

# Sulfonated graphene oxide with improved ionic performances

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**Abstract** Graphene oxide is well known as a new kind of functional materials because of its super-high specific surface area, mechanical strength, as well as excellent amphiphaticity. In this article, graphene oxide was further sulfonated via substitution reaction with diazo salt of sulfanilic in order to endow graphene oxide with better ion exchange capacity and proton conductivity. The microstructure and morphology of the obtained sulfonated graphene oxide were characterized by X-ray diffraction (XRD), Raman spectra, and TEM, while the sulfonation of graphene oxide was confirmed by energy-dispersive X-ray (EDX) and Fourier transform infrared spectroscopy (FTIR) spectra. As expected, ion exchange capacity and proton conductivity of sulfonated graphene oxide increased by about 0.589 and 33.6 times than those of graphene oxide, respectively.

**Keywords** Graphene oxide · Sulfonation · Functional carbon material · Ion exchange capacity · Proton conductivity

## Introduction

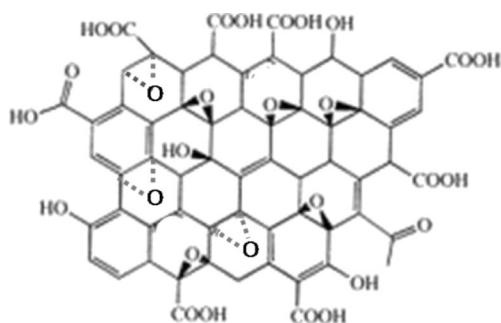
Graphene is well known as a new type of two-dimensional functional carbon materials, and it possesses some unique properties such as super-high electronic and thermal conductivity, excellent mechanical strength, Hall effect, and so on due to its unique perfect two-dimensional (2D) planar

microstructure [1–3]. Therefore, graphene exhibits wide applications in varied fields [4–10]. Graphene oxide is an intermediate during the synthesis of graphene by oxidation-reduction method [11]. On the one hand, graphene oxide consists of pseudo 2D planar nanosheets similar to those of graphene. As a result, graphene oxide also possesses high mechanical property and large surface area. On the other hand, to be different, there exist some oxygen-containing groups within graphene oxide, such as epoxy and hydroxyl groups at basal plane and carbonyl and carboxylic groups at the edge, as shown in Fig. 1. Resultantly, graphene oxide has higher amphiphaticity and reactivity than graphene [12, 13], thus making graphene oxide as more suitable filler to reinforce the mechanical strength of the substrates than graphene [14]. Additionally, these functional groups can negatively affect the electron conductivity as well as thermal stability of graphene oxide, that is, these functional groups can decrease its electron conductivity and thermal stability [15]. For example, graphene is well known to be the highest electron conductor, while graphene oxide is a good electron insulator. Recently, in order to improve its thermal stability, dispersibility, and compatibility with other substrates, graphene oxide was further functionalized [16, 17].

Sulfonated acid group is an important functional group. With the help of the solvation effect, it can dissociate the movable proton for ionic conductivity. Compared with the carboxyl group, sulfonated acid group is more efficient to dissociate the movable protons and to endow the substrate with higher ionic exchange capacity due to its stronger acidity [18, 19]. No doubt, functionalization of graphene oxide with sulfonated acid group will result in better ion exchange capacity as well as the proton conductivity. In principle, together with high mechanical strength and electronic insulator capacity of graphene oxide, sulfonation can make the graphene oxide as a promising multifunctional filler. In this work, sulfonation of graphene oxide was carried out: graphene oxide

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**Fig. 1** Scheme of microstructure of graphene oxide

was sulfonated via reaction with diazo salt of sulfanilic acid, and XRD, Raman, Fourier transform infrared spectroscopy (FTIR), TEM, and energy-dispersive X-ray (EDX) were used to probe the microstructure–property relationship of sulfonated graphene oxide.

## Experimental

### Materials

Graphite powders, 98 %  $\text{H}_2\text{SO}_4$ ,  $\text{NaNO}_3$ ,  $\text{KMnO}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HCl}$ ,  $\text{NaOH}$ , and *p*-aminobenzenesulfonic acid were purchased from Yunnan Keyi Chemical Glass Limited company and used as received without further being purified.

