Electronic Supplementary Material (ESI) for RSC Advances
This journal is © The Royal Society of Chemistry 2014

Supplementary Information

Green synthesis of thiolated graphene nanosheets by Alliin (garlic) and its effect on the deposition of gold nanoparticles

Sarvesh Kumar Srivastava,[a] Chiaki Ogino[a] and Akihiko Kondo*[a]

[a]Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, 1-1 Rokkodai-cho, Nada, Kobe, 657-8501, Japan.
E-mail: akondo@kobe-u.ac.jp

1. Experimental

1.1 Surface modification of graphene

Alliin and Graphene Oxide (GO) were purchased from Sigma Aldrich (Japan). 4 mg of alliin was dissolved in 2 mL of H_2O:EtOH (95:5 v/v) in plastic vials and sonicated till dissolved completely. To this alliin solution, 5 mg GO were introduced and sonicated for 30 minutes. The GO-alliin mixture was then heated at 100°C for 3 hours in sealed vials. Care should to be taken to seal the plastic vials properly as subsequent heating may resulting in accidental spillage.
This reaction mixture was sonicated for 15 seconds at every hour to homogenize the reaction solution. Excess of alliin solution was removed from the reaction mixture by centrifugation at 3500 × g for 5 minutes. Finally, the obtained organosulfur modified GNS (to be referred as OS-GNS) was dried at 60 °C and stored for further use.
At this stage, a notable color shift between GO and OS-GNS can be observed by the color change from brownish tint to black.

1.2 Synthesis and attachment of gold nanoparticles over modified GNS

Gold nanoparticles were prepared by the reaction of $HAuCl_4$ and citric acid. In a typical experiment, 0.016 g of $HAuCl_4$ and 0.019g citric acid, both dissolved separately in 5 mL of milliQ H_2O were stirred together for 60 minutes to produce Au NPs. These Au NPs were then allowed to stand overnight before being added drop-wise into the dispersion of OS-GNS to make sure that no Au NP attachment happens due to seeding over the graphene surface. 2mL of Au NP solution was added to 2 mg of OS-GNS in a clean plastic vial.

This dispersion was vigorously stirred at room temperature for 1 h to complete Au NP surface attachment. After this procedure, solid phase was separated by centrifugation (3500 × g for 10 min) and washed six times with milliQ water to remove any non-linking Au NPs over the OS-GNS surface. Finally, we obtained our desired product of OS-GNS decorated with Au NPs (Au-OS-GNS) which was dried at 60 °C and stored away from light in a vacuum desiccator. As a control test, same procedure of Au NP deposition was performed with pristine GO (referred as GO+Au NPs).

This journal is © The Royal Society of Chemistry 2014

1.3 Characterization studies

Preliminary analysis of Au NP deposition over the organosulfur modified GO surface was done by NanoDrop 3300 Fluorospectrometer operated at 400 nm – 600 nm with relative fluorescence units (RFU) at 540 nm.

GO – with and without Au NP attachment dispersed in H_2O were transferred to carbon coated grid for transmission electron microscopy (TEM) measurements by Joel JEM 1011 electron microscope operated at 200 kV r. Images obtained were analysed using ImageJ 1.43M software.

Transmission mode Fourier transform infrared (FT-IR) spectroscopy was carried out for using Jasco FTIR-680 plus coupled to a high performance computer. The results reported here were obtained from 200 scans at a 4 cm^{-1} resolution. Confirmatory analysis for sidewall addition of S-linkages/thiol onto CNT surface was done by X-ray photoelectron spectroscopy (XPS) obtained from JEOL JPS9010 MC photoelectron spectrometer operating at 10 kV and 30 mA. The results obtained were analysed by SpecSurf ver. 1.7.3.9 software.

