Supporting Information

Facile and simultaneous production of metal/metal oxide dispersed graphene nano composites by solar exfoliation

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Supporting Information

1. Preparation of Graphite Oxide (GO) and salt-GO composites

Graphite oxide (GO) was prepared according to Hummers method.[1] Briefly, graphite (SP-1 Bay Carbon) was grounded with NaCl and washed with DI water followed by filtration. After drying, the filtrate was stirred with conc. H_2SO_4 for 8 h. 6 g of $KMnO_4$ was gradually added while keeping the temperature less than 20ºC. The mixture was stirred at 35 to 40ºC for 30 min and 65 to 80ºC for 40 min. 92 ml water was added to the above solution and heated to ~ 100ºC. This was diluted by adding 280 ml of water followed by the addition of 30% H_2O_2. The mixture was washed followed by repeated centrifugation and filtration (first by 5 % HCl and then with water). The final product was washed and dried in vacuum. GO was dispersed in water by ultrasonication for 30 min. and this was then followed by the addition of metal salt precursors during magnetic stirring. The salt-GO composite thus obtained was evaporated directly in air atmosphere at 60ºC to get powder composites.

2. Reduction and exfoliation of salt-GO composites

Salt-GO composites were spread over petri dish and kept under sunlight. A convex lens of diameter 100 mm was used to focus the incoming radiation from the sun. The power of the focused radiation was ranging from 1.8 - 2.5W and temperature raised to more than ~300°C. At high temperature, GO exfoliates into graphene and at the same time, the metal salt get reduced to corresponding metal/metal oxide, with the release of chlorine gas. A pungent smell of the evolved gas was identified. Due to the rapid exfoliation of GO, defects are getting introduced which act as anchoring sites for the deposition of metal nano particles over solar graphene.

3. Characterization Techniques

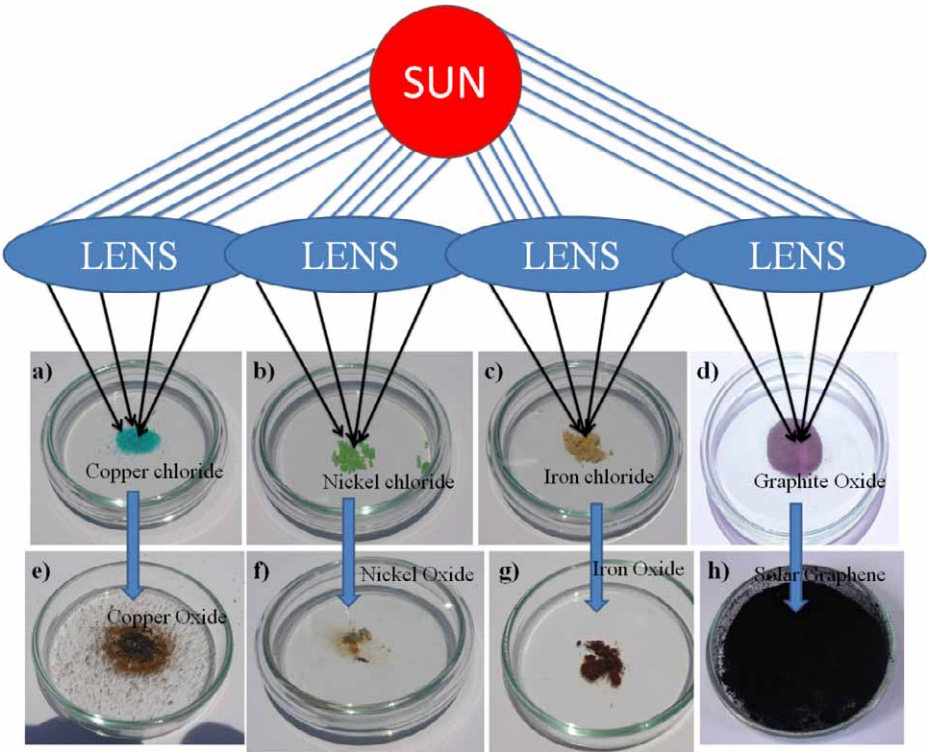
The XRD measurements were performed with a PANalytical X'Pert Pro X-ray diffractometer with nickel-filtered Cu Kα radiation as the X-ray source. The pattern was recorded in the 2θ

