Improvement of Dispersibility of Graphene Oxide by Surface Modification with Rare Earths

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Abstract

Rare earth-modified graphene oxide (RE-M-GO) materials were successfully prepared by infiltration and heating modifier method. The morphology and phase structure of RE-M-GO were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and energy dispersive spectrometer (EDS). The changes of the chemical structure were indicated by Fourier transform infrared (FTIR). X-ray photoelectron spectroscopy (XPS) was used to study the chemical state of the surface elements of graphene oxide which showed that the rare earth elements were added to the graphene oxide functional groups through the coordination reaction. Additionally, the findings concluded that the effect of modification by Ce is more obvious than La elements and the RE-M-GO materials prepared by the heating modifier method had better dispersibility than infiltration. With activating effect, the rare earth elements grafting to graphene oxide will contribute to its combination with other materials.

1. Introduction

Graphene has fetched much attentions recently after its discovery in 2004 by Kostya Novoselov and Andre Geim at the University of Manchester and numerous researches have been carried out on it [1]. Graphene oxide is blessed with extraordinary aspects including its excellent two-dimensional nanostructure, active surface groups, and mechanical properties. These special structural properties of graphene can be used to develop new and innovative composites [2–9].

However, there are certain limitations in its wide range of applications such as Graphene oxide is easy to agglomerate into the graphite form and not conducive to make complex with other substances. To tackle this dilemma, Graphene oxide surface modification must be carried out to improve the dispersion of Graphene oxide and its compatibility with the matrix. Nguyen Minh Dat et al^[10]. studied the surface modification of graphene oxide by silver nanoparticles. Through plate colony counting and optical density methods, the antibacterial activity of nanocomposites can be effectively improved. Ag/GO has shown sustainable development that can be used for multiple purposes. prospect. Priyanka Pareek et al^[11]. modified graphene oxide by microwave radiation. Microwave-modified graphene oxide can effectively improve the adsorption. microwave treatment of GO can be considered as a potential treatment method for adsorptive removal of dyes for treatment of industrial effluents.

Organic functionalization of Graphene oxide is one of the main research directions in its modifications. Although graphene composed of a stable six-membered ring and is chemically inert, graphene oxide has high reactivity^[12]. This is because there are hydrophilic groups on the surface of graphene oxide, which can facilitate the surface modification. To expand the application range of Graphene oxide and improve its dispersibility in an organic solvent, it needs to be modified by an appropriate organic surface. The functional organically modified Graphene oxide has been reported in the literature, mainly ocyanates, alkylamines, silane coupling agents, diazonium salts, and so on^[13–15].

The rare earth (RE) with an electronic structure ($-4f^{0-14}$) has special chemical properties. In the complex system of hydrogen, oxygen, nitrogen, carbon, and other typical nonmetallic elements, atomic size is bound to change greatly due to electron exchange and interatomic polarization resulting in that rare earth will be polarized to active element, which can be used as a surface-active agents and penetrate the shallow element^[16]. RE possess low electronegativity which contributes to not only clean the surface of graphene but also form a Re-C bond or hybrid to make its state more stable. Numerous pieces of research have revealed that the addition of rare earth elements can significantly reduce the surface energy of the nonmetallic elements, which makes the carbon nanotubes more dispersible and more easily fixed on the substrate during the reaction process^[17]. In another study Liu et al.,^[18] concluded that when the pair is rubbed, the rare earth oxide CeO_2 can accelerate the formation of the reaction membrane on the interface, which effectively reduced the friction. Also, the bond strength of the carbon fiber composite is enhanced and the interface toughness is improved after the surface modification of carbon fiber by rare earth^[19].

Therefore, in the current investigation, we proposed the preparation of RE-modified Graphene oxide by infiltration and heating modifier method; the leading goal of this study was to analyze the influence of modification induced by RE on the properties of Graphene oxide as well as the effect of different methods was also assessed. Besides, the mechanism of the surface modification of graphene oxide was discussed as well.

