

## A general strategy to prepare graphene-metal/metal oxide nanohybrids†

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Graphene sheets decorated with metal/metal oxide nanoparticles are gaining increasing attention. In this study, sulfhydrylated graphene was prepared by reducing the sulfonic acid groups on sulfonated graphene to thiol groups. We evaluated its ability to anchor different metal/metal oxide nanoparticles by simply mixing the sulfhydrylated graphene with the corresponding pre-prepared metal/metal oxide nanoparticles. The sulfhydrylated graphene and its nanohybrids were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS). We demonstrate that the obtained sulfhydrylated graphene can act as a general platform to anchor different kinds of metal/metal oxide nanoparticles with different shapes, structures or properties through thiol–metal bonds. These novel hybrids will render graphene with additional interesting properties and potential applications.

## Introduction

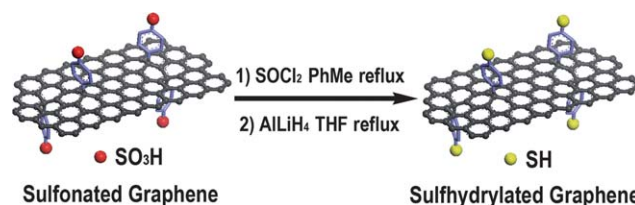
Graphene-based nanohybrids, especially graphene-metal/metal oxide nanohybrids, have potential applications in lithium storage materials, biosensor devices, heterogeneous catalysts, photo-thermal materials, composite reinforcement and solar cells, *etc.*<sup>1–14</sup> Recently, Yang *et al.* prepared graphene-encapsulated metal oxide hybrids by the co-assembly of negatively-charged graphene oxide and positively-charged metal oxides, which lead to a remarkable lithium storage performance.<sup>2</sup> Du and co-workers have prepared gold-graphene hybrids by electrodepositing Au ions to amplify electrochemical signals, and they could act as biosensors for the electrochemical detection of DNA-specific sequences.<sup>5</sup> Wang *et al.* have prepared graphene-Al<sub>2</sub>O<sub>3</sub> nanohybrids by directly depositing Al<sub>2</sub>O<sub>3</sub> nanoparticles on the surface of graphene sheets in the gas phase by atomic layer deposition.<sup>6</sup> Ourselves and the others have prepared graphene-metal/metal oxide nanohybrids by the *in situ* reduction of graphene oxide and corresponding metal ion precursors. The obtained nanohybrids could be successfully used as efficient heterogeneous catalysts in the Suzuki reaction and the degradation of dyes, *etc.*<sup>8–10</sup> By these methods, the amount and size of the metal/metal oxide nanoparticles on graphene can be controlled by altering the stoichiometric ratio, reaction

temperature and other experimental conditions. Metal/metal oxide nanoparticles with different shapes and structures, such as Au nanorods, have extraordinary properties and promising applications.<sup>15–18</sup> Their hybrids with graphene will endow upon graphene additional properties and potential applications. However, it is still an impossible task to prepare graphene-metal/metal oxide nanoparticle nanohybrids with controllable shapes and structures by existing methods. In this paper, we report a general strategy to fulfil this task. Considering that methods to prepare metal/metal oxide nanoparticles with desired shapes and structures are well established, we prepared sulfhydrylated graphene to anchor different metal/metal oxide nanoparticles with the strong thiol–metal bonds that are stable in a wide variety of temperatures, solvents and potentials.

Recently, we successfully prepared sulfonated graphene, with its surface being uniformly anchored with abundant phenyl-SO<sub>3</sub>H groups by covalent attachment, and proved its potential applications as a highly efficient water tolerant solid acid catalyst.<sup>19</sup> Later experiments revealed that the C–C bonds between the sulfonic acid containing aryl and the graphene were so strong that they could endure harsh reduction conditions, and the

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† Electronic supplementary information (ESI) available: Scanning electron microscope images, C 1s electron region of the X-ray photoelectron spectrum and a photograph of the graphene solution; TEM images of graphene-Au nanorods hybrids with different dosages; the XPS S2p peaks of graphene-Au hybrids and their corresponding TEM images; the fitting of the XPS S2p peaks. See DOI: 10.1039/c1jm12970h



**Scheme 1** Illustration of the preparation of sulfhydrylated graphene from sulfonated graphene.

terminated sulfonic acid groups could be successfully reduced to thiol groups by lithium aluminum hydride (Scheme 1).

## Experimental

### Preparation of sulfhydrylated graphene

The sulfonated graphene precursor was prepared by directly anchoring sulfonic acid-containing aryl radicals to the surface of reduced graphene.<sup>19</sup> Then, the  $-\text{SO}_3\text{H}$  groups were reduced by lithium aluminum hydride ( $\text{AlLiH}_4$ ) after chlorosulfonylation.<sup>20</sup> In brief, the prepared sulfonated graphene (60 mg) was added to a mixture of toluene (15 mL) and thionyl chloride (4 mL). Several drops of dimethylformamide (DMF) were then added as a catalyst and the mixture refluxed for 10 h to prepare the chlorosulfonylated graphene.