range of 5° - 90° with a step size of 0.016°. Raman spectroscopy was performed on Witec Raman microscope using green (532 nm) laser excitation, with excitation energy of 2.33 eV. Scans were taken on an extended range (500-3000 cm^{-1}) for an exposure time of 60 s. The samples were sprinkled over cleaned glass slides for observation and viewed under a maximum magnification of x20. Thermo gravimetric spectra were recorded with NETZSCH analyzer from ambient temperature to 800°C in air atmosphere with temperature heating of 10°C/min. Field emission scanning electron microscopy (FESEM, Quanta 3D) imaging was used to examine the morphology of the synthesized samples. The microscope was operated at an accelerating voltage of 5-30 kV. EDX spectra was recorded with Li doped Silicon X-ray detector equipped with FESEM. High resolution micrographs were obtained with FEI Tecnai G^2 transmission electron microscope operated at 200 keV. The samples were dispersed in ethanol and drop cast over holey carbon coated copper grid (200 mesh). The samples were dried over night in ambient atmosphere.

Supporting figures

Figure S1-1. Optical photographs of pure metal salts (a,b,c), reduced metal/metal oxide nanoparticles (e,f,g), graphite oxide (d) and solar graphene (h).

The photographs show clearly the colour difference observed in the metal salts before and after irradiation with focused sunlight. The change in colour as well as nature of the samples better illustrates the photoinduced reduction of metal salts to pure nanoparticles.



It is interesting to note that when iron chloride is irradiated with focused solar radiation, the immediate colour change is observed from pale yellow to dark red (popularly known as red iron oxide). The magnetic property of the reduced Fe_2O_3 nanoparticles and Fe_2O_3/sG has been analyzed by bringing an electromagnet towards them. The strong attraction of both the nanoparticle and nanoparticle-graphene composite strongly suggest the magnetic nature of the reduced samples. Hence, non magnetic ion chloride/ ion chloride -GO transforms into magnetic iron nanoparticle/iron nanoparticle dispersed solar graphene by a very simple, fast and green chemical dry process.

Figure S1-2. Optical images of (a) reduced iron oxide attracted to natural magnet and (b) strong attraction of iron oxide /graphene towards magnet.

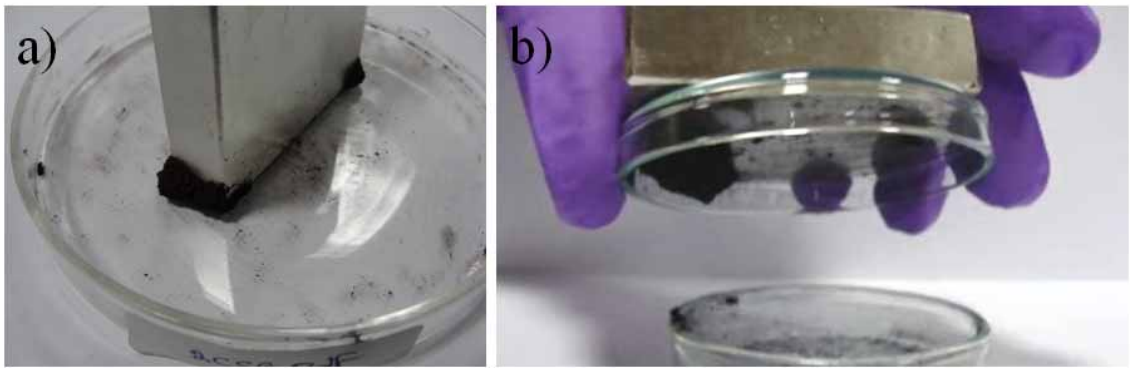


Figure S2-1. TGA spectra of iron chloride and iron oxide nanoparticles dispersed solar graphene.

