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COMMUNICATION

Synthetic possibility of polystyrene functionalization based on hydroxyl groups of graphene oxide as nucleophile

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Rationally designed polystyrene surface-functionalized graphene oxide nanohybrids were synthesized for the first time utilizing hydroxyl groups of graphene oxide (GO) as nucleophile. The successful wet chemical functionalization of GO with polystyrene containing phenyl groups convinced the possibility of nucleophilic substitution for heterogeneous phase reactions owing to rigid structure of graphene.

Research into graphene and graphene oxide has recently attracted extensive attention due to their outstanding physicochemical properties, which enable them to become fundamental building blocks in an emerging field of interdisciplinary science.^{1, 2} Synthetic and in particular wet chemistry are playing vital roles in the field of graphene and GO technology, which is always regarded as a most effective approach to overcome π - π stacking interactions to improve solubility and processibility, etc.¹

The various functionalization strategies based on graphene have been explored to meet the practical application, which mainly include doping of heterogeneous atoms and well-defined covalent/noncovalent modification. In terms of easier procedures and productivity, the chemical functionalization of graphene has been considered the most promising approach.^{1, 3-5} Especially, the numerous methods based on graphene oxide (GO) as precursor have been widely developed, and is summarized in several reviews.⁶⁻⁹ In the covalent modification systems reported, the numerous introduced functional molecules generally react with epoxy and carbonyl groups located on the surface and at the edge of GO through nucleophilic addition reaction, esterification and amidation.^{8, 10, 11} However, the hydroxyl groups of GO are seldom utilized as active sites to fabricate novel materials except several silane-functionalized products.^{12, 13}

In principle, wet chemical functionalization allows for covalent binding to both sides of the graphene plane due to the higher surface area of $2630 \text{ m}^2 \text{ g}^{-1}$. However, it is regrettably noticed that there are no exhaustive wet chemical functionalization of graphene with large organic molecules including polymers, such as phenyl groups, owing to stronger steric reasons.¹ Polymers are one of the most widely exploited classes of materials due to the incredible chemical structures, together with low cost, easy processing and potential recycling, etc. So, the combination of GO and polymer has the potential in developing some novel building blocks.

Nucleophilic substitution is a fundamental class of reactions in which an electron nucleophile selectively bonds with or attacks the positive or partially positive charge of an atom or a group of atoms to replace a so-called leaving group; the positive or partially positive atom is referred to as an electrophile. And, in organic synthesis, the size and steric hindrance of substituent of organic molecules play a crucial factor to affect the chemical activity between two molecules, which would directly result in success or failure of the reaction.⁴ But, it is well known that all the chemical reactions based on GO belong to heterogeneous phase reaction systems owing to rigid structure of graphene. So, it becomes possibly more difficult that the hydroxyl groups of GO as nucleophile would attack the C-Cl bonds of chloromethylated polystyrene. It is also undeniable that a more advanced rational design would further promote the in molecular level tuning and fabrication of hybrid nanomaterials for different purposes. And because of this, the modification of hydroxyl groups is still of great interest and challenge for synthetic chemists.

Herein, the chemical combination of polystyrene (PS) to graphene has been designed rationally and fabricated successfully under weak basic conditions, and the formed covalent linking for PS surface-modified GO still confirms to the typical $\text{S}_{\text{N}}2$ nucleophilic substitution mechanism. The polystyrene wrapped graphene oxide nanomaterials (GO@CMPS) convince the possibility of nucleophilic substitution for heterogeneous phase reactions owing to rigid structure of graphene, which would represent an interesting alternative for the development of novel composite materials with interfacial interaction.