The resulting mixture was washed with tetrahydrofuran (THF) several times and the chlorosulfonylated graphene finally dispersed in THF (15 mL). Lithium aluminum hydride (0.5 g) was then added and refluxed for 8 h. After the reaction was complete, the reaction was quenched with 1 M HCl, and the resulting suspension was centrifuged and washed several times with 1 M HCl to remove the Al and Li ions. The yielded suspension was dialyzed for 48 h to obtain a purified sulfhydrylated graphene suspension. The sulfhydrylated graphene was placed in an oxygen free environment to avoid oxidization.

### Preparation of metal/metal oxide particles

The cubic and rod structured gold particles were grown from spherical Au nanoparticles, which acted as seeds, according to research described by Sau *et al.* and Nikoobakht *et al.*, respectively.<sup>21,22</sup> In summary, Au seeds were prepared by the reduction of  $\text{HAuCl}_4$  (0.25 mL, 10 mM) by ice-cooled  $\text{NaBH}_4$  (0.6 mL, 10 mM) in the presence of CTAB (7.5 mL, 0.1 M). Au nanocubes were formed in a growth solution (10 mL) containing CTAB (1.6 mL, 0.1 M),  $\text{HAuCl}_4$  (0.4 mL, 10 mM),  $\text{AgNO}_3$  (60  $\mu\text{L}$ , 10 mM), ascorbic acid (64  $\mu\text{L}$ , 0.1 M) and Au seeds (5  $\mu\text{L}$ ,  $2.5 \times 10^{-5}$  M). Au nanorods were formed in a growth solution containing CTAB (4.75 mL, 0.1 M),  $\text{HAuCl}_4$  (0.2 mL, 10 mM),  $\text{AgNO}_3$  (60  $\mu\text{L}$ , 5 mM), HCl (0.5 mL, 0.1 M), ascorbic acid (32  $\mu\text{L}$ , 0.1 M) and pre-prepared Au seeds (10  $\mu\text{L}$ ). Spherical gold nanoparticles were prepared in a microwave reactor. Briefly, a trisodium citrate solution (2.5 mL, 38.8 mM) was added to de-ionized water (20 mL) with vigorous stirring; then, a  $\text{HAuCl}_4$  solution (0.25 mL, 10 mM) was added and reacted in the microwave reactor (373 K, 300 W) for 10 min.

Ag particles were prepared by the reduction of  $\text{AgNO}_3$ . In brief,  $\text{AgNO}_3$  (0.25 mL, 10 mM) was added to de-ionized water (20 mL) containing a trisodium citrate solution (2 mL, 38.8 mM). After stirring for 30 min, ice-cooled  $\text{NaBH}_4$  (1.0 mL, 10 mM) was added dropwise to the solution.  $\text{Fe}_3\text{O}_4$  particles were prepared by a modified co-precipitation method.<sup>23</sup>  $\text{FeCl}_3$  (0.2 mL, 10 mM) and  $\text{FeCl}_2$  (0.1 mL, 10 mM) were added to de-ionized water (20 mL). Under ultrasonic and gas protective conditions, an ammonia solution (1 mL, 25%) was added dropwise.

All of the prepared nanoparticles were centrifuged and washed with de-ionized water several times to remove stabilizer and unreacted metal ions.

## Characterization

Sulfhydrylated graphene and its hybrids were characterized by scanning electron microscopy (SEM) (Hitachi S4800), energy dispersive X-ray spectroscopy (EDS) (Hitachi S4800), high resolution transmission electron microscopy (HRTEM) (Philips Tecnai G2 F20) and X-ray photoelectron spectroscopy (XPS) (Perkin-Elmer, PHI 1600 spectrometer), and the gold spheres were prepared by a microwave reactor (Sineo, MAS-II).

## Results and discussion

X-Ray photoelectron spectroscopy (XPS) was used to determine the amount and valence states of the element S. As compared with the results of the full range XPS spectra in Fig. 1a and b, the O/C atomic ratio of the sulfonated graphene significantly decreased with a sulfur signal remaining ( $\sim 2.07\%$  atom percentage), suggesting the conversion of the  $-\text{SO}_3\text{H}$  to  $-\text{SH}$  groups. This speculation is associated with the results from the S 2p XPS spectra. As shown in Fig. 1a (inset), the sulfonated graphene shows a single S 2p peak at 167.8 eV, corresponding to the  $-\text{SO}_3\text{H}$  groups.<sup>19,24</sup> After reduction, however, it splits into two adjacent peaks with the dominant one at 163.7 eV (corresponding to  $-\text{SH}$  groups),<sup>25,26</sup> demonstrating that most the  $-\text{SO}_3\text{H}$  groups on the sulfonated graphene precursor have been successfully converted to  $-\text{SH}$  groups. According to a calculation of the peak area, the transformation extent of the  $-\text{SO}_3\text{H}$  groups from the sulfonated graphene precursor is about 75%.