2. Experimental Section

2.1 Materials

Ammonium chloride (with purity $\geq 99.5\%$), ethylene diamine tetra acetic acid (NH_4Cl , $\geq 99.5\%$), nitric acid (HNO_3 , $\geq 65\%$) and N,N-dimethylformamide (DMF, $\geq 99\%$) were all purchased from Daimao Chemical Reagent Factory (Tianjin China). Single-layer GO were obtained from Angstrom Graphene Investment Management Co.Ltd (GuangzhouChina), Lanthanumchloride ($LaCl_3$ 0.05 mol/L), Cerium chloride ($CeCl_3$ 0.05 mol/L) were purchased from Tianjin Institute of Fine Chemicals Retrocession .

2.2 Preparation of RE-M-GO composites

Two approaches were employed in this experiment, infiltration and heating modifier method, respectively.

2.2.1 Heating modifier method.

To prepare a modifier, lanthanum chloride was dissolved in 100 ml of ethanol with the addition of ammonium chloride, urea, etc. which consisted of rare earth compound lanthanum chloride (0.1wt.%~1wt.%), ethyl alcohol (96wt.%~99.7wt.%), ethylene diaminetetraacetic acid (0.05wt.%~0.5wt.%), ammonium chloride (0.1wt.%~1wt.%), urea (0.03wt.% ~ 1wt.%). Modifier was added cerium chloride prepared by the same method of experimental. This solution was stirred for 10 min on the magnetic stirrer at 80°C until the complete reaction. Then, the pH value of the modified solution was adjusted to 4~6 with

nitric acid. Meanwhile, GO (10 mg) was ultrasonically dispersed in DMF (8ml) for 10 min, followed by adding a prepared modifier and kept being sonicated for 5 h to form a stable colloid suspension. Finally, the RE-M-GO composites were collected by centrifugation, washed with hot ethanol, and de-ionized water until no other ions were detected, and finally dried in a vacuum drier (80°C) for 12 h.

2.2.2 Infiltration method

Firstly, the modifier is prepared as scheme 2.2.1. the pH value is adjusted to 4~6 and then the GO was directly dispersed into the DMF, followed by immersed in the modifier. After standing for 4 h, the obtained mixture was washed and dried.

Sample code and preparation methods are outlined in Table 1.

Table 1
Sample code and preparation method

Sample code	Preparation method	Content of CeCl ₃ /LaCl ₃ in rare earth(wt.%)
LaCl ₃ -M-GO-1	infiltration method	15%
LaCl ₃ -M-GO-2	heating modifier	15%
CeCl ₃ -M-GO-3	infiltration method	15%
CeCl ₃ -M-GO-4	heating modifier	15%

2.3 Characterization

Fourier transform infrared spectra (FTIR) were recorded from KBr pellets using a Bruker ALPHA.X-ray photoelectron spectroscopy (XPS) were performed using an ESCALAB 250 Xiand Al Kα radiation (hν=1486.6 eV). X-ray powder diffraction (XRD) patterns were collected using Cu Kα radiation (λ = 0.154 nm) at the scanning speed of 10 ° min⁻¹ and the accelerating voltage 40 KV. The elemental distribution of the boundary film and the morphology of the surface were observed on Scanning electron microscopy (SEM) of FEI-MLA650F field emission microscope with an energy dispersive spectrometer (EDS). Transmission electron microscopy (TEM) images were obtained on Tecnam G2-20 microscope.

3. Results And Discussion

3.1 Characterization of RE-M-GO composite

The SEM images of GO, LaCl₃-M-GO-1, and LaCl₃-M-GO-2 are shown in Fig. 1 (d), (e), and (f), are magnified views of the above-mentioned three cases, respectively. Fig. 1 (g) and (h) are magnified views of 240000 times that of LaCl₃-M-GO-1, LaCl₃-M-GO-2. Compared to the graphs (a), (b), (c), (d), (e), and (f), the agglomeration of graphene oxide with modification is significantly reduced. We can also observe the

modified graphene oxide obtained by the heating method has better dispersibility than the infiltration. It can be seen that there are a lot of wrinkles on the surface of the modified graphene oxide from the high magnification of graphs (g) and (h). Earlier studies^[20] have found that the presence of a large number of wrinkles can improve the electrochemical properties of graphene compared to a flat graphene layer and it can increase the electrochemical current density as the battery electrode. The EDS showed that the La element has already been presented in the graphene oxide (Fig. 2).

