

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

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A novel green one-pot approach for surface modification of graphene oxide into organosulfur modified graphene nanosheets (OS-GNS) is being reported. Alliin (garlic phytochemical) mediated organothiol linkages over OS-GNS facilitated one-step attachment of pre-synthesized gold nanoparticles. In absence of alliin treatment, no Au NP attachment was observed.

Graphene has attracted tremendous attention and vast amounts of research for various applications within a decade.¹ This relatively new two-dimensional nanomaterial comprising of sp²-bonded carbon atoms promises to be the next generation building block for composite materials.² Attachment of nanoparticles on graphene has offered greater opportunities in application of graphene oxide (GO) and graphene nanosheets (GNS).^{3–5} Several chemical methods for surface modification of graphene⁶ have been reported including exfoliation by chemicals/strong acids,⁷ sheet formation by carbon vapour deposition (CVD)⁸ and thermal reduction of GO under high temperature conditions.⁹ Also, non-covalent functionalization techniques exploit π - π stacking of graphene sheets *via* peptides,¹⁰ surfactants¹¹ and direct reduction of metal salts¹² in presence of GO. However, direct in-situ reduction of metallic salts over GO sheets has resulted in poor control over the particle size and morphology thereby affecting metal-GO composite properties in general.¹³ Therefore, there is an urgent need for providing eco-friendly alternative for graphene functionalization without using toxic chemicals, excessive solvents, expensive instruments and tedious process control. Here, we report a unique green functionalization technique for GO surface modification *via* alliin (3-(2-propenylsulfinyl)alanine) under ambient temperature conditions in aqueous solution and its effect on gold nanoparticle attachment. In our previous

research, we reported that organosulfur compounds in garlic particularly alliin/allicin are responsible for carbon nanotube surface thiolation and subsequent attachment of Au NPs.¹⁴ In this study, we extended the application of alliin^{15–17} found in garlic cloves (*Allium sativum*) in preparation of thiolated-GO from GO and subsequent attachment of Au NPs. Gold was selected as an ideal recipient for S-linkages attachment¹⁸ (like thiol) along with several potential applications in catalysis, optics and nanobiotechnology.¹⁹

Graphene oxide and alliin (AR grade) were commercially obtained. To modify GO, 4 mg of alliin was dissolved in 2 mL of H₂O–EtOH (95 : 5 v/v) in plastic vials and sonicated until dissolved completely. To this alliin solution, 5 mg of GO was introduced and sonicated for 30 minutes. This GO–alliin mixture was then heated at 100 °C for 3 hours in sealed vials. 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 to as OS-GNS) was dried at 60 °C and stored for further use.

Gold nanoparticles were prepared by the reaction of HAuCl₄ and citric acid. In a typical experiment, 0.016 g of HAuCl₄ and 0.019 g citric acid, both dissolved separately in 5 mL of milliQ H₂O were stirred together for 60 minutes to produce Au NPs.²⁰ 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.²¹ This dispersion was vigorously stirred at room temperature for 1 h to complete Au NP surface attachment. After this procedure, the solid phase was separated by centrifugation (3500 × *g* for 10 min) and washed six times with milliQ water to remove any non-linked 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.

Preliminary analysis of Au NP deposition over the modified GNS surface was carried out by observing characteristic localized surface plasmon resonance peak (L-SPR) at 540 nm. GO

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with and without Au NP attachment dispersed in H₂O–EtOH was also analysed by transmission electron microscopy (TEM). Finally, confirmatory analysis for surface modification and subsequent organosulfur addition onto the GNS surface was done by X-ray photoelectron spectroscopy (XPS). Both Au NPs and Au–OS-GNS samples showed distinct localized SPR peak at around 540 nm when laser excitation was made in the white light region as shown in Fig. 1. This characteristic absorbance at 520–540 nm suggests the presence of gold nanoparticles linked over the GNS surface. The L-SPR peak remained after vigorous sonication and repeated washing. No L-SPR peak was otherwise observed in the control sample consisting of GO only and OS-GNS sample.

This preliminary result indicated that Au NPs are attached onto the GNS surface resulting in the formation of Au–OS-GNS. Also, retention of optical absorption spectra suggested that there is no adverse influence on nanoparticles. The TEM image of Au–OS-GNS was compared with the control as shown in Fig. 2.

Fig. 2b (Au–OS-GNS) clearly shows Au NPs attached on to the alliin modified GNS sheets while no such attachment was observed in the control sample. Several Au NPs in the size range of 60–80 nm were found to be adhered to alliin treated GO sheets (OS-GNS). Further, GO, OS-GNS and Au–OS-GNS were analysed by FTIR (Fourier Transform Infrared spectroscopy) as shown in Fig. 3. The FTIR spectra were analysed for different densities of oxygen functionalities present at the surface of GO, OS-GNS, and Au–OS-GNS. The absorption band corresponding to the C=O carbonyl and carboxyl stretching was represented at 1706 cm⁻¹ and 1251 cm⁻¹ respectively.^{22,23} The C–O (epoxy) and C–O (alcoxy) stretches were at 1251 cm⁻¹ and 1057 cm⁻¹ respectively.²⁴ Note that all the spectra showed a C=C peak centred around 1550–1650 cm⁻¹ corresponding to the remaining sp² character of the C-linkages. It is evident that oxygen functionalities decreased drastically in the case of OS-GNS and Au–OS-GNS. Both the reaction samples showed a decrease in C=O functionalities in particular, suggesting decreased oxygen double bond character in GNS post-alliin treatment.

