pH-responsive dispersed reduced graphene oxide using poly (3-aminophenylboronic acid) via in situ polymerization method

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Abstract. Homogeneous aqueous suspensions of graphene have been prepared by chemical reduction of graphene oxide in the presence of poly(3-aminophenylboronic acid) (PABA) in alkale solution. The graphene sheets in thus prepared suspensions can stable several months and can be switch to aggregated state with low-er pH values.

Introduction

Reduced graphene oxide (RGO), a single layer of sp2-bonded carbon atoms, has attracted enormous attention owing to its unique structure and its exceptional electronic, mechanical, and thermal properties [A. K. Geim. 2007]. These properties make graphene a highly promising material for many potential applications such as logic devices, transparent electrodes and sensors [Y. -M. Lin, 2010]. Unfortunately, as-produced graphene generally shows limited solubility in conventional solvents, which has severely hindered its practical application. Noncovalent functionalization has provided a simple but effective route to solve this problem. Up to now, various polymers and surfactants such as chitosan [Jiyang Liu. 2012], lysozyme [Fan Yang. 2010], poly(ethyleneimine) [Angus Griffith. 2011], have been used to facilitate the dispersion of graphene. However, little attention has been paid to the possibility of controlling the dispersion/aggregation of graphene in solutions using Polyaniline (PANI) and PANI derivatives due to the poor solubility of PANI.

poly(3-aminophenylboronic acid) (PABA) is self-doped PANI derivatives, which is a stimulus-responsive polymer with a solubility that can be reversibly alerted by pH changes [Bhavana A. Deore. 2003]. Using PABA as a mediating agent for graphene dispersing may bring about an interesting system that is possible integrated with both the merits of graphene and PABA. Here, we demonstrate the fabrication of such graphene/PABA system and discuss the pH-responsiveness of the system. Homogeneous aqueous suspension of graphene has been prepared by chemical reduction of graphene oxide (GO) in the presence of PABA in basic condition, and the graphene in the as-prepared suspension can be switched irreversibly to a more aggregated state with reducing pH value as a stimulus due to the strong van der Waals interactions between them. This perhaps provides a new way to preparation of unique graphene composite.

Experimental section

Materials

Graphite powder, 3-aminophenylboronic acid hemisulfate salt (ABA), potassium fluoride, fructose, were purchased from Aldrich. Other reagents were analytical grade and used as received. All of the solutions were prepared using deionized water (18.2 MΩ).

General Methods

GO nanosheets were prepared from natural graphite powders by a modified Hummer's method1. In the first step, preoxidized graphite powder was synthesized through reaction of natural graphite (1 g), sulfuric acid (4 mL), K2S2O8 (0.8 g), and P2O5 (0.8 g), the reaction mixture was maintained at 80 oC for 5h and was terminated by adding 170mL deionized water. This preoxidized graphite powder (600 mg) was further oxidized by sulfuric acid (24 mL), KMnO4 (3 g), the reaction mixture

was stirred at 35 oC for 2h. In the end, the reaction mixture was maintained at 98 oC for 0.5h and was terminated by adding 50 mL deionized water. It was then further treated with H2O2 (30 wt %, 6 mL). The resulting GO solution was filtered and washed with deionized water several times, and complete remove of metal ions by dialysis membrane for a week, and vacuum dried overnight at 40 oC.

In a typical synthesis, GO was dispersed in deionized water to create 0.1 mg/mL dispersion with the aid of ultrasonication. After dissolving g PABA in pH=12 NaOH solution, homogeneous GO/PABA solution was prepared by simply mixing 6 mL PABA and 2mL GO suspension under stirring (the amount of PABA should be at least 50 times larger than that of GO). g Hydrazine monohydrate (0.1 mL, 98％) was then added, and the suspension was heated at 80 oC for 24h. Finally, black RGO dispersion was obtained and be stabled more than half a year.

Results and analysis

Characterization

To identify the crystalline phase and the extent of surface functionalization of GO and RGO, X-ray diffraction (XRD) patterns and Elemental analyses data were collected using a Rigaku D/MAX 2400 diffractometer and an elementar analysensysteme GmbH varioEL cube analyzer, respectively. The conductivities of GO and RGO were also explored by the four-point probe system (ST2253, Suzhou Jingge Electronic Co., China). Figure 1 shows the XRD patterns of pristine graphite powder, GO and RGO. Graphite powder shows a sharp (002) peak at 26.4o with a typical d-spacing of 3.37 Å. GO exhibits a diffraction peak (002) at 2theta of 11.37o corresponding to a d-spacing of 7.82 Å, which suggests that graphite has been successfully oxidized by Hummers' method. It is also seen that the corresponding peak disappears after reduction, indicating the successful formation of RGO.