This journal is © The Royal Society of Chemistry 2014

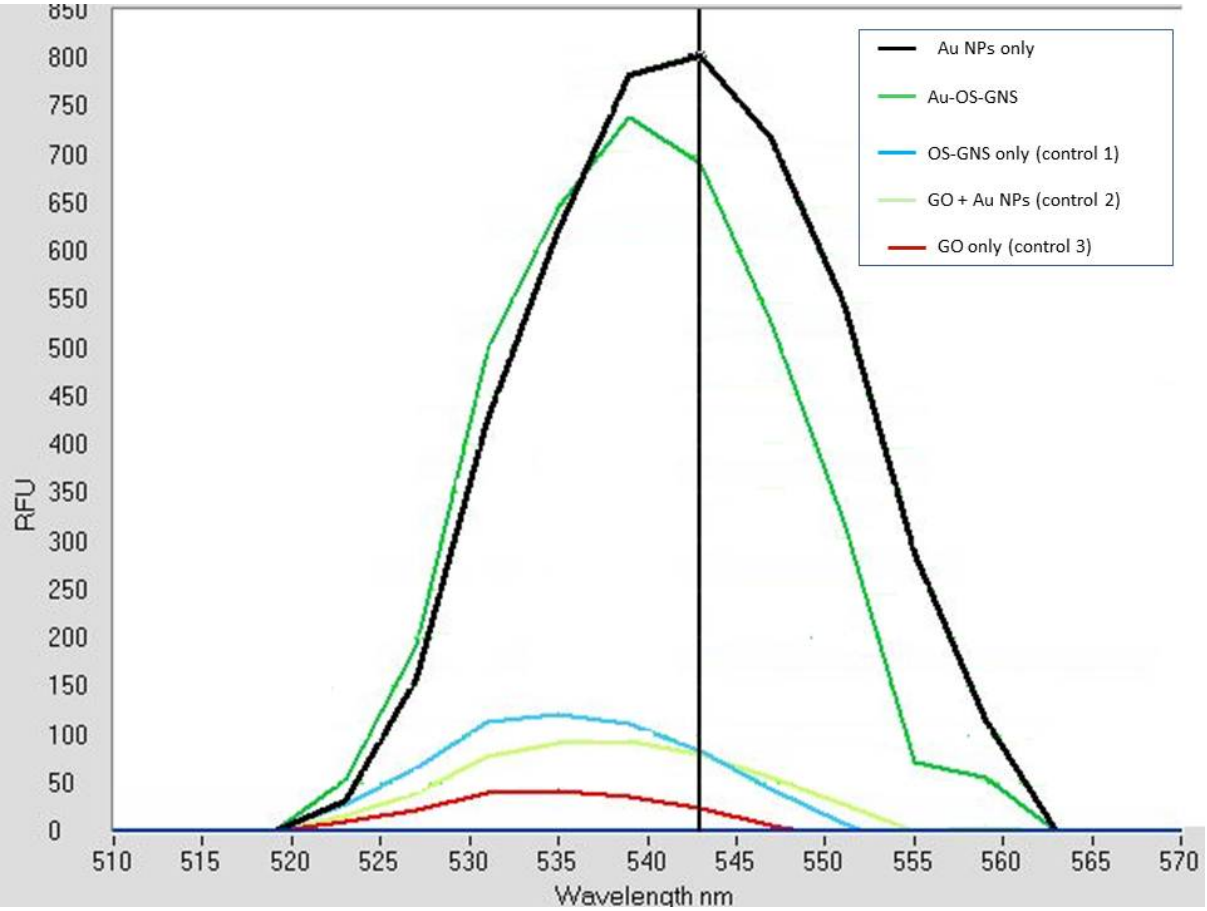

Figure S1. Vis-spectra of all reaction and control mixtures for the presence/absence of L-SPR at 540 nm.

In figure S1, L-SPR was clearly observed in case of Au NPs and Au-OS-GNS (after washing) at 540 nm. No such pattern was observed in our controls (sonicated aqueous solution dispersions): pristine GO, OS-GNS only and GO+Au NPs (without alliin treatment). All the control underwent same washing/sonication conditions as of reaction mixture thereby confirming that no Au NP attachment is taking place in absence of alliin treatment.

Most importantly, this study also indicates that no Au NP particle attachment is observed due to seeding over the GO substrate and thereby indicating that overnight Au NP storage resulted in stable nanoparticle formation.

