Supporting Information

Scrolling up graphene oxide nanosheets assisted by self-assembled monolayers of alkanethiols

Lin Wang,[a,§] Peng Yang,[a,§] Yang Liu,[a] Xiangru Fang,[a] Xiaotong Shi,[a] Shiyu Wu,[a] Ling Huang,[a] Hai Li,[a,*] Xiao Huang,[a] Wei Huang[a,b]

[a]Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (Nanjing Tech), 30 South PuZhu Road, Nanjing 211816, China

[b]Key Laboratory for Organic Electronics & Information Displays (KLOEID), and Institute of Advanced Materials (IAM), Nanjing University of Posts and Telecommunications, Wenyuan Road 9, Nanjing 210023, China.

§ These authors contributed equally to this work.

*Author to whom correspondence should be addressed. E-mail: iamhli@njtech.edu.cn

Experimental Section

1. Materials

Methanol, ethanol, acetone and isopropanol were obtained from Shanghai Ling Feng Chemical Reagent Co., Ltd. 99.99 % gold and 99.99% chromium were bought from Zhong Nuo New Material Technology Co., Ltd. Silver nitrate was obtained from Xiya Reagent Co., Ltd. $N_2H_4 \cdot H_2O$ solution, 97% 1-Octanethiol, 1-dodecanethiol, 1-Octadecanethiol were bought from Shanghai Aladdin biochemical Polytron Technologies Inc. Silicon wafers were purchased from Jing Xi Co., Ltd (Su Zhou, China).

2. Synthesis

2.1 Synthesis of large sized graphene oxide (GO) nanosheets

The GO nanosheet was prepared using modified Hummers' method.[1]

2.2 Synthesis of large sized GO-Ag nanosheets

10 mL GO solution (5 mg/mL) was added in a bottle containing 10 mL 0.1 M $AgNO_3$ solution. After it was heated to 85 °C and maintained for 30 min, the suspension was washed three times with distilled (DI) water at 7000 rpm to remove free Ag NPs. Finally, GO-Ag nanosheets were dispersed in 10 mL DI water to form a stable dispersion.

2.3 Langmuir-Blodgett (LB) assembly of single layer GO film and single layer GO-Ag film

An LB trough (KSV3000) was carefully cleaned with acetone, isopropanol and then filled with DI water. The mixture of 0.5 mg/mL GO solution and methanol with an optimal ratio (v : v) of 1:5 was dropwise deposited over the water surface. The GO nanosheets were slowly spread on the water surface and the monolayer was kept undisturbed for 240 min to allow methanol evaporation. Monolayer GO film was transferred onto gold substrates by vertical dipping into the trough and slowly pulling it up (1 mm/min) at target surface pressure of 0.5 mN/m. Monolayer GO-Ag film was fabricated through the same procedure.

2.4 Synthesis of GO nanoscrolls and GO-Ag nanoscrolls

GO or GO-Ag nanosheets deposited on gold substrate by LB technique were immersed into OTT, DDT and ODT solution with concentration of 0.3%, 0.5%, 1%, 2% and 3% (v : v) for 1, 3, 6 and 12 h, respectively. Then the substrates were washed by ethanol and dried with N_2.

2.5 Sensing Applications

Saturated K_2CO_3, NaCl and K_2SO_4 solutions were selected as standard humidity solution (43%, 75% and 97% RH, respectively) for humidity detecting. 50 nm thick gold and 10 nm thick chromium were deposited to rGO nanosheet, rGO-Ag nanosheet, rGO nanoscroll and rGO-Ag nanoscroll by using TEM grid as mask in thermal evaporator, respectively. Thus the devices based rGO nanosheet, rGO-Ag nanosheet, rGO nanoscroll and rGO-Ag nanoscroll can be obtained. Keithley 4200 semiconductor characterization system was used to monitor the real-time current change of as-prepared devices exposed to different humidity (43%, 75% and 97% RH, respectively).

