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Hybrid Graphene - Metal Nanoparticle Systems: Electronic Properties and Gas Interaction

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Supporting Info

Experimental Section

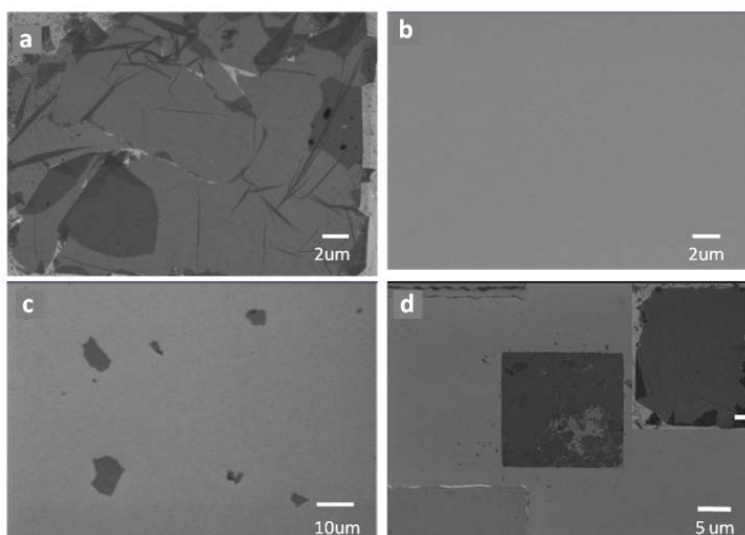
GO was synthesized chemically by oxidation of graphite using modified Hummer's and Offeman's method⁶. 0.5g graphite powder (Bay carbon, SP1), 0.55g Sodium Nitrate (Sigma Aldrich, >99.999%) and 23ml Sulfuric acid (Sigma Aldrich, 99.999%) were mixed and stirred for 10 minutes. Then, 3g Potassium Permanganate (Sigma Aldrich, >99.0%) was added slowly and temperature maintained below 20°C. DI water added slowly and the temperature raised to 90°C. The solution turned bright yellow when 3ml of Hydrogen peroxide (30%) was added. The mixture was filtered while warm and washed with warm DI water. Purification was done by centrifugation. Highly doped silicon with 50nm SiO₂ were used as substrate. The substrate was plasma cleaned and modified using Aminopropyl-Trichloroethoxysilane (APTES, Sigma Aldrich, 99%) to create predefined areas for GO localization. The substrate was immersed in GO aqueous solution washed with DI water.

Electron beam resist (PMMA – Microchem corp, A3) was spin coated on the substrate before performing e-beam lithography to define the electrodes. The channel dimensions were defined as 2µm by 15µm.

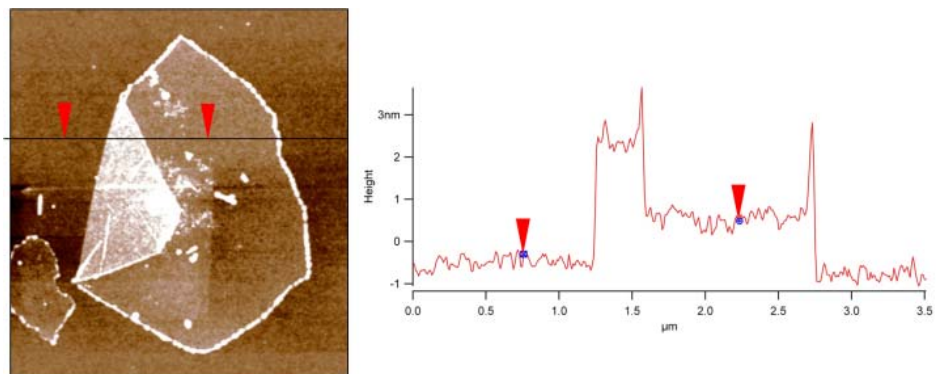
Decoration of gold was obtained by using 1ml of 10mM Chloroauric acid (HAuCl_4) (Strem Chemical, 99.9%) diluted with 9ml DI water. The mixture was heated to 80°C together with the graphene oxide deposited substrate. Next, 77mM sodium citrate (Sigma Aldrich, ACS reagent) was added. The substrate was then washed with DI water and kept under N_2 to avoid contamination. Briefly for silver decoration⁹, AgNO_3 (Sigma Aldrich, 99.9999%) solution was injected to closed cells with GO substrate while continuously flushed with N_2 . After 20 minutes, the substrate was taken out and rinsed with DI water. Graphene oxide and the hybrid devices then underwent chemical reduction using Hydrazine Monohydrate vapor for 18 hours at 140°C in a closed flow cell. The chip is then flushed with N_2 for 6 hours to remove the excess hydrazine, baked for 1 hour to clean the PMMA residue, and stored in N_2 before measurement.