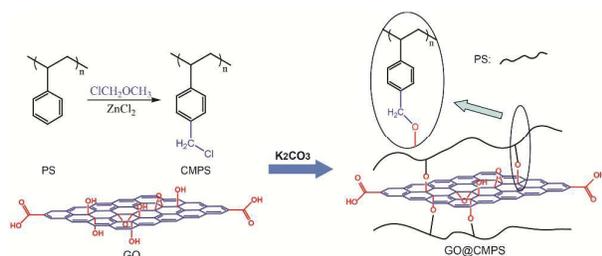
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The fabrication process of GO@CMPS is illustrated in Scheme 1. In the S_N2 reaction, the addition of the nucleophile and the elimination of leaving group take place simultaneously (i.e. concerted reaction). S_N2 occurs where the central carbon atom is easily accessible to the nucleophile. So, the chloromethylation reaction of PS was first accomplished according to Blanc mechanism so as to fabricate partially positive carbon atom due to introduction of Cl atoms. In addition, for S_N2 reactions, there are a few conditions that affect the rate of the reaction. The first one, an aprotic solvent is best, such as acetone, DMF, or DMSO. Another one is reaction temperature. So, in the whole reaction, DMF is employed as a reaction solvent. In order to accelerate the reaction, the K_2CO_3 as catalyst is also added to reaction, which could promote the more oxygen anions (O⁻) with the stronger nucleophilic ability appear. Besides, the reaction is performed at different reaction temperature to investigate the functionalization degree. (The detailed experimental procedure could be found in ESI†)

Though the GO has the rigid structure and PS has phenyl groups with stronger steric hindrance, the PS surface-functionalized graphene nanomaterials have been successfully fabricated. The "effective collision" in organic synthesis especially for the heterogeneous phase reaction could be controlled by adjusting the reaction conditions rationally. The synthetic structure could be strongly confirmed by FT-IR spectra (Fig. 1). As shown in Scheme 1, the CMPS modification of GO could occur between the hydroxyl groups of GO with chloromethyl groups (Cl-CH₂-) of CMPS to yield new C-O bonds according to S_N2 nucleophilic substitution. As seen in Fig. 1(a) and (b), the FT-IR spectra of PS and CMPS show the peaks at about 2848 and 2919 cm⁻¹ attributed to -CH₂- groups, and peaks at about 1452 and 1421 cm⁻¹ ascribed to phenyl groups. After chloromethylation of PS, three new peaks at 1265, 824 and 676 cm⁻¹ appear due to -CH of Ph-CH₂-Cl, *p*-substituted phenyl groups and C-Cl bonds, respectively. These observations strongly support the successful preparation of CMPS. The FT-IR spectra of GO exhibit representative peaks at 3370, 1727, 1629 and 1073 cm⁻¹, corresponding to OH stretching, C=O stretching, C=C stretching of the aromatic ring and alkoxy C-O stretching, respectively.^{15, 16} After CMPS modification, one new absorption peak at 2921 cm⁻¹ appears, assigned to the C-H stretch in the -CH₂-groups of CMPS.¹⁷ Another new peak located at 700 cm⁻¹ is due to the unreacted substituted benzene. The peaks at 3370 and 1073 cm⁻¹ for GO are blue-shifted to 3417 and 1118 cm⁻¹ for GO@CMPS respectively (Fig. 1c), and the intensity of the adsorption peak at 3417 cm⁻¹ decrease significantly.



Scheme 1 Scheme illustrating the fabrication process of GO@CMPS by a facile one-pot route.

While the peaks at 1727 cm⁻¹ remain unchanged, demonstrating the only OH groups reacted with the CMPS. Besides, the peak at

1629 cm⁻¹ owing the C=C bonds shifted to 1578 cm⁻¹, which is due to the π - π interactions between the benzene groups of CMPS and C=C bonds.