This result is further supported by scanning electron microscopy (SEM) and quantitative energy dispersive X-ray spectroscopy (EDS) element mapping (Fig. 2). Compared with the sulfonated graphene precursor,<sup>19</sup> the obtained sulfhydrylated graphene shows a similar two-dimensional layer structure (Fig. S1, see ESI†) and homogeneous distribution of the element S (the S signal of the obtained sulfhydrylated graphene should come from both the  $-\text{SH}$  and  $-\text{SO}_3\text{H}$  groups), whereas the element O significantly decreases (due to the transformation of  $-\text{SO}_3\text{H}$  to  $-\text{SH}$  groups). Further reduction of trace epoxide, hydroxyl and carboxyl groups on the sulfonated graphene precursor may also contribute to the decrease of the element O.

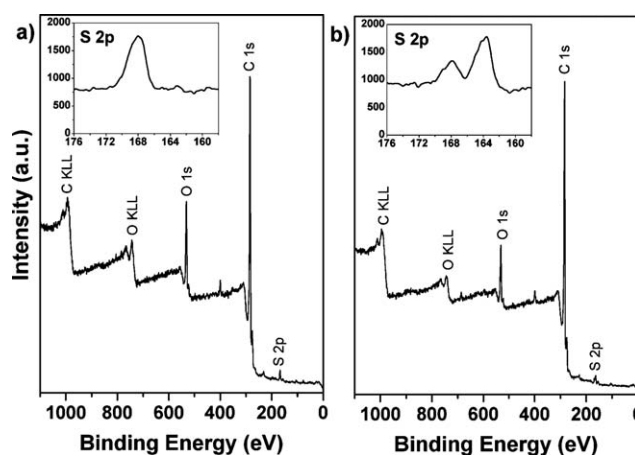
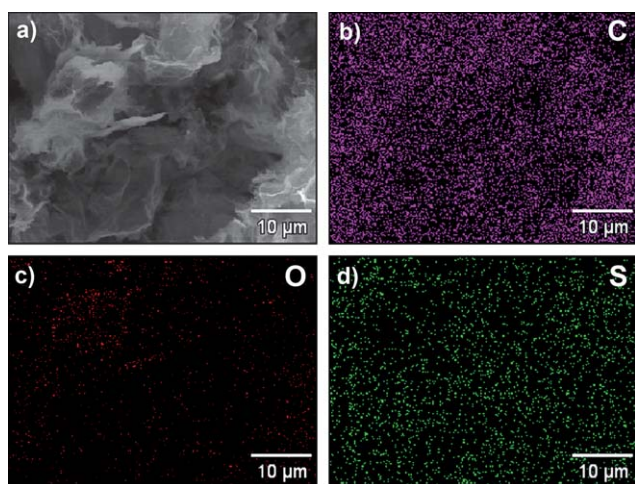


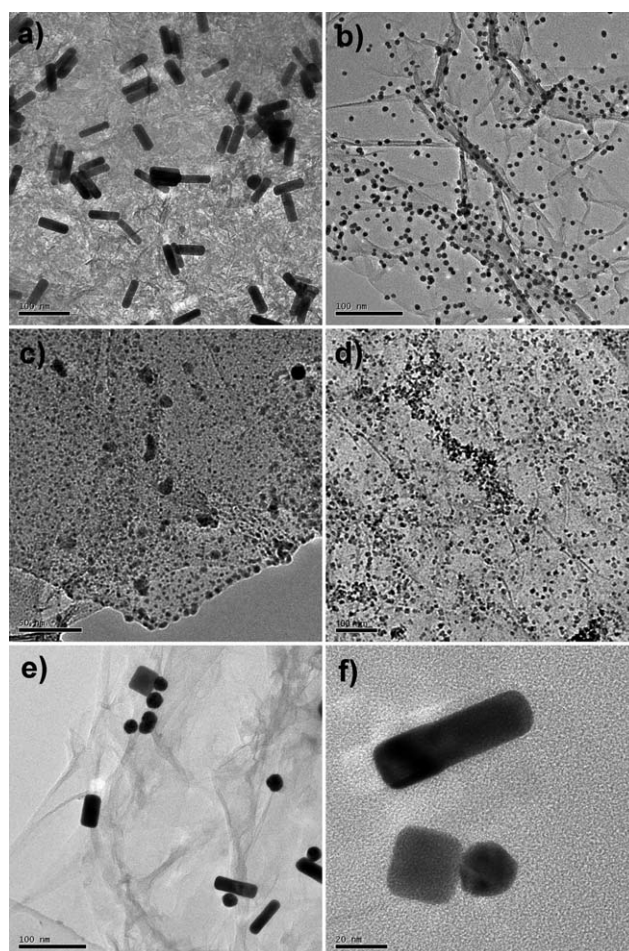
Fig. 1 XPS spectra of the sulfonated graphene (a) and sulfhydrylated graphene (b).