### Preparation and functionalization of graphene oxide

Graphene oxide was prepared by modified Hummers method as follows: firstly, 5 g graphite powders and 2 g  $\text{NaNO}_3$  were added into 120 mL 98 %  $\text{H}_2\text{SO}_4$ , which was stirred for 30 min in the ice bath and followed by the addition of 20 g  $\text{KMnO}_4$ . After stirring for another 60 min, the color of the mixture became dark green and the mixture was kept at 40 °C for 90 min. The mixture was diluted by adding 240 mL deionized water many times, during which the temperature was controlled below 98 °C. Then, 5 %  $\text{H}_2\text{O}_2$  was added into the mixture until no gas was produced; as a result, the color of the mixture changed from dark green to gold yellow. Finally, the hot mixture was filtered and washed by 5 %  $\text{HCl}$  solution and deionized water, respectively.

Five grams of *p*-aminobenzenesulfonic acid was dissolved into 50 mL 10 %  $\text{NaOH}$  solution. After being cooled to room temperature, 2 g  $\text{NaNO}_2$  was added into the solution. Under the condition of ice bath, this solution was dropped into 10 mL concentrated  $\text{HCl}$ , and white crystal was produced. After being filtered, the white crystal was added into graphene oxide solution for sulfonation reaction in the ice bath. Finally, the brown gel of sulfonated graphene oxide can be obtained by washing with deionized water many times. For further

characterization, powder-like or paper-like sulfonated graphene oxide can be also obtained by the following treatment.

### Characterization of sulfonated graphene oxide

XRD patterns of the samples were obtained with a Rigaku X-3000 X-ray ( $\lambda=0.154$  nm) powder diffractometer using  $\text{Cu K}\alpha$  radiation with a Ni filter. The scan range was from 5 to 80°, and the scan rate was 5°/min. TEM analysis was carried out on a JEM-2100 microscope at 100 kV. Synchronous elemental analysis was performed with an EDX spectroscope (Oxford INCA). Raman characterizations of the samples were carried out on Laser Raman spectrometer (785 nm Renishaw invia). FTIR spectrum was collected on Nicolet Avatar 370 equipped with DTGS detector and ZnSe crystal (45°) as attenuated total reflection accessory (ATR) (resolution 4  $\text{cm}^{-1}$ , wave number 400~2000  $\text{cm}^{-1}$ ). The ion exchange capacity (IEC) of the sample was determined by titration as follows: (i) the dry sample with a given weight was immersed in 0.1 M  $\text{NaCl}$  solution for ion exchange at room temperature for 24 h, (ii) the resultant  $\text{HCl}$  in the mixture was titrated with 0.1 M  $\text{NaOH}$  solution, and (iii) IEC was calculated using the dry weight of the sample and the mole number of exchanged protons. The proton conductivity of the sample along the direction parallel to the membrane plane was obtained from AC impedance spectroscopy in the frequency range from 100 to 100 KHz with oscillating voltage of 10 mV, as reported elsewhere [20]. The paper-like sample was sandwiched between two Teflon plates with platinum wires as the electrodes and measured at room temperature on the potentiostat (Princeton Park 4000).

## Results and discussion

### Sulfonation reaction mechanism of graphene oxide

Diazonium salts are a kind of materials with a very high reactive diazo group ( $-\text{N}=\text{N}^+$ ). Compared with aliphatic diazonium salt, phenyldiazonium salt is more useful due to its higher stability. Generally speaking, in the case of phenyldiazonium salt, there are two kinds of reactions: (i) diazotization reaction, that is, diazo group can be substituted by some groups such as  $-\text{H}$ ,  $-\text{OH}$ ,  $-\text{X}$ ,  $-\text{CN}$ , and  $-\text{NO}_2$ . Therefore, phenyldiazonium salts are also called as aromatic “Grignard” reagents. (ii) Coupling reaction with arylamine or phenol. Obviously, sulfonation of graphene oxide in this work was achieved via substitution reaction of graphene oxide and diazo salt of sulfanilic acid, in which diazo group may be substituted with  $-\text{OH}$  within graphene oxide. Diazo salt of sulfanilic acid can be easily obtained via the

reaction of *p*-aminobenzenesulfonic acid with HNO<sub>2</sub> at the temperature from 0 to 5 °C in alkaline medium, as described in the “Experimental” section.