3. Characterization

3.1 Raman characterization

Raman spectra of GO nanosheet, GO-Ag nanosheet, GO nanoscroll and GO-Ag nanoscroll were collected on HR Evaluation spectrometer (Horiba) with a 532 nm laser focused through a 100× objective lens. The Raman band of a Si wafer at 520 cm^{-1} was used as a reference to calibrate the spectrometer.

3.2 Atomic force microscopy (AFM) characterization

A commercial AFM instrument (Dimension ICON with Nanoscope V controller, Bruker) equipped with a scanner (90 × 90 μm^2) was used to image the samples in tapping mode in air.

3.3 Scanning electron microscopy (SEM) characterization

Morphology of GO nanosheets and nanoscrolls was captured by using a JEOL JSM-6700 field-emission scanning electron microanalyzer at accelerating voltage of 5 and 10 kV, respectively.

3.4 Transmission electron microscopy (TEM) characterization

GO and GO-Ag nanoscrolls were imaged by using a JEM-1200EX transmission electron microscope (TEM) (JEOL, Japan) operating at an accelerating voltage of 100 kV.

4. Measurement of scroll yield (S_Y)

The scroll yield (S_Y) is defined as the percentage of GO nanosheets converted to GONSs, which can be described by equation (S1),

$$S_Y=A_0-A \quad (S1)$$

Here, A_0 is the original area percentage of gold substrate covered by single-layer GO nanosheets. A is the area percentage of gold substrate covered by partially or completely formed GONSs after being immersed into alkanethiol solution. Therefore, the difference between A_0 and A is the percentage of GO nanosheets converted to GONSs, *i.e.*, S_Y.

5. Measurement of the area percentage of gold substrate covered by GO naosheets or GONSs

a) Open ImageJ software.

b) Click File→Open in ImageJ to open SEM or OM image of single-layer GO nanosheets on gold substrate prepared by LB technique.

c) Click Image→Adjust→Threshold. Adjust suitable threshold value to mark all GO nanosheets on gold substrate in black (Figure S2b).

d) Click Analyze→Measure, and the area percentage of gold substrate covered by GO nanosheets (A_0) is shown in %Area (Figure S2c).

e) Repeat steps a-d to measure the area percentage of gold substrate covered by partially or completely formed GONSs (A), which is shown in Figure S3.