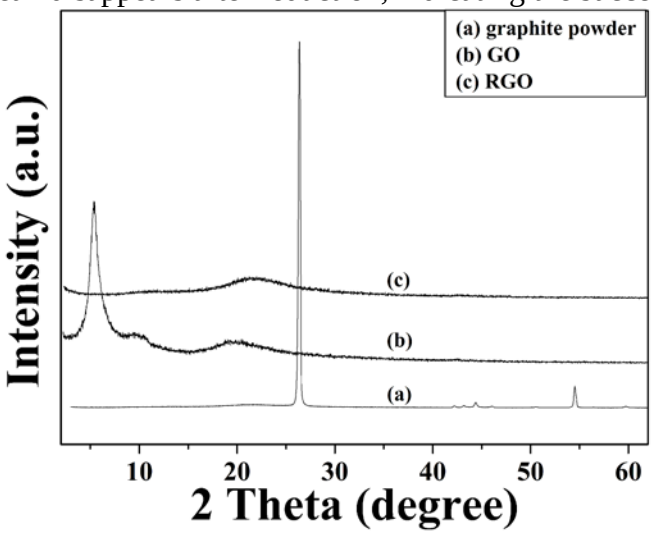

Fig. 1 XRD patterns of pristine graphite powder, GO and RGO

Likewise, elemental analyses revealed deoxygenation of GO to form RGO. An increase in the C/O atomic ratio of RGO was found to be 2.66 compared to 1.08 in as-prepared GO (Table. 1).

	C (wt%)	*N (wt%)*	*H (wt%)*	*O (wt%)*	*C/O*
GO	43.40	0.24	3.06	53.39	1.08
RGO	62.58	4.03	1.99	31.4	2.66

Table 1 Elemental analysis results of GO and RGO

It is well-known that, during reductions, GO gradually loses its oxygen-containing groups and becomes hydrophobic, so that direct reduction of GO in water without proper mediating agents generally causes irreversible aggregations. PABA is a weak polyelectrolyte and its molecular conformation and solubility can be reversibly altered by pH changes (Figure 2). Therefore, noncovalent

bonding of RGO with PABA offers the possibility of controlling the behaviors of RGO in suspensions by using pH as a stimulus.

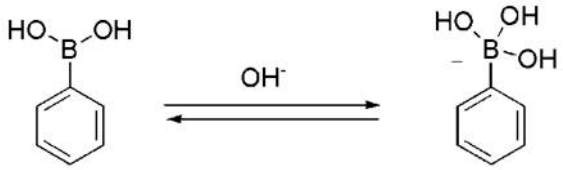

Figure 2 the transformation of PABA in acidic and basic condition

pH-responsive dispersibility

PABA can just be dissolved at basic conditions. figure 3 shows the photographs of PABA which dissolved in solution with different pH value. When pH was tuned as 3 by HCl (left photo), PABA aggregated together with blue color after centrifuging. And in neutral water, PABA shows the same poor dispersibility in green color (middle photo). However, even after 400 rmp centrifuging, PABA in basic resolution with pH=12 still dissolved evenly. This fact indicated that the possibility to desolve reduced graphene oxide by PABA via π-π interaction between them.

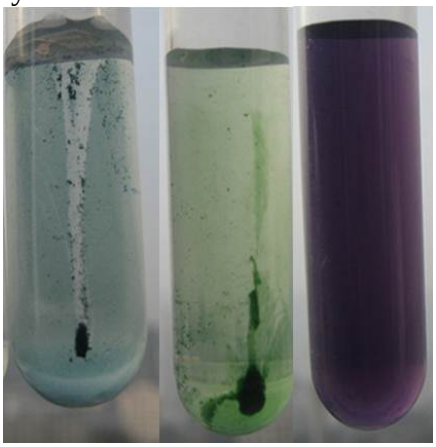

Figure 3. Photographs of PABA in water with pH=3 (left), 7 (middle) and 12 (right)

When individually dispersed GO sheets were chemically reduced in the presence of PABA (with the decrease of oxygen-containing groups on GO surface), the repulsion power changed to attract power, the domain interaction is the π-π stacking interaction between RGO and PABA, by which PABA could be noncovalently functionalized on RGO surfaces and endowed with dispersibility to RGO in water (Figure 4).

We reduced GO in the presence of PABA in alkaline media and the suspension changed to dark (Figure 4 right). The suspension remained homogeneously dispersed more than six months. On the other hand, if we tuned the solution to neutral or acidic condition, RGO aggregated immediately (Figure 4 left).

Figure 4. Photographs of the RGO/PABA suspension at pH= 7 (middle) and 12 (right).

Obviously, RGO/PABA in suspension showed a pH-dependent dispersibility. The suspension

was homogeneous with a transmittance of about 20% when the pH was higher than 12. As the pH decreased from 12 to 9, the suspension became cloudy, and the transmittance abruptly increased to 72% after sedimentation. The transmittance mildly approached about 80% with a further increase of the pH. The pH-responsiveness of the suspension was further supported by ζ potential analyses.