XRD

As shown in Fig. 2, the microstructures of graphite, graphene oxide, and sulfonated graphene oxide were characterized by XRD method. It was found that graphite exhibited a sharp strong diffraction peak at  $2\theta=26.5^\circ$  and a weak peak at  $2\theta=55^\circ$ , which are corresponding to (002) and (004) crystal planes of graphite, respectively. Especially, the former was widely considered as characteristic of graphite [21]. When it was oxidized to be graphene oxide, the diffraction peak at  $2\theta=26^\circ$  shifted left to  $2\theta=10.6^\circ$ , indicating the expanded interlayer spacing by the incorporation of some oxygen-containing spacers such as epoxy, carboxyl, and carbonyl [21]. At the same time, the weak peak at  $2\theta=55^\circ$  disappeared. In the case of XRD pattern of sulfonated graphene oxide, there was no significant difference from that of graphene oxide, indicating that the introduction of sulfonated acid groups did not greatly affect the crystal structure of graphene.

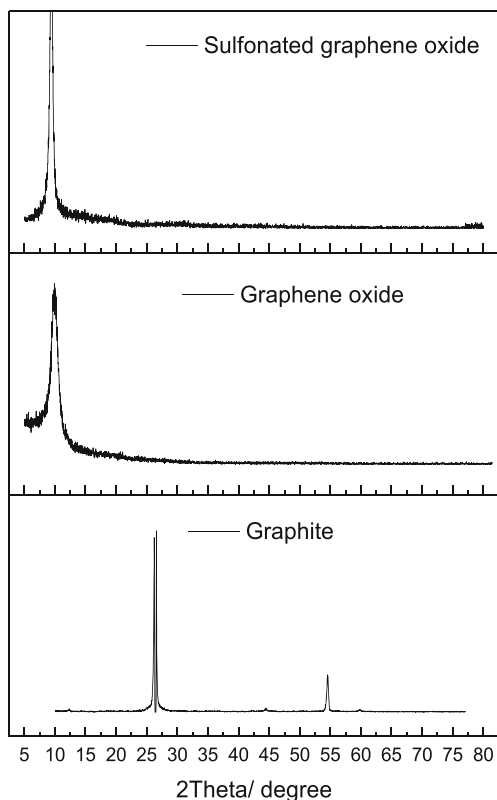


Fig. 2 XRD spectra of graphite, graphene, and sulfonated graphene oxide

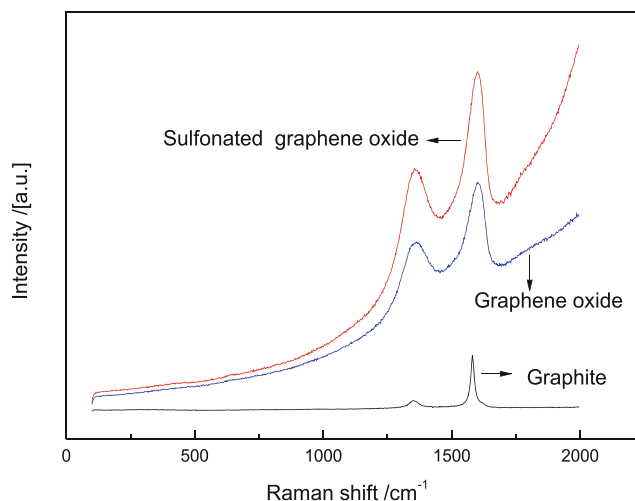


Fig. 3 Raman spectra of graphite, graphene, and sulfonated graphene oxide

Raman characterization

The microstructures of the samples were further characterized by nondestructive Raman spectroscopy, as shown in Fig. 3. It can be seen that graphite exhibited only G peak at  $1570\text{ cm}^{-1}$ , indicating regular microstructure of graphite. In the case of graphene oxide, G peaks became wider and shifted right to  $1590\text{ cm}^{-1}$ . Additionally, a new peak at about  $1357\text{ cm}^{-1}$  appeared, corresponding to D peak, meaning that part of  $\text{sp}^2$  hybrid carbon atoms of graphene oxide changed into  $\text{sp}^3$  hybrid carbon atoms, that is, C=C double bonds were broken after oxidation [22]. Furthermore, the strength ratio of G peak to D peak stood for the ratio of  $\text{sp}^2$  hybrid carbon atom to  $\text{sp}^3$  hybrid carbon atoms. Similar to XRD results, sulfonated graphene oxide did not exhibit significant changes compared to graphene oxide.