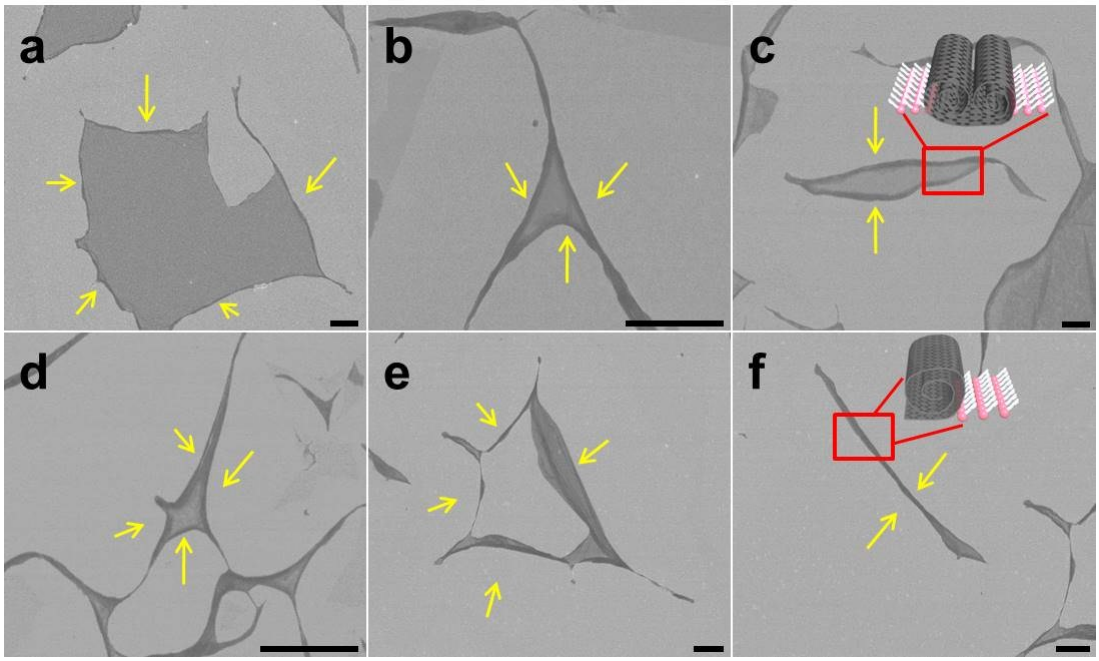
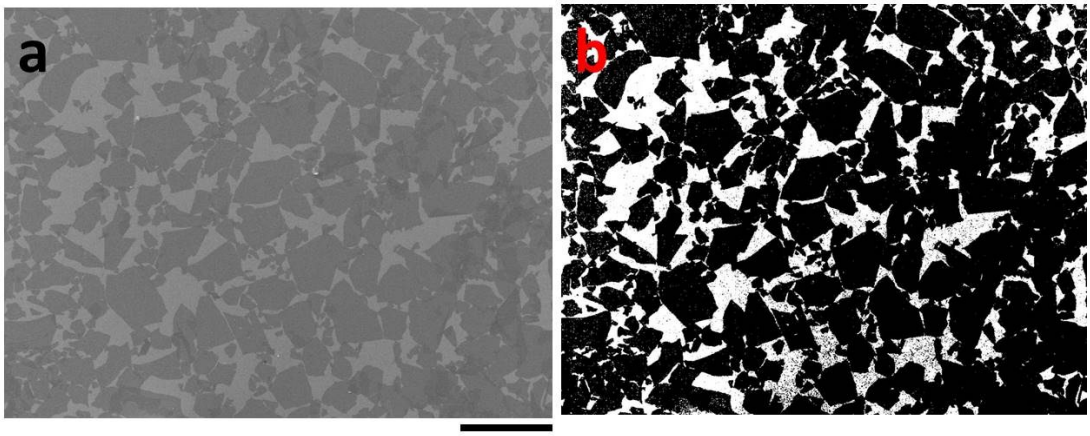


Figure S1. SEM images (a-f) of GO nanosheet rolled up by alkanethiol self-assembled monolayers in random orientation. All scale bar is 5 μm.



c

	Area	Mean	StdDev	Min	Max	%Area
1	1278720	176.701	5.747	146	255	79.573

Figure S2. The area percentage of gold substrate covered by single layer GO nanosheets before immersion.