XPS analysis was done to further study the surface of each graphene substrate (GO, OS-GO and OS-GNS–Au) and confirms the chemical groups responsible for Au NP attachment. Although the presented C1s spectra (Fig. 4a) and O1s (Fig. 4b) can be further divided into smaller components to precisely

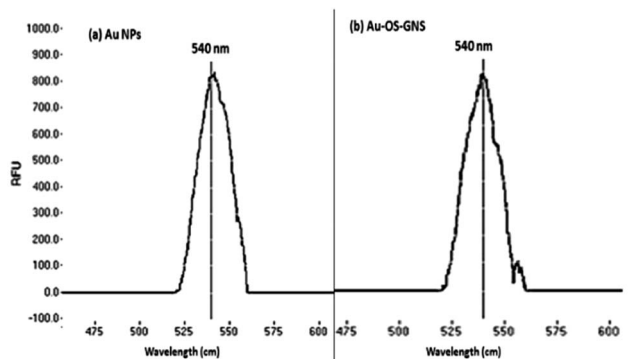


Fig. 1 L-SPR observation of (a) Au NPs; (b) Au–OS-GNS.

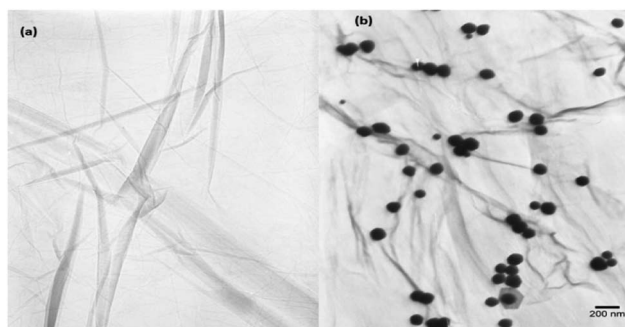


Fig. 2 TEM images of (a) GO (control); (b) Au–OS-GNS.

allocate the different bonding regions, for the ease of comparison and data interpretation, we intended it be unaltered. In the present case (Fig. 4a), pristine GO sheets exhibit a C 1s spectrum at 288.4 eV and 286.2 corresponding to O=C–OH/C=O and C–O groups respectively.²⁵

This C 1s spectrum of GO sheets when compared with OS-GNS and Au–OS-GNS clearly confirmed a major peak shift from a carbon–oxygen bond majority to a carbon–carbon bond majority (the binding energy of C 1s spectrum shifted from higher energy to lower energy). The same was highlighted by FT-IR analysis.

The O=C–OH peak region arising due to the carboxylate carbon was completely absent in OS-GNS and Au–OS-GNS with the appearance of prominent C–C/C=C at lower energy regions. The C 1s spectra of OS-GNS showed two major peaks at 285.8 and 283.5 corresponding to singlet C-bound oxygen moieties like C–OH and C–C/C=C respectively.²⁶ Similarly, Au–OS-GNS (Fig. 4c) showed two major peaks at 286.3 eV and 283.1 eV corresponding to singlet C–O and C–C/C=C bonds. Both reaction mixtures (OS-GNS and Au–OS-GNS) showed an absence of peaks at higher binding energies in the C 1s spectrum suggesting that –C=O and –O=C–OH groups are absent once GO is treated with alliin.

This decrease in oxygen bonded groups in GO and its subsequent reduction to GNS was also confirmed when the O 1s

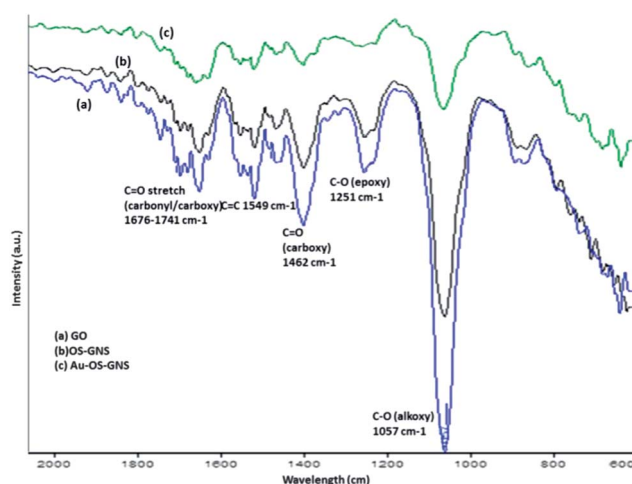


Fig. 3 FT-IR spectra of (a) GO; (b) OS-GNS; (c) Au–OS-GNS.