Figure 3 (a) and (b) presents the $\text{CeCl}_3\text{-M-GO-3}$ at a magnification of 1600 times and a magnification of 50,000 times. The same SEM magnification graphs of $\text{CeCl}_3\text{-M-GO-4}$ are present in Figure 3 (c) and (d). It can be seen that the surface of the graphene oxide distributes a large number of particles. Combined with the energy spectrum (Fig. 4), it was determined that the particles are Ce. In addition, the modified graphene oxide is obtained by the heating modifier method exhibited a better dispersibility contrasted to infiltration.

To further confirm the structure of modified GO, XRD was used for phase identification, and the size of the rare earth oxide was calculated by the Debye-Scherr formula. The graphene oxide displayed a characteristic peak at $2\theta = 11^\circ$, with a d value of 8.81 angstroms. As shown in Fig. 5, the characteristic diffraction peaks of $2\theta = 11^\circ$ in the other three disappeared in contrast to $\text{LaCl}_3\text{-M-GO-1}$, while $\text{LaCl}_3\text{-M-GO-1}$ weakened a lot at 11° without disappearing completely. The diffraction peaks of graphene were observed at about $2\theta = 23^\circ$ in $\text{LaCl}_3\text{-M-GO-1}$ and $\text{LaCl}_3\text{-M-GO-2}$ indicating that the graphene lamellar spacing changed and the graphene oxide was partially reduced in the modification. Further, La_2O_3 appeared after modification, and its grain size is about 16 nm. However, $\text{CeCl}_3\text{-M-GO-3}$ and $\text{CeCl}_3\text{-M-GO-4}$ only revealed the diffraction peaks of CeO_2 , and their grain sizes are about 16 and 14 nm. Combined with rare-earth compound particles appearing in the results of SEM, the main reason for the disappearance of characteristic diffraction peaks of GO can be attributed to the destruction of the regular layer of GO due to crystal growth of CeO_2 between the intermediate layers of GO. The good crystallinity of CeO_2 providing strong reflection coverage of the GO signal is another reason.

TEM images of GO, $\text{LaCl}_3\text{-M-GO-1}$, $\text{CeCl}_3\text{-M-GO-3}$ and $\text{CeCl}_3\text{-M-GO-4}$ are shown in Fig. 6. A small number of particles appeared in graphene oxide in Fig. 6(b), which explains the reason why the graphene oxide diffraction peak of $\text{LaCl}_3\text{-M-GO-1}$ in Fig. 5 did not completely disappear. Combined with the above EDS (Fig. 2) and XRD (Fig. 5), it is certain that the particles were lanthanum oxide. As presented in Fig. 6 (c), the surface of modified graphene oxide was densely covered with the aggregates of CeO_2 nanoparticles comparing with GO (Fig. 6(a)). The dispersion of $\text{CeCl}_3\text{-M-GO-4}$ was relatively not so dense but more uniform. The size of the nanoparticle in $\text{CeCl}_3\text{-M-GO-3}$ was around 18 nm, while 16 nm in $\text{CeCl}_3\text{-M-GO-4}$. the particle produced by the heating method is smaller aggregates than that of infiltration. These findings demonstrate that the modification effect of Ce is more obvious than La.