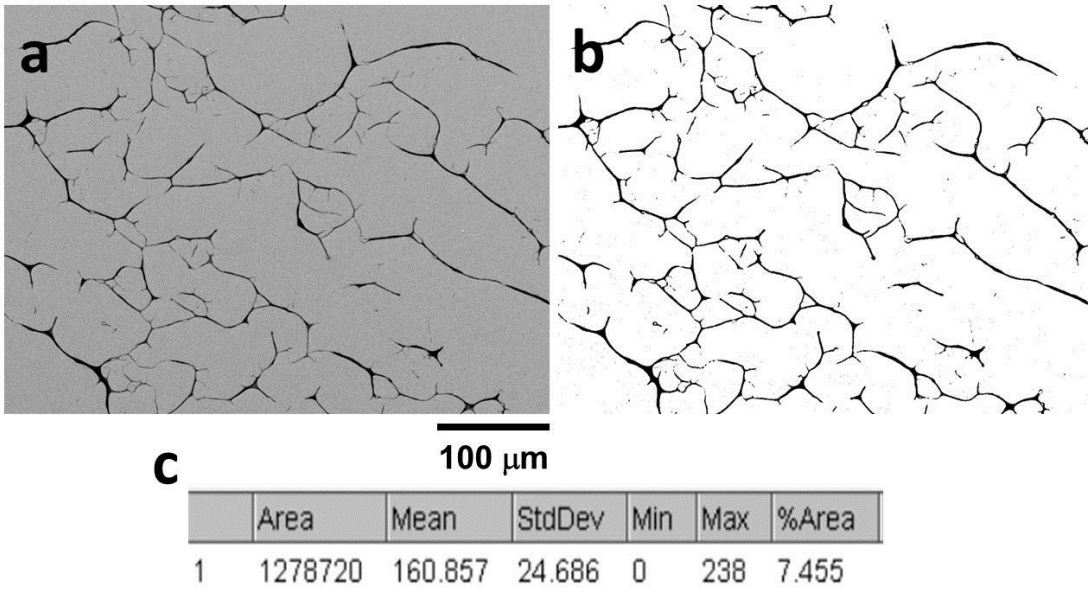


Figure S3. The area percentage of gold substrate covered by GO nanoscrolls after being immersed into thiol solution.

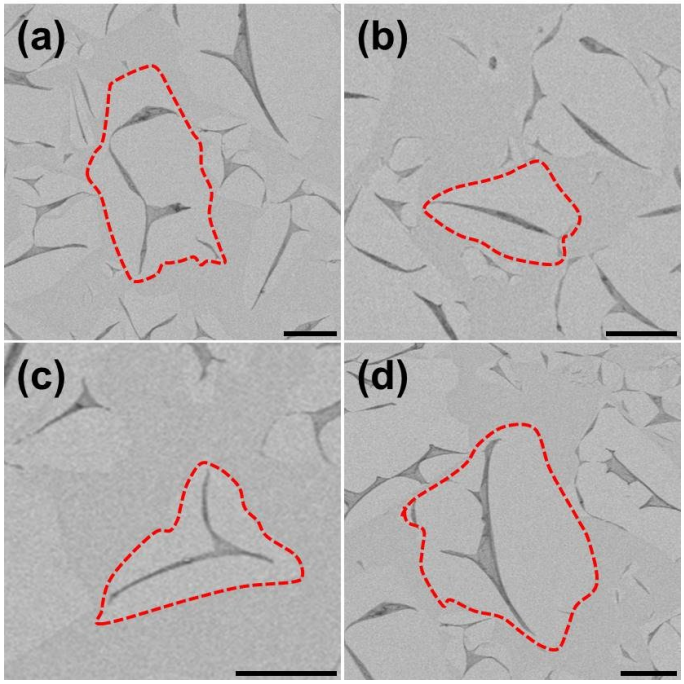


Figure S4. (a-d) SEM images of GONSs rolled up from individual GO nanosheets. The original shapes of GO nanosheets are marked by red dashed lines. All scale bar is 10 μm.

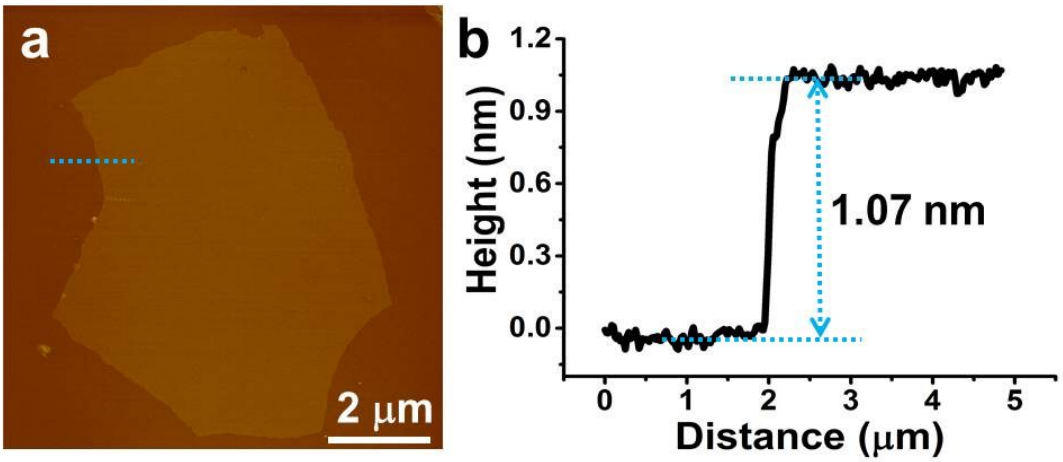


Figure S5. AFM image (a) and the corresponding height profile (b) of GO nanosheet.