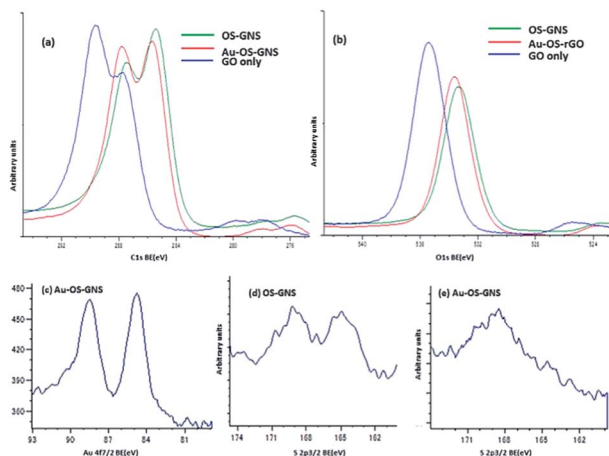


Fig. 4 XPS spectra of (a) C 1s region; (b) O 1s region; (c) Au 4f region in Au-OS-GNS; (d) S 2p region in OS-GNS; S 2p region in Au-OS-GNS.

spectrum of the reaction and control mixtures were compared. Fig. 4b shows a comparison of the O1s spectrum of GO with OS-GNS and Au-OS-GNS. A distinct peak shift and decrease in intensity was observed when GO (con) at 535.4 eV was compared with GNS and Au-OS-GNS at 533.6 and 533.3 respectively. The relative decrease in O1s peak intensity and peak shift towards lower BE values clearly suggest that GO has successfully undergone partial reduction with formation of graphene sheets (GNS). It should be noted that the essence of reduction is the transformation of sp^3 -C to sp^2 -C. Also, the presence of single bonded oxygen groups over the GO surface reduces the van der Waal's forces between the C-layers and improves the stability and facilitates easy exfoliation of GO into monolayers for subsequent chemical reduction.

To further confirm Au NP particle attachment, Au 4f and S 2p bands were observed in OS-GNS and Au-OS-GNS. OS-GNS after treatment with Au NP solution (Au-OS-GNS) showed the distinct presence of Au NPs linked to the resulting Au-OS-GNS nanocomposite surface as evidenced in Fig. 4c. In Fig. 4c, XPS peaks at 84.7 eV and 88.5 eV correspond to Au NPs present over the OS-GNS sheets in the metallic state. Also, a change in the peaks was observed in the S 2p region in the case of OS-GNS and Au-OS-GNS which were responsible for Au NP attachment as shown in Fig. 4d and e. It is interesting to note that in the case of OS-GNS, the S 2p component clearly showed two peaks at 169.2 eV and 164.9 eV. Characteristic oxygen-sulfur interactions are generally observed at higher energy levels at around 168 eV in the case of natural organosulfurs. The lower binding energy around the 164 eV region corresponds to characteristic thiocarbonyl-sulfhydryl interactions. The S2p component of OS-GNS when compared with Au-OS-GNS showed the absence of free thiocarbonyl linkages over OS-GNS at around 164 eV²⁷ and peak shifting of organothiol groups (168.4 eV) due to S-linked interactions with Au NP. This clearly demonstrates that the resulting Au-OS-GNS was being formed by attachment of Au NPs *via* virtue of these organothiol interactions imparted over the OS-GNS surface by alliin treatment. Similar results were reported by Nakamura *et al.*²⁸ for carbon surface modification

via elemental sulfur and subsequent interaction with Au NPs. Based upon our initial observations, a free-radical mechanism comprising of (H_3C-O-S^*) and ($HC^*=S$) resulting from thermal decomposition of alliin into methyl methane thiosulfonates²⁹ may be responsible for this reaction. The thiolated GNS obtained as the end-product can then be used for Au NPs deposition over the modified OS-GNS surface. This preliminary study highlights the chemical modification of graphene oxide by a natural phytochemical and adds valuable information to the ever growing community of biogenic/biomimetic materials. It is interesting to note that very recently, a few research works have been reported suggesting the use of natural products³⁰⁻³² in surface modification of graphene but no study until now claimed one-step thiolation or subsequent nanoparticle attachment.

Conclusion

In summary, we have demonstrated one-step thiolation of graphene and subsequent preparation of a Au-graphene nanocomposite by a green process *via* garlic plant extract (alliin). As per our knowledge, this is the first study to effectively utilize plant phytochemicals for rapid thiolation of graphene oxide under moderate temperature conditions. Finally, an interdisciplinary research will aid in better understanding of the underlying mechanism this bio-inspired material may possess and offers a promising sustainable alternative for Au-graphene nanocomposite production.

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