Simultaneous Reduction and Covalent Combining of Tetraethylenepentamine on Graphene Oxide

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Abstract. [Objective] To prepare tetraethylenepentamine functionalized reduced graphene oxide (TEPA-Gn) by a one-step process. [Method] Tetraethylenepentamine (TEPA) was grafted with graphene oxide (GO) under mild condition of 70 °C and in the presence of sodium hydroxide which acted as a catalyst. [Results] The structural analysis of TEPA-Gn by FTIR and XPS showed that tetraethylenepentamine was attached to the six-membered ring of graphene by forming a covalent bond with an epoxy group in GO. Raman spectrum showed that the disorder of TEPA-Gn increased. [Conclusion] The tetraethylenepentamine was both a linker agent and a reducing agent in the reaction of preparing TEPA-Gn.

1. Introduction
Graphene has some excellent performance, such as high specific surface area, excellent electrical conductivity, outstanding mechanical properties and high thermal conductivity [1-6]. The van der Waals force between the graphene sheets is very large, and it is easy to cause aggregation, making it difficult to dissolve in water and common organic solvents, which has caused great difficulty for further research and application of graphene. The introduction of functional groups onto the graphene surface by chemical modification is the main way to solve its dispersion. There are oxygen-containing groups on the surface of GO, like hydroxyl group, epoxy group, carbonyl group, carboxyl group and ester group. These oxygen-containing groups can easily react with compounds containing amino group, carboxyl group, and isocyanate group, so as to realize covalent modification of GO [7-9]. The thickness of the modified GO is higher than that of graphene. At the same time, the conjugated structure of GO is damaged, resulting in a significant reduction in its electrical and mechanical properties [10-11]. However, some of the conjugated structures can be recovered by chemical reduction to improve their performance.

In this work, the graphene oxide was simultaneously modified and reduced with amino acid-rich tetraethylenepentamine under the catalysis of sodium hydroxide to prepare tetraethylenepentamine functionalized reduced graphene oxide with good dispersion performance. The reaction condition was mild and the operation process was simple without hydrazine hydrate or sodium borohydride reduction steps.

2. Experimental

2.1. Reagents
Tetraethylenepentamine, graphite powder, H₂SO₄, KMnO₄, NaNO₃, HCl, NaOH and absolute ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd., and all the above reagents were of analytical grade.
2.2. Apparatus
DF-101S collector thermostatic magnetic stirrer produced by Gongyi Yuhua of China, ESCALAB250 multi-functional surface analysis system of Thermo VG Company of USA, 2000 type Fourier transform infrared spectrometer produced by American PE Company and the DXR Raman spectrometer produced by Thermo Fisher Company of the United States.

2.3. Preparation of TEPA-Gn
The graphene oxide was prepared using the improved Hummers method [12]. 25 mg of graphene oxide was dissolved in 25 mL of deionized water, and after 1 hour of sonication, a homogeneous dispersing solution was formed. 3 ml of a 0.2 mol/L NaOH solution was added dropwise with stirring and after ultrasonication for 20 minutes, 25 μL of tetraethylenepentamine was slowly dropped under stirring. The solution was stirred at 70 °C for 20 hours, centrifuged by a centrifuge, and washed three times with deionized water. The product after centrifugation was redispersed in deionized water and no precipitation occurred within three months.