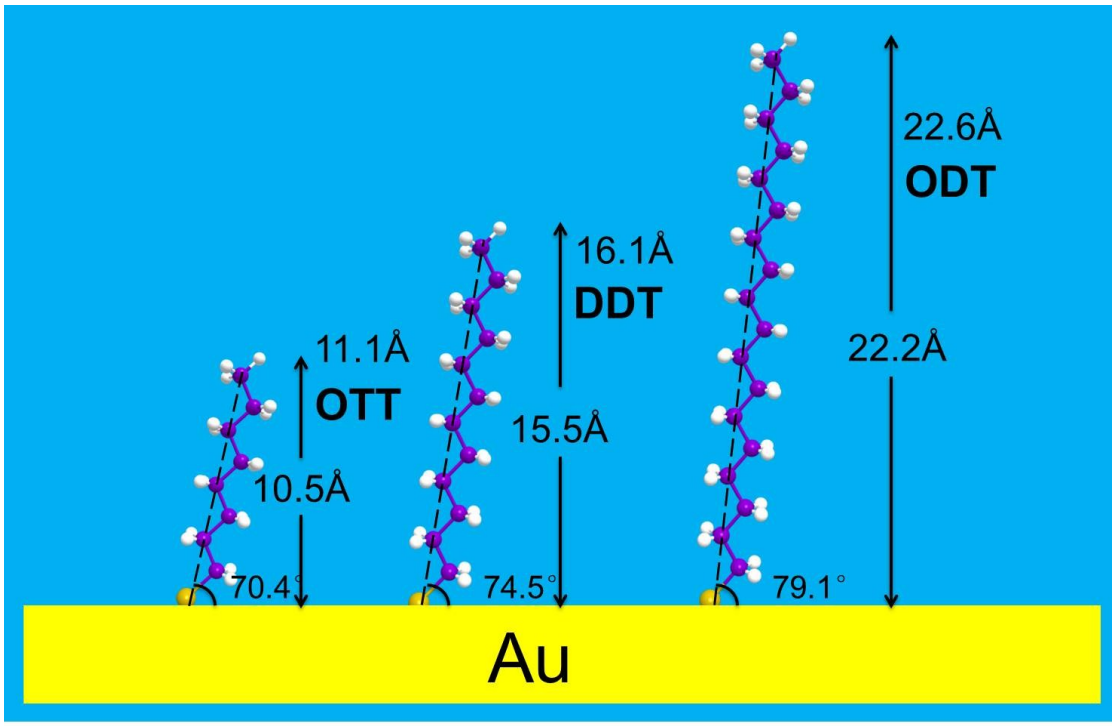


Figure S6. The schematic structure of OTT, DDT and ODT molecules immobilized on gold substrate.