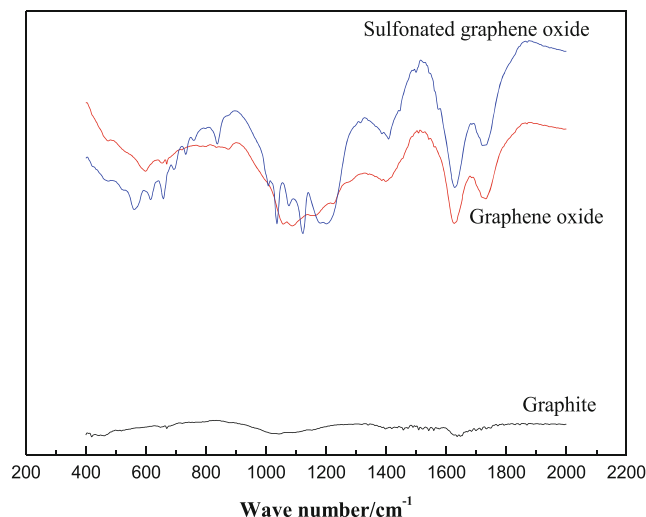
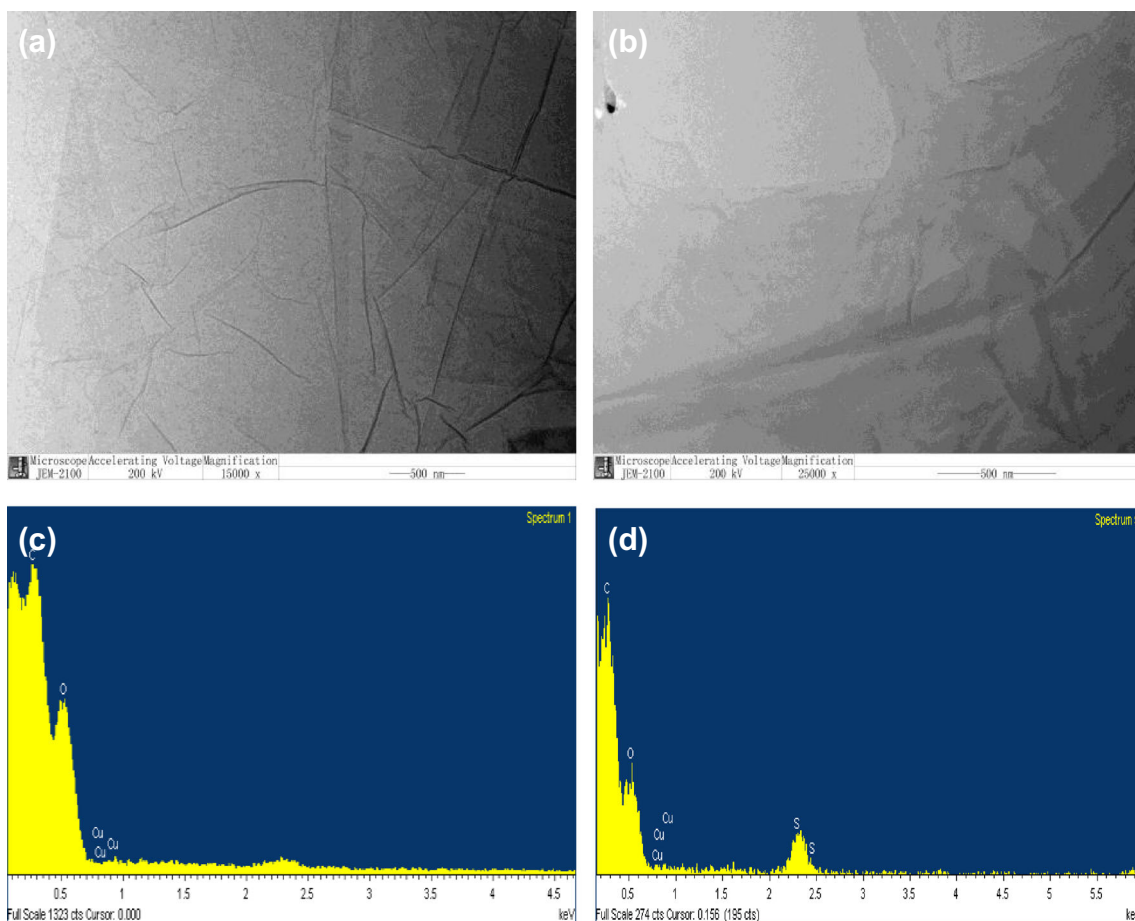


