative AuNW with the length more than 100 μ m (100,000 nm). (b) A higher magnification SEM image of the nanowire showing the diameter ~ 20 nm. (c) and (d) More representative morphologies of G/AuNWs assembly.



Figure S4. (a) Representative SEM images of AuNWs obtained on graphene template without using ultrasonication. AuNWs obtained with this method show a wide range of diameters from \sim 20 nm (b) to more than 100 nm (c).



Figure S5. XRD of Graphene-Au nanowires. Five characteristic Au peaks, i.e. Au (111) $\{38.2^{\circ}\}$, Au (200) $\{44.4^{\circ}\}$, Au (220) $\{64.6^{\circ}\}$, Au (311) $\{77.5^{\circ}\}$ and Au (222) $\{81.8^{\circ}\}$ are observed, corresponding to the typical FCC Au structure.

Au	Texture Coefficient	
lattice plane	Randomly orientated Au powder (polycrystalline)	G/Au nanowires
{111}	1.00	0.92
{200}	0.48	0.81
{220}	0.29	1.21
{311}	0.33	1.01
{222}	0.10	1.05

Table S1. G/Au nanowires texture coefficient compared with polycrystalline Au powder.

The calculation of texture coefficient (TC) was carried out using the following equation:

$$\mathrm{TC}_{(h_{i}k_{i}l_{i})} = \frac{\mathrm{I}_{(h_{i}k_{i}l_{i})}}{\mathrm{I}_{0(h_{i}k_{i}l_{i})}} \left\{ \frac{1}{N} \sum_{i=1}^{N} \frac{\mathrm{I}_{(h_{i}k_{i}l_{i})}}{\mathrm{I}_{0(h_{i}k_{i}l_{i})}} \right\}^{-1}$$

Where

 $I_{(h_ik_il_i)}$: intensity of the $h_ik_il_i$ peak of the sample;

 $I_{0(h_ik_il_i)}$: intensity of the $h_ik_il_i$ peak of the randomly oriented powder;

N: number of diffraction considered in the analysis



Figure S6. Elemental spectrum of G/AuNWs assembly from the area shown in Fig. 1(d). Silicon peak is from the sample substrate.



Figure S7. (a) Low magnification TEM image including the area of Fig. 2(c). (b) The fast-Fourier transformation (FFT) of the area shown in Fig. 2(c).



Figure S8. Shape evolution of AuNWs on graphene template in different timeframes (a) 1 hr. (b) 4 hrs. (c) 12 hrs. (d) 24 hrs.



Figure S9. Relations of diameters and Aspect ratios (R) of AuNWs with time t.



Figure S10. (a) Atomic structure of highly dense stacking faults in Fig. 3(c). (b) The FFT pattern of (a). The atomic structure reveals that stacking faults are gathered in the <111> direction, which is identified by FFT spots streaking along the <111> vector on the $\{110\}$ basal planes.