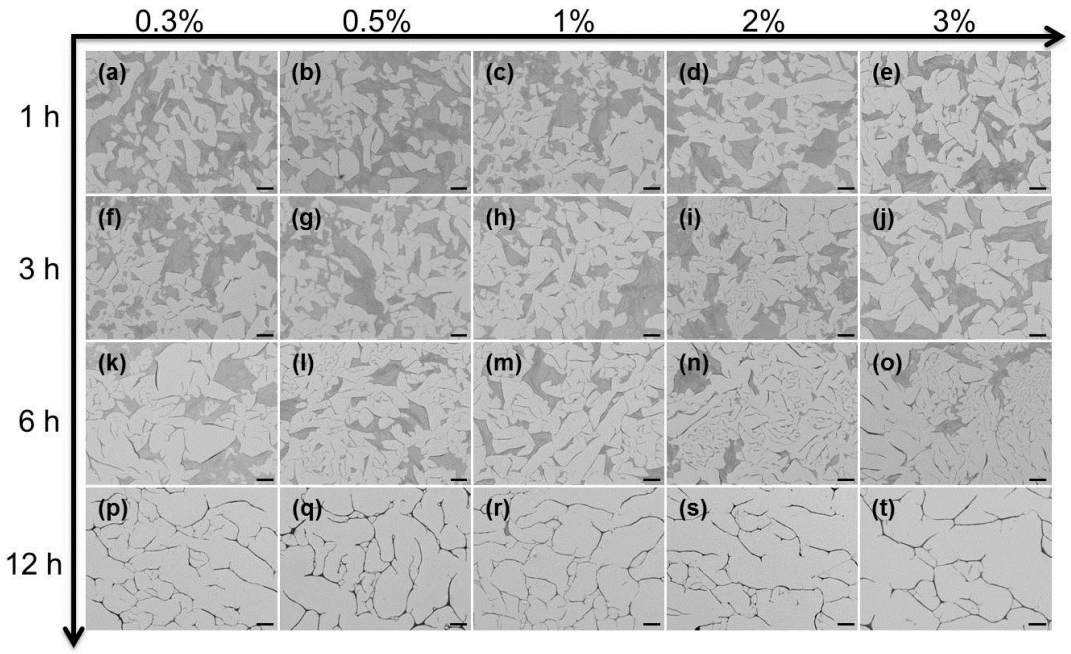


Figure S7. SEM images of GO nanosheets after being immersed into 1-Dondecanethiol solutions with concentration of 0.3, 0.5, 1, 2 and 3% for 1, 3, 6 and 12 h, respectively. All scale bar is 20 μm.

Table S1. Comparison of GO nanoscrolls fabricated by this work and refs 9-10.

Method	Materials	Process	Size of GO nanosheet	Width of GO scroll	Density	Morphology	Orientation	Mechanism	
Molecular combing	GO nanosheet	Fast (seconds)	> 10 μm	~1□μm	Low	Long, straight scroll	Parallel to dragging direction	Capillary interaction	Ref 9
Molecular combing	GO nanosheet	Fast (seconds)	> 10 μm	~1 μm	Depending on the template	Bead-like structure	Parallel to dragging direction	Capillary interaction	Ref 10
Immersing in alkanethiol solution	GO nanosheet and GO-Ag sheet	Slow (hours)	No limitation	~200 nm	High	Dendritic scroll	Random	Rolling up by self-assembled monolayer of alkanethiol	This work

Table S2. Constants of equation (1) for GO nanosheets immersed into 1-Octanethiol, 1-Dondecanethiol and 1-Octadecanethiol solutions with concentration of 0.3%, 0.5%, 1%, 2% and 3% for 1, 3, 6 and 12 h, respectively.

		1 h	3 h	6 h	12 h
1-Octanethiol	a	77.78	83.77	88.57	90.71
	b	0.006	0.04	0.005	0.01
1-Dondecanethiol	a	53.69	59.63	69.17	83.09
	b	0.05	0.029	0.04	0.047
Octadecanethiol	a	10.36	23.79	36.31	45.57
	b	0.36	0.19	0.08	0.07