3. Results and Discussion

3.1. FTIR spectra of GO and TEPA-Gn
As shown in Figure 1a, GO has a large number of hydrophilic functional groups. The broad absorption peak at 3397 cm⁻¹ corresponds to the stretching vibration of the hydroxyl group in graphene oxide, the absorption peak at 1731 cm⁻¹ is attributed to the stretching vibration of the carbonyl group, and the absorption peak at 1623 cm⁻¹ is derived from the stretching vibration of the aromatic ring C=C. The absorption peaks at 1050 cm⁻¹ and 853 cm⁻¹ are symmetric and asymmetric stretching vibration peaks of the epoxy group. In the IR spectrum of TEPA-Gn, the absorption peaks at 1050 cm⁻¹ and 853 cm⁻¹ disappear because the amino group in tetraethylenepentamine reacted with the epoxy group in graphene oxide. The absorption peak at the 1731 cm⁻¹ also disappears, which can be attributed to the reduction of graphene oxide. Several new absorption peaks appeared in the FTIR spectrum of TEPA-Gn because of the introduction of tetraethylenepentamine. The attribution of these peaks can be divided as follows: N−H stretching vibration absorption peak (3407 cm⁻¹), N−H bending vibration peak (1583 cm⁻¹), and C−N stretching vibration absorption peaks (1351 cm⁻¹ and 1221 cm⁻¹). The results of IR spectra show that graphene oxide reacted with tetraethylenepentamine and was reduced to form tetraethylenepentamine functionalized reduced graphene oxide.

![Figure 1. FTIR spectra of GO (a) and TEPA-Gn (b)](image-url)
3.2. XPS characterization of GO and TEPA-Gn

The XPS full spectra of GO and TEPA-Gn are shown in Figure 2. There are only C1s (284 eV) peaks and O1s (532 eV) peaks in the full XPS spectrum of GO while a new N1s peak (399 eV) appears in the full XPS spectrum of TEPA-Gn, indicating that tetraethylenepentamine has been grafted on graphene oxide. The intensity ratio of C/O in TEPA-Gn is higher than that of GO, which is due to the removal of oxygen-containing groups after the reaction of tetraethylenepentamine and graphene oxide under the presence of sodium hydroxide.

Figure 3 is the C1s high-resolution XPS spectra of GO and TEPA-Gn. The combined states of C in graphene oxide are C=C and C=O (284.5 eV), C-OH (286.6 eV) and C=O (288.1 eV), respectively [13]. Compared with graphene oxide, the content of C-OH and C=O in TEPA-Gn is significantly reduced, indicating that most of the oxygen-containing groups have been reduced. And the presence of a new carbon-bonded C-N (285.5 eV) in TEPA-Gn much more confirms the combination of graphene oxide and tetraethylenepentamine, which is consistent with the results confirmed by FTIR spectra and XPS full spectra.

Figure 2. XPS spectra of GO (A) and TEPA-Gn (B)
Figure 3. Peak deconvolution of C (1s) of GO (A) and TEPA-Gn(B)

Figure 4. Raman spectra of GO (a) and TEPA-Gn (b).
3.3. Raman spectra of GO and TEPA-Gn

Raman scattering is a method that can directly observe the interaction of electrons and phonons without damage, it has high sensitivity to electronics and crystallographic structure so it has been widely used for structural detection of carbon materials [14]. Graphene is composed of symmetrical carbon-carbon covalent bonds, and its structure can be detected by Raman spectroscopy even with slight changes. Raman spectrum of the graphene oxide shows two sharp peaks. The G peak is located in around 1590 cm\(^{-1}\) produced by the stretching motion of the sp\(^2\) hybrid orbital. And the D peak is located in around 1350 cm\(^{-1}\) which represents sp\(^2\) hybridization defects. The sp\(^2\) hybridization defects are caused by crystal defects and disorder induction. Generally, the disorder degree of graphene is measured by the intensity ratio of D peak to G peak (I\(_D\)/I\(_G\)), and the larger the ratio, the higher the degree of disorder of graphene. The I\(_D\)/I\(_G\) ratio of GO was 0.92; while the I\(_D\)/I\(_G\) of TEPA-Gn prepared in this study was 1.07, which shows that the degree of disorder of graphene oxide was increased because of the introduction of tetraethylenepentamine.

4. Conclusion

The tetraethylenepentamine was both a linker agent and a reducing agent in the reaction of preparing TEPA-Gn. Sodium hydroxide can catalyze the ring-opening reaction of tetraethylenepentamine and graphene oxide epoxy, and at the same time, it can reduce graphene oxide. The mild reaction conditions avoided the aggregation of the TEPA-Gn. The TEPA-Gn can further participate in the reaction because of its good dispersion and active amino group, which creates conditions for further utilization of functionalized graphene.

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