SEM image (Figure. 5) were utilized to analyze the dispersing state and morphology of the RGO with PABA in the suspension at basic or neutral condition. “transparent” separated RGO sheets appeared on the substrate (Fig. 5(a)), suggesting the RGO/PABA in the suspension was well dispersed at pH=12. In contrast, RGO with PABA at neutral condition produced black clusters in which the reduced product exhibited a highly agglomerated morphology (figure 4(b)). This indicated that the pH value playes an important role for the dispersion of the RGO/PABA composite in water.

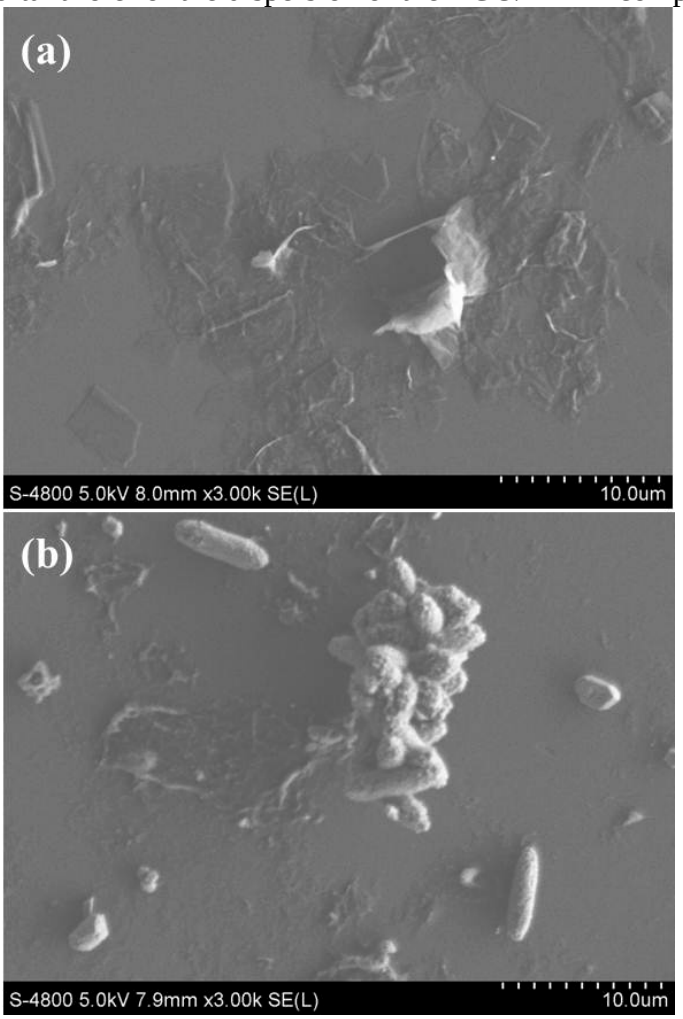

Figure 5. SEM images of (a) RGO/PABA suspension at pH= 12 and (b) RGO/PABA aggregation at neutral condition

ζ potential measurements showed that while the RGO/PABA suspension had –38.7 mV negative ζ potential at pH value equals 12. As we know, that in colloidal science, suspensions with ζ potential values higher than 30 mV are generally considered to be stable. Thus, the mixture of RGO and PABA were stable. And when the pH value lower than 10, ζ potential fell to -15.8 mV, indicating the interparticle repulsion is poor, and in this range, agglomerations occurred. However, when pH decreased to 9, the agglomerations performe totally.

The pH-responsive behaviors of RGO/PABA suspension could be understood by taking pH-stimulated alterations of the molecular conformation and charging state of PABA into consideration. The surfaces of RGO were noncovalently anchored with PABA molecular chains, so that the states of RGO were closely related to the behaviors of PABA. At high pH, the groups of PABA are negative charged and backbone of PABA is highly extended which stabled RGO due to intersheet electrostatic repulsion. With decreasing of pH, PABA molecules become neutral and intersheet electro-

static repulsion is minimized. At the same time, intermolecular association (π-π stacking interaction) of PABA molecules become dominant, so that RGO become aggregated. In general, the negative charged/neutral of PABA can be viewed as an engine for the dispersion/aggregation of RGO in the suspension.

The strategy using pH-responsive polymer to control the behaviors of graphene in solution may open a window for constructing homogeneous nanocomposites of graphene.

Conclusion

In summary, we have demonstrated that homogeneous aqueous suspensions of graphene can be prepared by chemical reduction of GO in the presence of PABA in basic condition, and the well dispersed RGS/PABA can be switched to aggregated stete with pH as a stimulus. Noncovalent interactions between RGO and PABA played an important role in both the initial formation of homogeneous graphene suspension and the further states (dispersion/aggregation) manipulation of RGO.

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