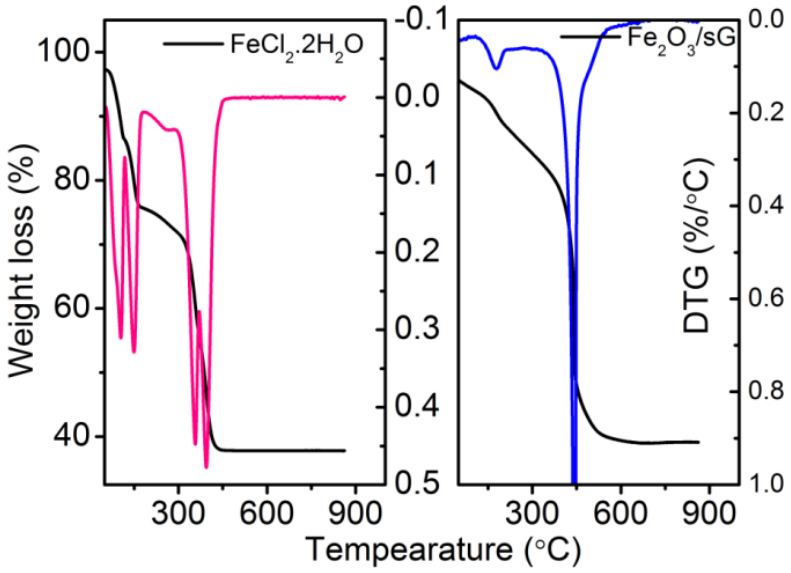


Figure S2-2. TGA spectra of gold chloride and gold nanoparticles dispersed solar graphene.

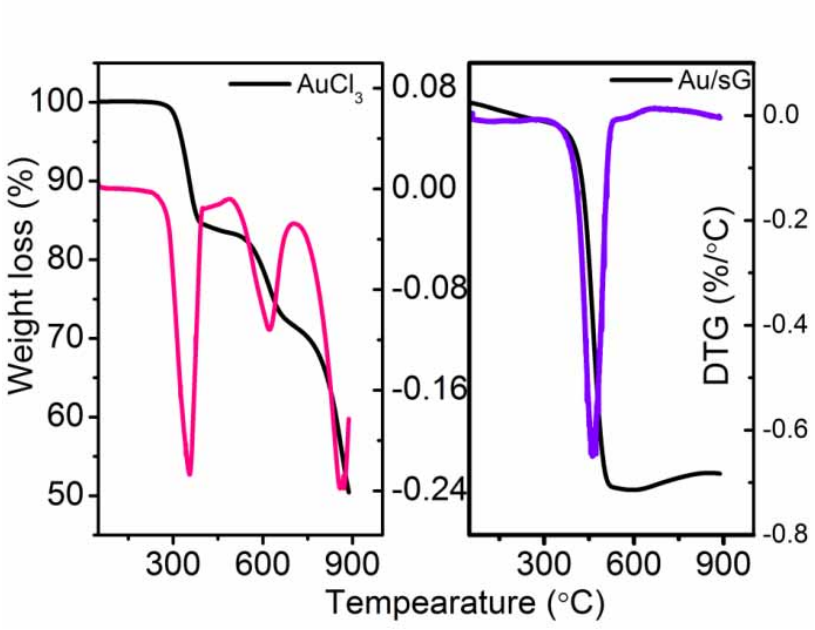
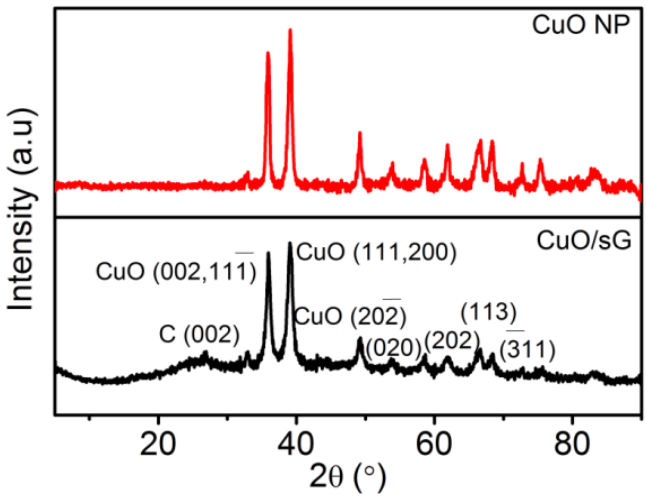
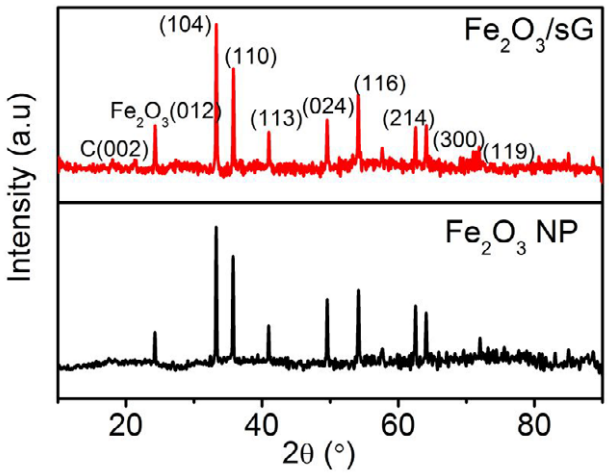