This journal is © The Royal Society of Chemistry 2014

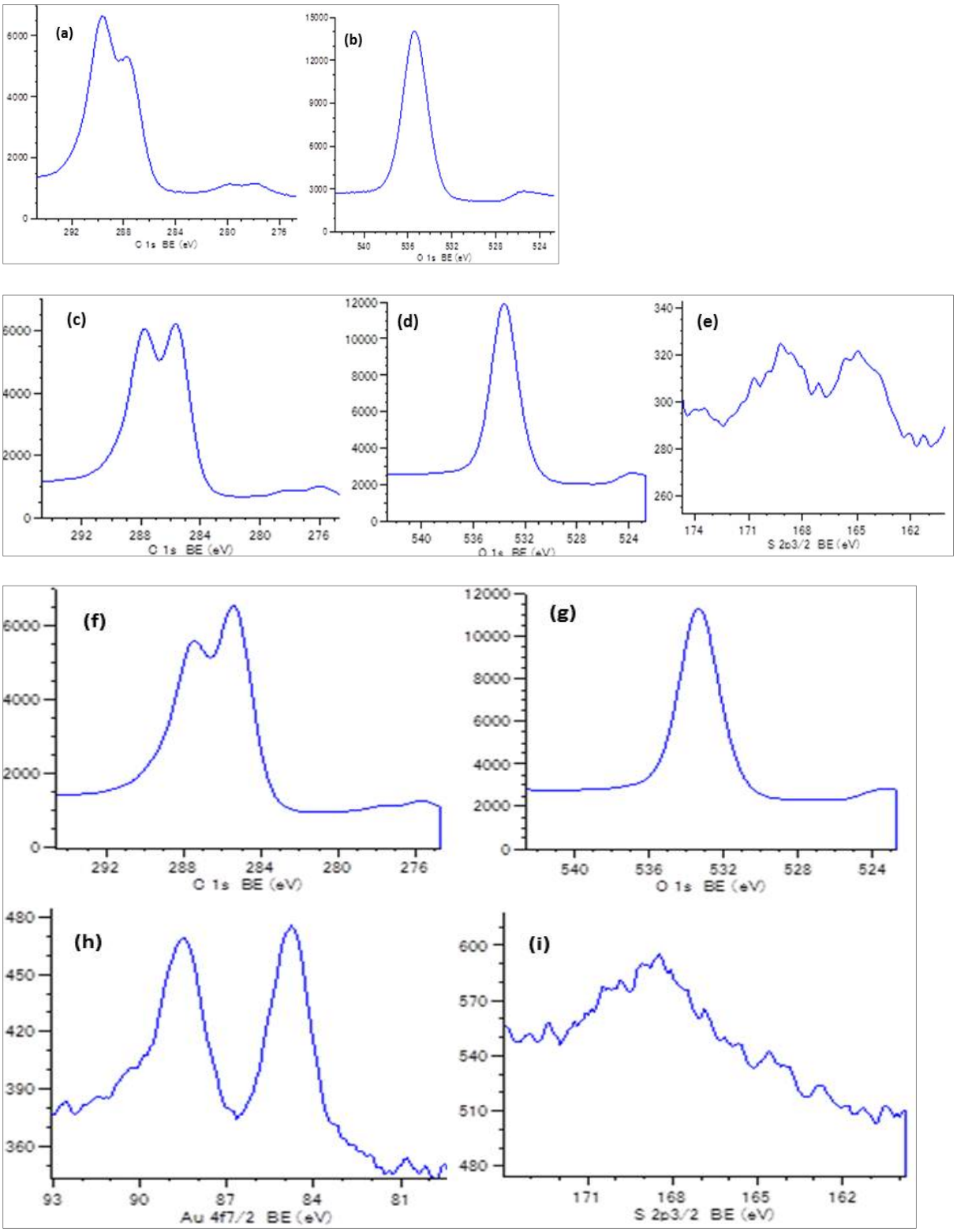

Figure S2. Showing XPS spectra of pristine GO (a) C1s, (b) O1s;
OS-GNS at (c) C1s, (d) O1s (e)S2p;
Au-OS-GNS at (f) C1s, (g) O1s, (h) Au4f, (i) S2p