Field emission scanning electron microscopy (FE-SEM, JEOL JSM7600F) at 1kV and transmission electron microscopy (TEM JEOL2100F) at 200kV were used to characterize various specimens in this experiment. Electrical measurements were done with Keithley 4200 on a probe station (TTP-6, Desert Cryogenic) under ambient temperature and vacuum in both transistor and resistor configurations. Raman measurements were performed using a Witec system at 488 nm. Gas sensing measurement was done in a home-made setup using manual air flow controller in a closed chamber at room temperature and atmospheric pressure.

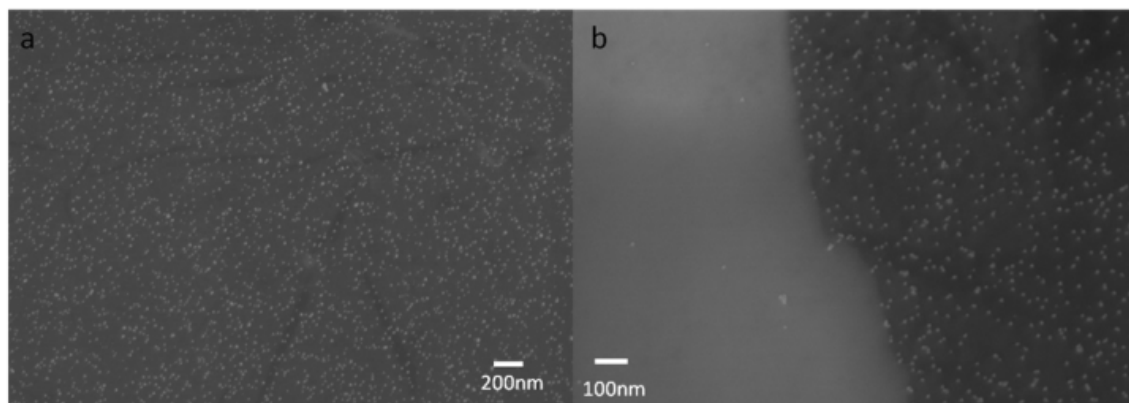
Supporting figures



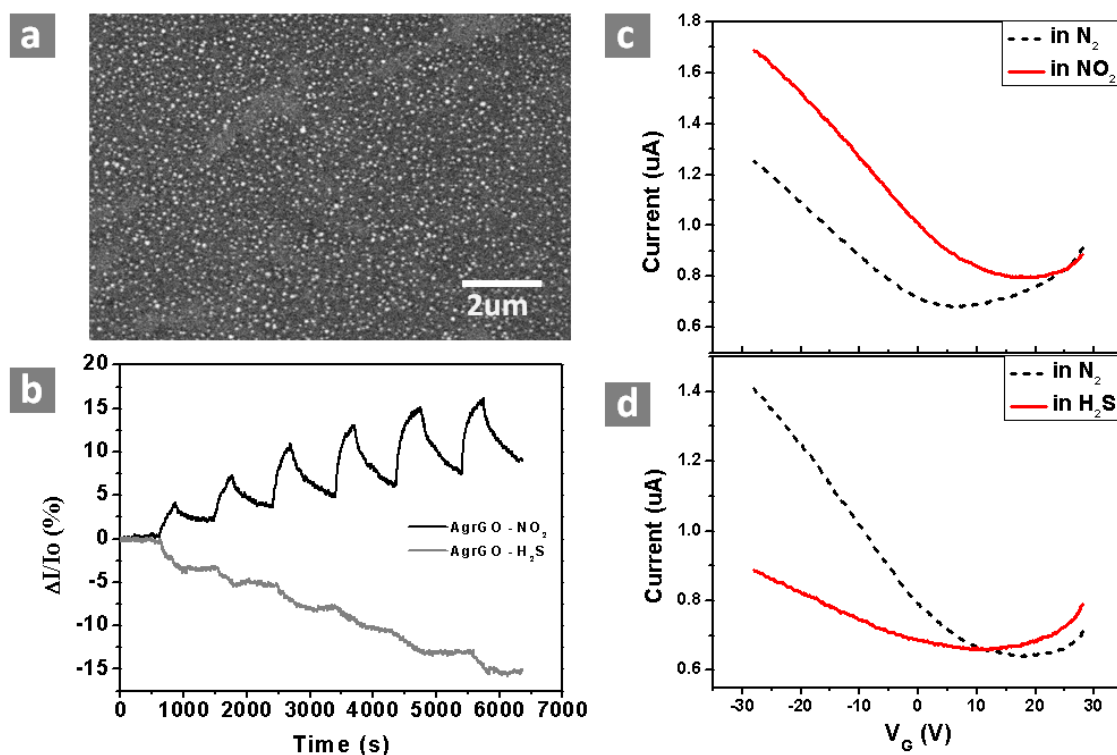
SI 1. a) APTES functionalization gives amine termination that attract GO to stick on the substrate thus securing the single layer. b) Octadecyltrichlorosilane (OTS) treated substrate which gives hydrophobic surface repels GO from sticking on the substrate. Surface appears clean from GO. c) Plasma cleaned substrate which gives hydrophilic surface allows some GO to stick on the substrate. d) Localized single GO layer on desired position. Inset showed big piece of GO layer (around 15 μm) is deposited through this method. Scale bar is 2 μm.