Figure S3-1. XRD spectra of CuO nanoparticle and copper oxide dispersed solar graphene.



The CuO particle size over sG calculated using Scherrer formula came out to be ~ 13 nm.

Figure S3-2. XRD spectra of Fe_2O_3 nanoparticle and Fe_2O_3 dispersed solar graphene.



The Fe_2O_3 particle size over sG calculated using Scherer formula came out to be ~ 50 nm.

Figure S4-1. EDX spectra of copper chloride, copper oxide nanoparticles, copper chloride-GO composite and copper oxide nanoparticles dispersed solar graphene.

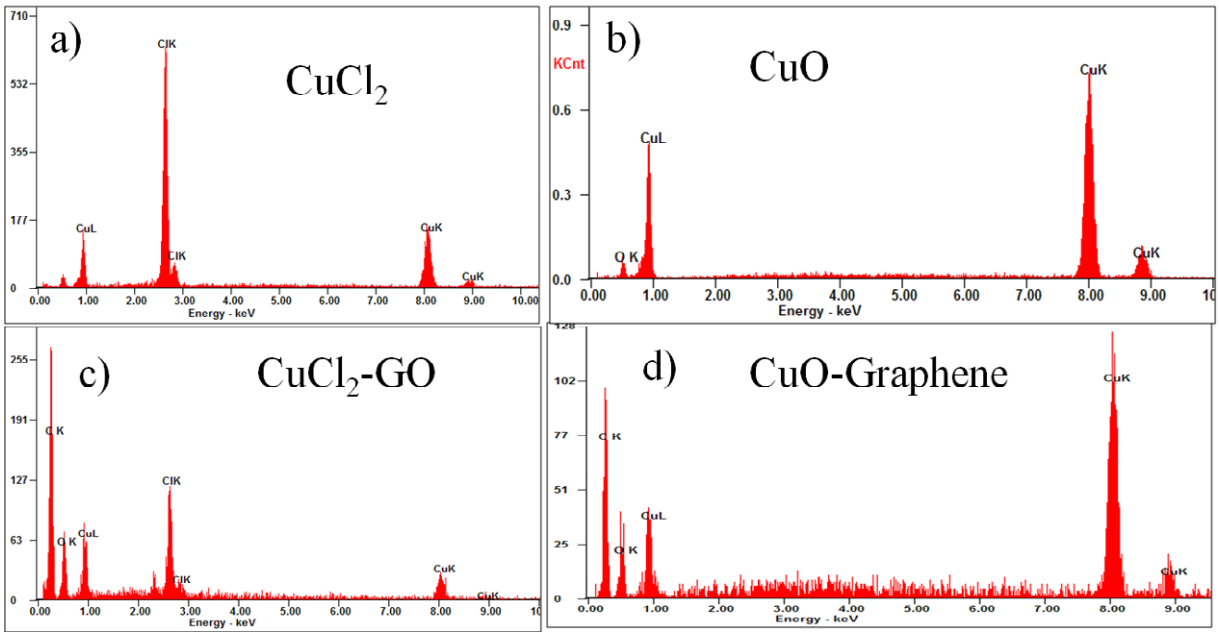


Figure S4-2. EDX spectra of nickel chloride, nickel oxide nanoparticles, nickel chloride-GO composite and nickel oxide nanoparticles dispersed solar graphene.

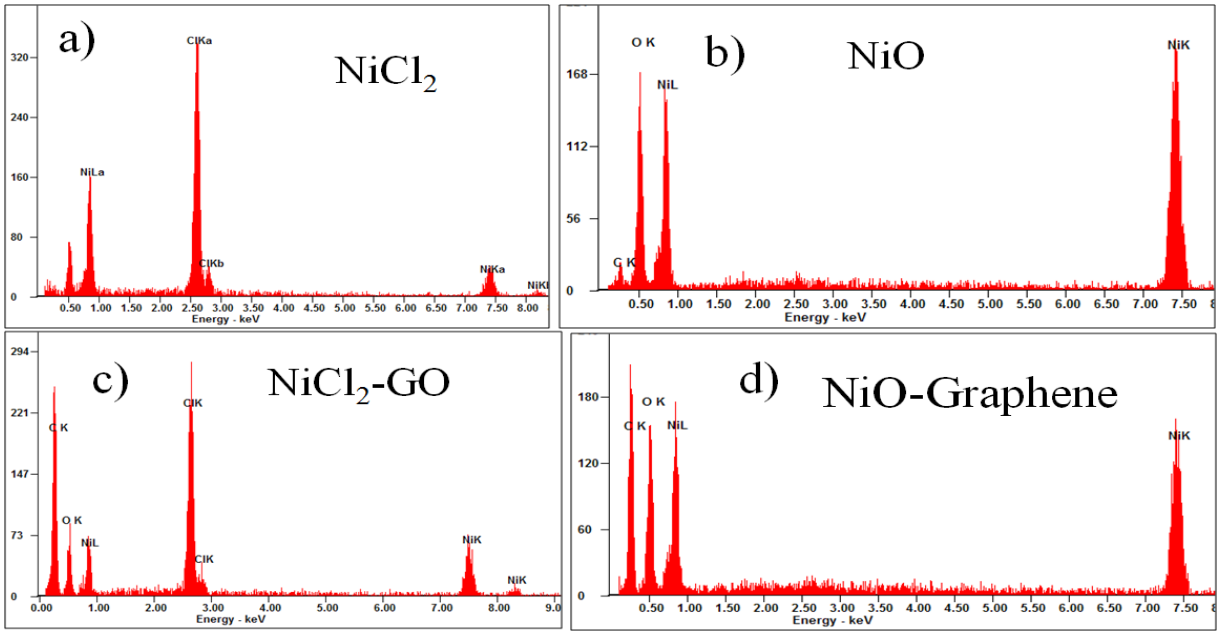


Figure S4-3. EDX spectra of silver chloride, silver nanoparticles, silver chloride-GO composite and silver nanoparticles dispersed solar graphene.