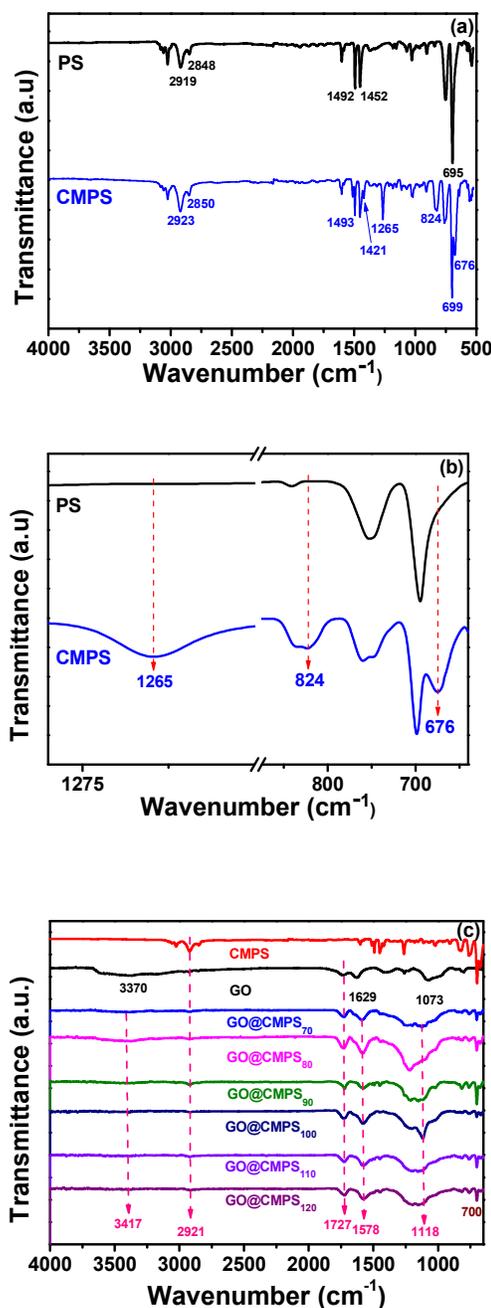


Fig. 1 FT-IR spectra of PS, CMPS (a and b) and GO@CMPS (c).

Raman spectroscopy is one of the most powerful methods for characterizing graphene, GO and their covalent derivatives. As shown in Fig. 2, both GO and GO@CMPS exhibit a typical broad D-

band ($\sim 1335\text{ cm}^{-1}$) due to A_{1g} breathing mode and G-band ($\sim 1580\text{ cm}^{-1}$) owing to in-plane bond-stretching motion of pairs of C sp^2 atoms, E_{2g} mode. They are attributed to defect-/disorder-induced modes and in-plane graphene vibrations, respectively. The I_D/I_G ratio is often used to evaluate the degree of functionalization of GO. The I_D/I_G ratio of GO is 1.02, because of the increase of nanoscale oxidized domain comparing with the aromatic domain during the GO fabrication process. After CMPS functionalization of GO, the I_D/I_G ratios of GO@CMPS nanomaterials obtained decreased from 1.02 for GO to 0.89~0.98, indicating an increase in the number of smaller sp^2 domains. This is attributed to the successful introduction of PS chains with the higher ratio of sp^2 to sp^3 hybrid carbon structures. In this study, GO@CMPS₁₀₀ exhibits the smallest value, demonstrating the maximum modification can be obtained at the 100 degree centigrade. In all, these observations indicate the successful formation of covalent bond of C-O groups.

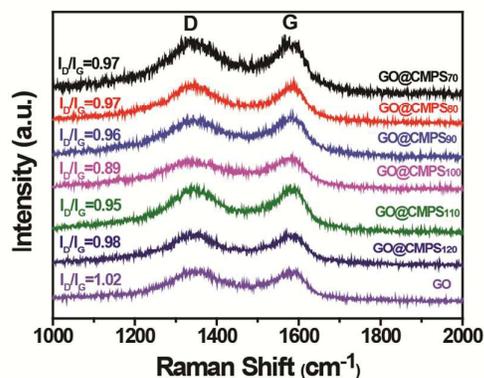


Fig. 2 Raman spectra of GO and a series of GO@CMPS.

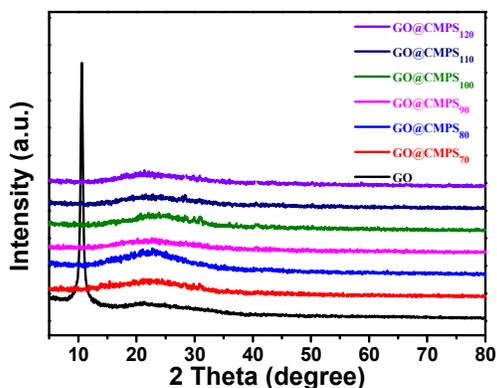


Fig. 3 XRD patterns of GO and a series of GO@CMPS.

Fig. 3 shows the wide angle XRD profiles of GO and GO@CMPS. The GO exhibits a typical sharp peak at 10.6° , which can be assigned to the (001) reflection.^{18, 19} The pattern of GO@CMPS contains a very broad reflection at $\sim 23^\circ$, indicating the formation of a poorly