XPS studied the chemical state of the surface elements and reveals whether RE is grafted onto the surface of the graphene oxide. Considering the electron binding energy of C1s 284.6eV as an internal

standard, the elemental content of the surface of the M-GO and GO was determined as shown in Table 2. Meanwhile, Table 2 also summarized the changes of the percentage of C and O elemental content in GO, CeCl₃-M-GO-3 and CeCl₃-M-GO-4. Compared with the GO, the content of the C element in CeCl₃-M-GO-3 and CeCl₃-M-GO-4 were decreased and oxygen was increased. Moreover, the change in the content of C and O elements prepared by the infiltration is larger than that of the heating method. Due to the low content of La oxide in LaCl₃-M-GO, the signal-noise ratio of the XPS test was poor and the La spectrum was not obvious. Fig. 7 (a) is the survey of CeCl₃-M-GO-3 spectrum. It can be seen from the figure that the surface of modified graphene oxide contains Ce elements, which is consistent with the previous SEM, TEM, and XRD findings. The binding energy of the trivalent cerium ions of CeCl₃ in Fig. 7 (b) are 606.32 eV, 601.63 eV, 587.63 eV, and 583.27 eV, respectively. When Ce and O form oxides, both Ce3d_{3/2} and Ce3d_{5/2} produced shake-up peaks. Therefore, the tetravalent Ce3d in CeCl₃-M-GO-3(Fig. 7 (C) has an absorption peak at 912.02 eV, 908.42 eV, 901.54 eV, 898.99 eV, 889.44 eV and 882.95 eV, respectively. Comparing with the binding energy of CeCl₃ in Fig. 7 (b), it is indicated that Ce has been successfully added to the surface of graphene oxide^[21]. Therefore, the Ce3d in Ce-M-GO-3 produced a chemical shift, indicating the formation of Re-O complexes^[22]. Fig. 7.(d) is a sub-peak fitting of the oxygen element of GO, from which it can be seen that the combination of oxygen contains O = C-O, C-O, C-O-C, -OH. Fig. 7 (e) and (f) is a sub-peak fitting of the oxygen elements of CeCl₃-M-GO-3 and CeCl₃-M-GO-4. Compared with the oxygen element of GO (Fig. 7 (d) and combined with Table.3, it can be seen that the binding energy of O = C-O, C-O, C-O-C, -OH in CeCl₃-M-GO-3and CeCl₃-M-GO-4 all moved toward the low potential field, indicating that the oxygen element in the coordination process to get electrons^[23].

Table.2 Percentage of elemental content in graphene oxide

	Elementary composition/%			Atom ratio
	C1s	O1s	Ce3d	O/C
GO	95.4	4.6	—	0.048
M-GO-3	74.95	19.85	5.2	0.264
M-GO-4	91.4	8.05	0.55	0.088

Table.3 The form and content of oxygen in the graphene oxide

	O1S	Energy(eV)	Percentage composition(%)
GO	C-O-C,-OH	531.03	39.06
	O=C-O	533.46	42.32
	C-O	534.64	18.62
CeCl ₃ -M-GO-3	C-O-C,-OH	529	46.05
	O=C-O	530.98	40.52
	C-O	532.76	13.44
CeCl ₃ -M-GO-4	C-O-C,-OH	529.09	35.56
	O=C-O	530.70	50.39
	C-O	532.56	14.06

FTIR spectra of RE-M-GO composite are exposed in Fig. 8. GO shows a peak around 3442 cm⁻¹ attributed to -OH vibration. This part of the peak is mainly from the adsorption of water molecules, The peak near 1749 cm⁻¹ corresponds to the C = O double-bond stretching vibration in the carboxyl group and the absorption peak at 1615 cm⁻¹ is assigned to -C=C-. The peak near 1380 cm⁻¹ corresponds to the C-O-C stretching vibration region and 1176 cm⁻¹ belongs to the C-OH bending absorption vibration peak in the GO structure [24]. From the infrared spectra, it can be shown that the structures of graphene oxide contain -OH, C-O-C, and C = O. From the figure, we can see the peak of 1380 cm⁻¹ corresponding to C-O-C was enhanced after modification, 1749 cm⁻¹, 1615 cm⁻¹ and 1176 cm⁻¹ were weakened and red-shifted in the vicinity of LaCl₃-M-GO-1 and LaCl₃-M-GO-2. However, all these peaks in CeCl₃-M-GO-3 and CeCl₃-M-GO-4 disappeared and shifted to a red shift. At the same time, a new peak appeared at 557 cm⁻¹, which belongs to C-O-Ce [25]. while no new peak appeared at LaCl₃-M-Go, indicating that the modification effect of La was not obvious. Surface functional groups of GO sheets can interact with RE elements causing reduced intensities and even disappearance of characteristic bands. However, the attachment of RE to GO seems to prevent the out-of-plane oscillations of functional groups [26].