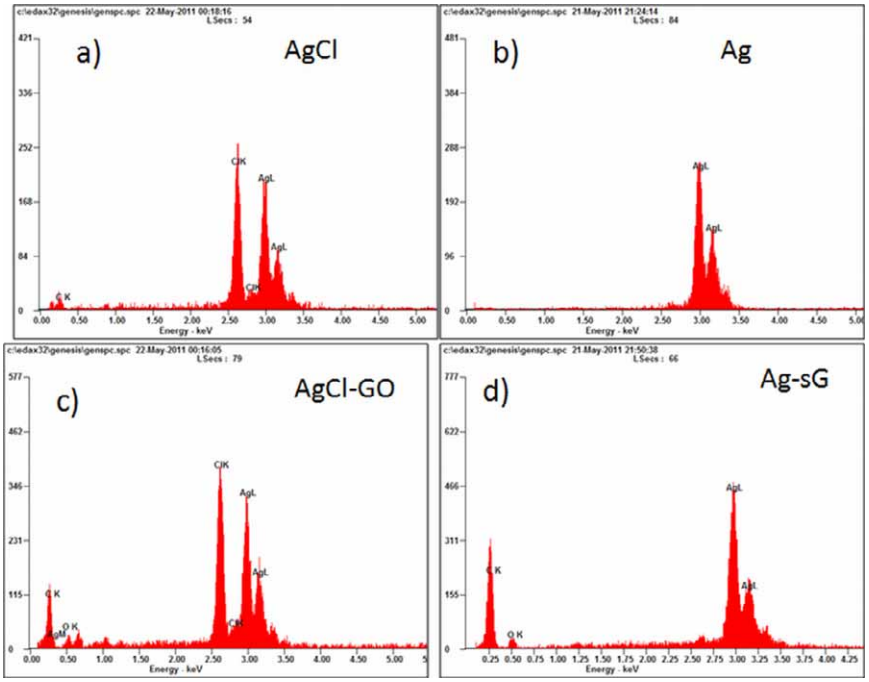


Figure S5. Raman spectra of silver-graphene, silver nanoparticles, nickel oxide-sG and nickel nanoparticles.

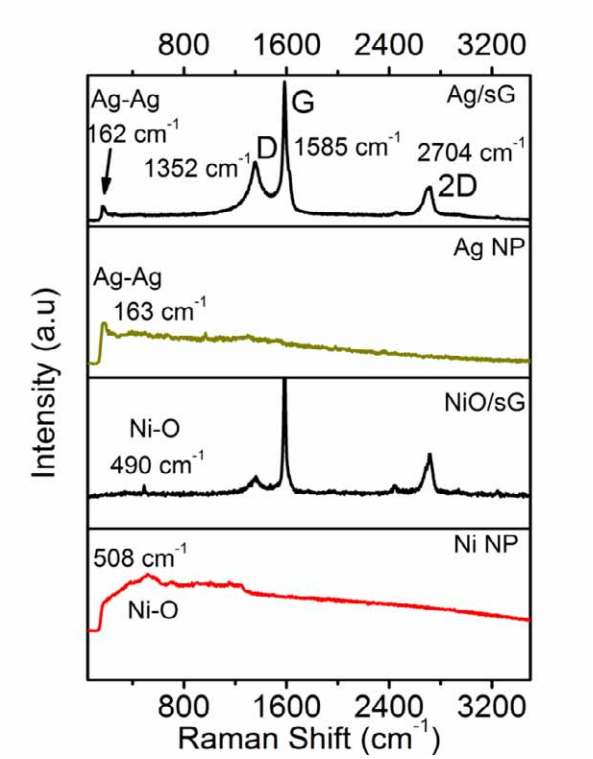


Table 1: Comparison of atomic % of chlorine in metal salts before and after focused solar irradiation.

Before focused solar radiation		**After focused solar radiation**
Metal salt	Chlorine (at%)	Chlorine (at%)
$NiCl_2$	58.6	~1
$AuCl_3$	76.5	~0.66
$CuCl_2$	68.1	~0.5
$FeCl_2$	64.98	~0
AgCl	48.4	~0

Table 2: Comparison of the amount of chlorine and oxygen in metal/metal oxide/graphene composites after being exposed to focused solar radiation.

After focused solar irradiation		
Metal-graphene	***Chlorine (at%)***	***Oxygen (at%)***
CuO-graphene	~0.4	2.9
Au-graphene	~1	3
NiO-graphene	~1.2	~7
Fe_2O_3-graphene	~0.9	~10
Ag-graphene	~0	~4

References

1. W. S Hummers and R.E. Offeman, J. Am. Chem.Soc.80, (1958) 1339.