randomly ordered graphene sheets with a corrugated structure. The GO and GO@CMPS were dispersed in water and eight organic solvents at a 1 mg/mL concentration in an attempt to evaluate the dispersibility of GO@CMPS, as shown in Fig. 4 and Fig. S1. All the GO@CMPS nanomaterials exhibit the better performance, which would promote the fabrication of polymer nanocomposites. Fig. 5 shows the TGA curves for GO and GO@CMPS. The main weight loss of GO was found at 150-250 °C because of the decomposition of oxygen-containing functional groups to CO, CO₂ and H₂O. The weight loss between 250-700 °C was 21% associated with the removal of more thermally stable oxygen functionalities and thermal decomposition of GO. After CMPS modification, the thermal stability of GO@CMPS is superior to GO obviously. Especially, the char yield of GO@CMPS₁₀₀ with increased onset degradation temperature (T_{onset}) of 277.0 °C is 67.4%, which is higher than 48.5% of GO. These results can be attributed to the formation of a CMPS wrapping on the GO surface that decreased the maximum rate of weight loss and increased T_{onset} .

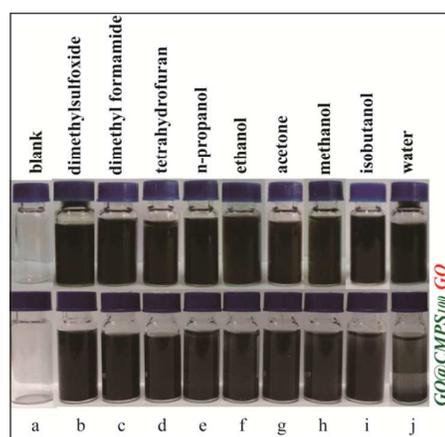


Fig. 4 Digital pictures of GO and GO@CMPS₁₀₀ dispersed in water and 8 organic solvents through both ultrasonication

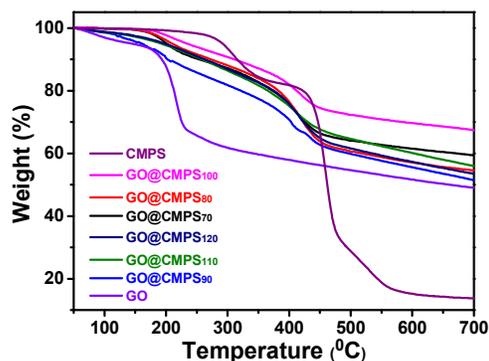


Fig. 5 TGA curves of GO, CMPS and GO@CMPS

For the chemical reactions based on graphene oxide, the controlled functionalization of GO is always a very valuable basis and still a challenge for synthetic chemists. Especially it would become more difficult that wet chemical functionalization of

graphene with large organic molecules owing to stronger steric reasons. How to apply famous organic reaction theories in practical synthesis of graphene-based nanostructure, and confirm the accurate structure would be important and challengeable issues.

In this work, polystyrene surface-functionalized graphene oxide nanohybrids have been successfully achieved by famous nucleophilic substitution reaction utilizing hydroxyl groups on the surface of GO with CMPS. The enhanced thermal stability and better dispersibility could make the nanohybrids to be incorporated into polymer matrix by easy solution-processing method. It is hoped that our current work could provide an effective and promising approach for preparing graphene-based nanomaterials and the corresponding polymer nanocomposites.

Experimental

The chloromethylation of PS (Shanghai Saik Company, China) was first carried out by the following steps. PS solution is prepared by dissolving 2 g of PS in 30 mL of CHCl_3 . After adding anhydrous ZnCl_2 (1.6 g) and chloromethyl ether (Xinyi Yonglong Chemical Co., Ltd, China), the mixture was stirred at 40 °C for 12 h. The suspension was dropped into methanol solvent. The precipitate was filtered and washed three times with ethanol. The product was denoted as CMPS. Graphite oxide was prepared according to the modified Hummer's method. 200 mg of graphite oxide was diluted with DMF to a homogeneous dispersion in an ultrasonic bath. Delamination of graphite oxide to GO in DMF can be facilitated by sonication. Reaction solution was prepared by dissolving 400 mg of CMPS and 60 mg of K_2CO_3 at the room temperature. The mixtures were stirred at the different reaction temperature for 2 days. Then, the suspensions were filtered and washed three times with CHCl_3 and hydrochloric acid water solution (1.0 mol/L). The obtained products are denoted as $\text{GO@CMPS}_{\text{reaction temperature}}$.

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Notes and references

† Electronic Supplementary Information (ESI) available: [Characterization, Digital pictures of GO and GO@CMPS dispersed in water and 8 organic solvents through bath ultrasonication]. See DOI: 10.1039/b000000x/

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