Fig. 4 FTIR spectra of graphite, graphene oxide, and sulfonated graphene oxide



**Fig. 5** TEM images (a, b) and EDX spectra (c, d) of graphene oxide and sulfonated graphene oxide

### FTIR spectra

Figure 4 showed FTIR spectra between 400 and 2000  $\text{cm}^{-1}$  of graphite, graphene oxide, and sulfonated graphene oxide. Obviously, graphite did not exhibit interesting signals expect for one peak at 1620  $\text{cm}^{-1}$ , which can be assigned to the stretching vibration of double bond C=C [23]. In the case of graphene oxide, beside the peak at 1620  $\text{cm}^{-1}$  as mentioned above, it also exhibited other signals corresponding to oxygen-containing groups. For example, the peak at about 1731  $\text{cm}^{-1}$  was resulted from the stretching vibration of carbonyl group ( $-\text{C}=\text{O}$ ), and the peaks at 1410  $\text{cm}^{-1}$  was due to the bending vibration of  $-\text{OH}$  in  $\text{H}_2\text{O}$  adsorbed in graphene oxide; the peak at about 1100  $\text{cm}^{-1}$  was from the stretching vibration of ether group (C–O–C) [24]. After further functionalization by sulfonation, sulfonated graphene oxide exhibited some new additional peaks at about 650 and 790  $\text{cm}^{-1}$  corresponding to aromatic ring and the peaks at 1076, 1124, and 1209  $\text{cm}^{-1}$  corresponding to sulfonated acid group [25]. Obviously, from FTIR spectra, it can be confirmed that graphite was oxidized and further sulfonated successfully.

### TEM

TEM is a common technology to probe the micromorphology of sample, and synchronous elemental analysis can be also performed to explore the element component of the samples by combining EDX with TEM technology. Here, such an effort was made in order to gain the insight into the micromorphology as well as element ingredient of graphene oxide and sulfonated graphene oxide, as shown in Fig. 5. Obviously, graphene oxide exhibited transparent wrinkled voile-like morphology, indicating that graphene oxide consisted of one or a few layer of nanosheets. Likewise, sulfonation did not

**Table 1** Ion exchange capacity and proton conductivity of graphite, graphene oxide, and sulfonated graphene oxide

Samples	Graphite	Graphene oxide	Sulfonated graphene oxide
Ion exchange capacity (meq/g)	0	1.12	1.78
Proton conductivity ( $\text{S cm}^{-1}$ )	–	$1.02 \times 10^{-8}$	$3.53 \times 10^{-7}$

significantly affect the morphology of graphene oxide, either. To be interesting, EDX spectra provided convictive evidences of sulfonation of graphene oxide. As shown in Fig. 5c, d, compared to graphene oxide, sulfonated graphene oxide exhibited not only the signals of C and O but also the signal of sulfur element from sulfonated acid group, indicating the successful sulfonation of graphene oxide. This point was in good agreement with FTIR spectra.

#### Ion exchange capacity and proton conductivity

The effect of sulfonated acid groups on ion exchange capacity of graphene oxide was evaluated by titration method, as listed in Table 1. Ion exchange capacities of graphite, graphene oxide, and sulfonated graphene oxide were 0, 1.12, and 1.78 meq, respectively. As expected, graphene oxide exhibited higher ion exchange capacity than graphite due to the presence of  $-\text{COOH}$  and  $-\text{OH}$ . After sulfonation, ion exchange capacity of sulfonated graphene oxide further increased by 58.9 %, attributed to sulfonated acid groups. Furthermore, the proton conductivity of dry paper-like samples was also measured at room temperature, as listed in Table 1. The absolute values of proton conductivity of the samples seemed low, possibly depending on the experimental conditions such as dry sample and low temperature. Interestingly, the proton conductivity of sulfonated graphene oxide also exhibited about 34.6 times of that of graphene oxide. These results also confirmed successful grafting of sulfonated acid groups onto graphene oxide via substitution reaction with diazo salt of sulfanilic.

#### Conclusions

Sulfonated graphene oxide was prepared via substitution reaction of graphene oxide with diazo salt of sulfanilic. The as-synthesized sulfonated graphene oxide displayed transparent wrinkled voile-like morphology. Especially, sulfonated graphene oxide exhibited higher ionic performances (such as ion exchange capacity and proton conductivity) than graphene oxide, indicating promising applications in many fields such as water treatment and energy.

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