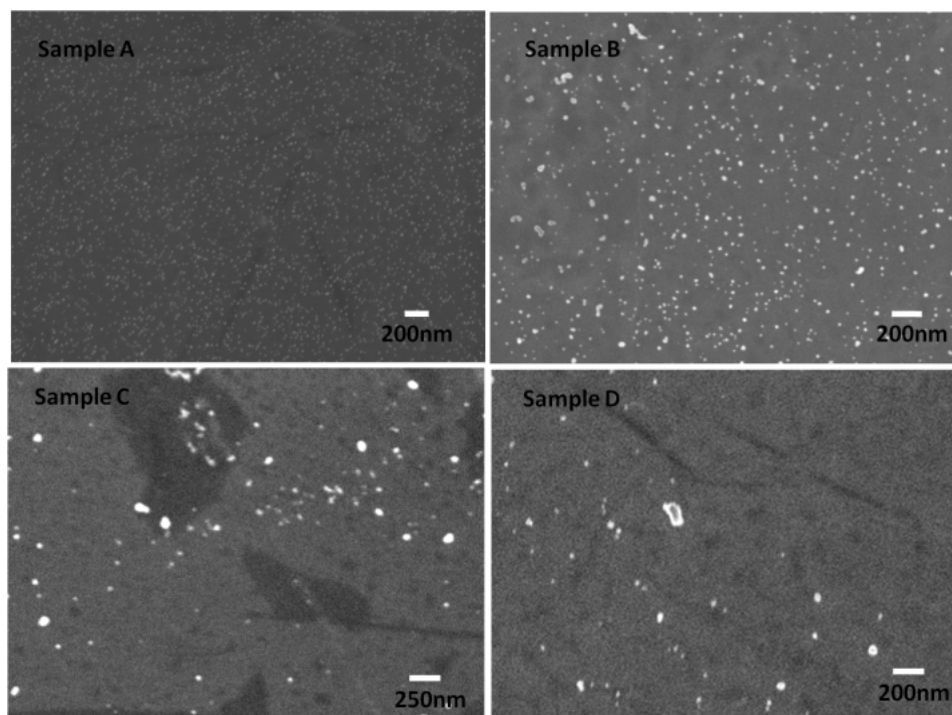
SI. 2. AFM measurement of rGO. Average thickness of the layer is around 0.65nm, which may be contributed to un-removed oxygen functionalities on the layers.



SI 3. a) SEM image of Au-rGO, b) SEM image shows selective decoration of Au nanoparticle on single GO sheet. The free standing particles on the substrate (appear lighter in color) are easily removed by mild sonication.



SI 4. AgrGO gas detection; a) SEM images for Ag decorated GO by chemical synthesis. The particle size is found to be 7.05 ± 2.10 nm with particle density of 949 particles / μm^2 , b) Transient measurement in NO_2 (black) and H_2S (gray) respectively, c) Transfer characteristic in NO_2 – 2 ppm, threshold voltage is positive shifted as result of p-type doping and mobility increases by 46% with relative to mobility calculated in N_2 ; d) Transfer characteristic in H_2S – 8ppm, threshold voltage is negative shifted as result of n-type doping and mobility decreases by 37% with relative to mobility calculated in N_2 . Limit of detection in NO_2 is 39ppb and in H_2S is 900ppb.



SI 5. SEM images for Au-rGO taken directly from the device used in figure 4d, showing different Au nanoparticle density (decreasing density from sample A, B, C to D). For samples A, B, C and D respectively, mean size of the nanoparticle was found to be around 13nm, 20nm, 28nm and 40nm; the density of nanoparticles are 335 particle/ μm^2 , 120 particle/ μm^2 , 50 particle/ μm^2 and 10 particle/ μm^2 .