3.2 Principle of RE Modified graphene oxide

Belonging to hard acid, rare earth elements can form a coordination bond with hard base atoms. Since the valence electron structure of rare earth elements is (n-1) d^m4f⁰⁻¹⁴ns² (m = 0 or 1) and the 4f electron layer cannot completely cover the nuclei of the rare earth resulting in a strong effective charge, they have a strong affinity with H, O, N, C and other typical non-metallic elements [18]. The interfacial and surface energy of these elements can be significantly reduced by the addition of rare earth elements [27]. In the oxygen element, rare earth elements are more inclined to form coordination bonds with oxygen elements. Oxygen atoms can either provide an empty 2p orbital accepting external coordination electron pairs or lend two pairs of orphan electron feedback to the original coordination atom empty orbit forming the feedback key. As graphene oxide contains a large number of oxygen-containing functional groups which

can react with rare earth elements to form coordination bonds. The scheme of surface functionalization of graphene presented in Fig. 9 illustrates the reaction steps involved in the above discussion.

4. Conclusion

The results of FTIR, XPS spectra and XRD revealed that RE elements are chemically bonded with GO during the formation of the composite through the coordination reaction, which reduced the interfacial energy and the surface energy of the graphene oxide. Meanwhile, the results showed that the modification effect of Ce is more obvious than La and the dispersibility of M-GO prepared by heating modifier is better than that of infiltration method. Additionally, by the modification, the dispersibility of Graphene oxide has been effectively improved which contributes to its combination with other materials.

Declarations

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Figures

Figure 1

Scanning electron microscope (SEM) of LaCl_3 modified graphene oxide (M-GO) at different magnifications

(a) GO (b) LaCl_3 -M-GO-1, (c) LaCl_3 -M-GO-2, (d) 100000 magnification figure of GO, (e) 100000 magnification figure of LaCl_3 -M-GO-1, (f) 100000 magnification figure of LaCl_3 -M-GO-2, (g) 240000

magnification figure of LaCl₃-M-GO-1, (h) 240000 magnification figure of LaCl₃-M-GO

Figure 2
Surface scanning spectra of LaCl₃ modified graphene (M-GO)

Figure 3

Scanning electron microscope (SEM) of CeCl_3 modified graphene-oxide (M-GO) at different magnifications

(a) 1600 magnification of CeCl_3 -M-GO-3, (b) 50000 magnification of CeCl_3 -M-GO-3, (c) 1600 magnification of CeCl_3 -M-GO-4, (d) 50000 magnification of CeCl_3 -M-GO-4

Figure 4

EDS spectra of CeCl_3 modified graphene oxide (M-GO)

Figure 5

XRD spectra of modified graphene oxide (M-GO)

Figure 6

Transmission electron microscopy(TEM)of modified graphene oxide(M-GO)

(a)GO, (b)LaCl₃-M-GO-1, (c)CeCl₃-M-GO-3, (d) CeCl₃-M-GO-4,

Figure 7

The XPS spectra of GO, CeCl₃-M-GO-3, and CeCl₃-M-GO-4

(a) The survey CeCl₃-M-GO-3 spectrum, (b) The Ce3d XPS spectra of CeCl₃,

(c) The Ce3d XPS spectra of CeCl₃-M-GO-3, (d) The curve-fitted of O elements of GO, (e) The curve-fitted of O elements of CeCl₃-M-GO-3, (f) The curve-fitted of O elements of CeCl₃-M-GO-4

Figure 8

FTIR spectra of modified graphene (M-GO)

Figure 9

schematic representation of the mechanism of RE Modified graphene oxide