**Fig. 2** SEM image of the sulfhydrylated graphene (a) and the corresponding quantitative EDS element mapping of C (b), O (c) and S (d).

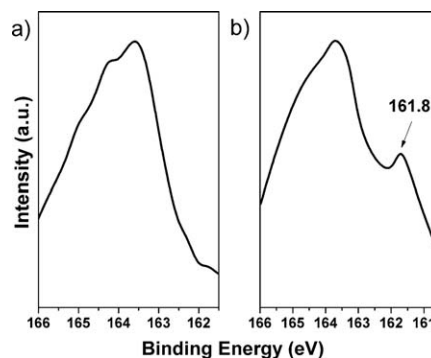
However, this contribution can be neglected when considering the difficulty of further reduction and the XPS C 1s spectra before and after the reduction (Fig. S2, see ESI†), which demonstrate that the amount of these residual oxidation functional groups on the sulfhydrylated graphene remain the same. Combining the results of XPS and EDS, the amount of thiol groups were calculated; about eight six-membered carbon rings of the graphene sheet correspond to one thiol group on the sulfhydrylated graphene sheet.

As the sulfhydrylated graphene was successfully prepared, we evaluated its ability to anchor different metal/metal oxide nanoparticles by simple mixing. Due to the successful conversion of hydrophilic  $-\text{SO}_3\text{H}$  to hydrophobic  $-\text{SH}$ , the obtained sulfhydrylated graphene showed an impressive dispersibility in ethanol, while it was difficult to disperse it in water (Fig. S3a–d, see ESI†). By simply mixing water dispersions of the sulfhydrylated graphene and the desired pre-prepared metal/metal oxide nanoparticles (Au nanorod, Au/Ag/ $\text{Fe}_3\text{O}_4$  nanoparticles are used) under ultrasonic conditions, we successfully prepared graphene-Au nanorods and graphene-Au/Ag/ $\text{Fe}_3\text{O}_4$  nanoparticle hybrids (Fig. 3a–d), proving that the prepared sulfhydrylated graphene can act as a general platform to anchor different kinds of metal/metal oxide nanoparticles. Notably, the nanoparticles were uniformly distributed on the graphene surface, matching with the above EDS mapping results, and no free Au nanorods escaped capture by the thiol groups on the sulfhydrylated graphene (Fig. S3e–f, see ESI†). In addition, the specific composition of the graphene-Au nanorod hybrid could be easily controlled by changing the dosage of Au nanorods and sulfhydrylated graphene (Fig. S4, see ESI†). XPS analysis (Fig. 4) revealed that the S 2p peak of the  $-\text{SH}$  groups (163.7 eV) on the sulfhydrylated graphene formed a shoulder peak at a lower binding energy (161.8 eV) after mixing with Au nanoparticles due to the formation of abundant S–Au covalent bonds (see Fig. S5 and S6 in ESI† for detailed discussions).<sup>25,26</sup> As a general platform, the sulfhydrylated graphene could also be used to prepare various designed graphene-metal/metal oxide



**Fig. 3** TEM images of the graphene-Au nanorod hybrid (a), graphene-Au nanoparticle hybrid (b), graphene-Ag nanoparticle hybrid (c), graphene- $\text{Fe}_3\text{O}_4$  nanoparticle hybrid (d) and the designed hybrid of graphene with Au nanorod, nanocube and nanosphere particles (e, f).

nanoparticle nano hybrids with multifunctional properties. For example, as shown in Fig. 3e–f, simply by mixing the Au nanorod, nanocube and nanosphere particles resulted in complicated graphene-nanoparticle hybrids.



**Fig. 4** The XPS S 2p spectrum of the sulfhydrylated graphene before (a) and after (b) mixing with Au nanoparticles.

## Conclusions

In summary, we have successfully prepared sulfhydrylated graphene by reducing sulfonated graphene with lithium aluminum hydride. This new derivative is an ideal platform for graphene to anchor different metal/metal oxide nanoparticles through strong thiol–metal bonds. The strategy reported here provides a general way to prepare different graphene-metal/metal oxide nanohybrids with interesting properties. In addition, it could be also used to readily prepare mixed hybrids with different compositions (such as a graphene-Au nanorod/nanocube/nanoparticle mixed hybrid).

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