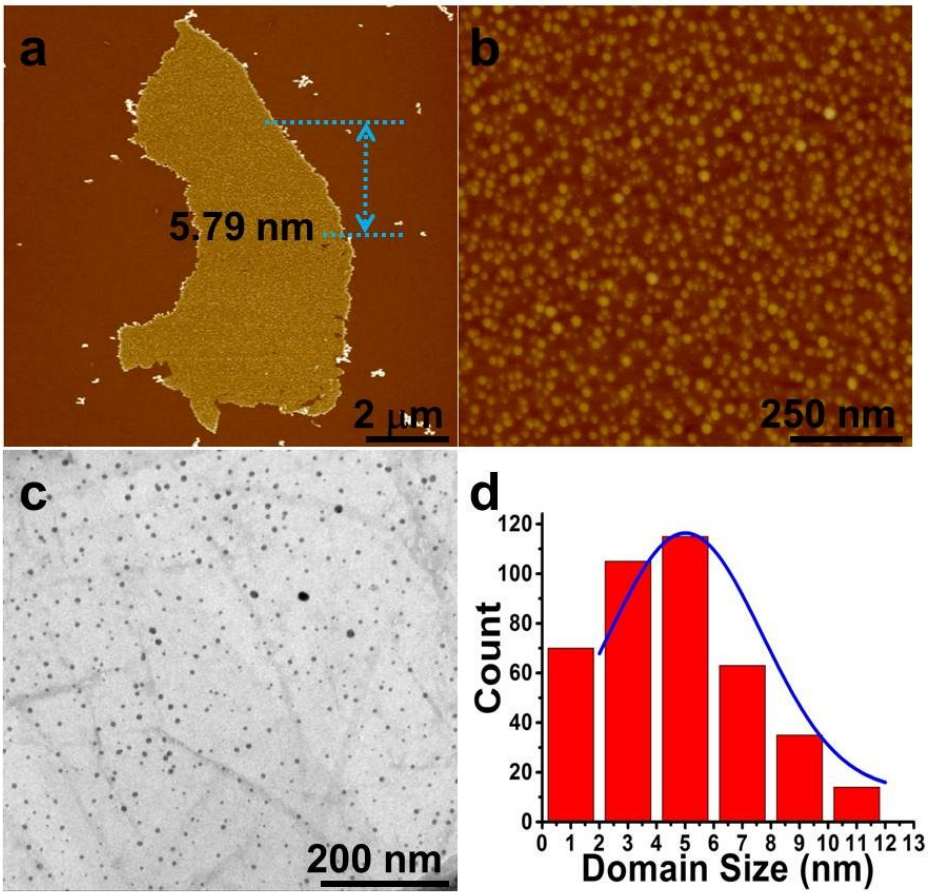


Figure S8. (a-b) AFM and (c) TEM images of GO-Ag nanosheet. (d) Size distribution of Ag nanoparticles on GO nanosheets.

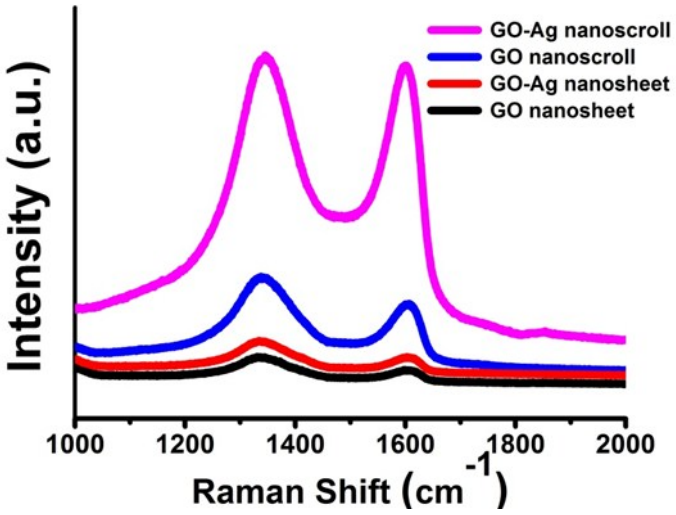


Figure S9. Raman spectra (a) of GO nanosheet, GO-Ag nanosheet, GONS and GO-Ag NS.

Reference

1 X. Zhou, X. Huang, X. Qi, S. Wu, C. Xue, F. Y. C. Boey, Q. Yan, P. Chen and H. Zhang, *J. Phys. Chem. C,* 2009, **113**, 10842-10846.