Reversible adsorption of conjugated amphiphilic dendrimers onto reduced graphene oxide (rGO) for fluorescence sensing

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A new class of smart complexes with reduced graphene oxide (rGO) and fluorescent amphiphilic dendrimers with triphenylamine cores, benzothiadiazole branches and poly(ethylene oxide) shells (RD) were prepared. The RD can adsorb onto rGO to enhance the dispersibility of rGO in aqueous media. The adsorbed dendrimers can be replaced by other amphiphiles, such as sodium dodecylbenzene sulfonate (SDBS) and lysophospholipid (LPC 18 : 0). This replacement was confirmed by photoluminescent spectra, X-ray photoelectron (XPS) and FT-IR spectroscopic measurements. These unique features could lead to the development of novel fluorescent turn-on biosensors based on the newly developed smart RD–rGO complexes.

1. Introduction

Graphene, a single-atom-thick two-dimensional carbon based sheet with close-packed conjugated hexagonal lattices, has attracted great interest due to its unique properties such as high mechanical strength, excellent optical transmittance and good electrical conductivity. Various methods, including mechanical exfoliation from graphite, chemical vapour deposition and epitaxial growth, have been developed to prepare graphene. However, graphene sheets produced from these methods have suffered from poor processability. Thus, the production of solution processable graphene by exfoliation of graphite into graphene oxides (GOs), followed by solution reduction, is regarded as one of the most promising approaches to effectively produce large-scale reduced graphene oxide (rGO). The highly exfoliated rGO with hydrophilic surface functionalities, such as epoxides, carboxyl and hydroxyl groups, has allowed for the formation of a stable graphene dispersion in an aqueous medium and the functionalization of graphene via various solution chemistries. On the other hand, amphiphilic materials, such as certain surfactants and polymers, have been used for direct exfoliation of graphene from graphite and/or enhancement of the GO and rGO dispersion via non-covalent functionalization.

We have previously reported that an amphiphilic dendrimer with triphenylamine cores, benzothiadiazole branches and poly (ethylene oxide) (PEO) shells (RD, Fig. 1) can greatly improve the dispersibility of single walled carbon nanotubes (SWNTs) in water, and that the pre-adsorbed dendrimers can be replaced by other amphiphiles, such as sodium dodecylbenzene sulfonate (SDBS) and lysophospholipid (LPC 18 : 0). These findings prompted us to use RD to enhance the dispersion of graphene-based materials, specifically rGO, and to study the substitution of pre-adsorbed RD by SDBS and lysophospholipid for many potential applications. Fig. 1 shows chemical structures of RD, SDBS and lysophospholipid (LPC 18 : 0) used in this study, along with a diagram schematically showing the substitution reaction.

2. Experimental

2.1 Materials and equipment

Graphite nanopowders (450 nm APS, 99.9% purity) from Nanostructured & Amorphous Materials Inc. were used in this study.

Fig. 1 Schematic diagram of the replacement of RD pre-adsorbed onto the surface of reduced graphene oxide (rGO) with SDBS and LPC (18 : 0) and chemical structures of dendrimers (RD), sodium dodecylbenzene sulfonate (SDBS) and lysophospholipid (LPC 18 : 0) used in this study.
study as the starting material. Sodium dodecylbenzene sulfonate (SDBS) was obtained from ACROS and lysophospholipids (LPC 18:0) were purchased from Avanti Polar Lipids Inc. The RD was synthesized and characterized according to our previously published procedures.10 Graphene oxide (GO) was synthesized from graphite by the modified Hummers method12 and reduced graphene oxide (rGO) was prepared by a hydrazine-mediated thermal reduction process.13 UV-vis and photoluminescent spectra were recorded on a Perkin-Elmer Lambda 35 and a Perkin-Elmer LS 55 spectrometer, respectively. Thermal gravimetric analysis (TGA) was performed using a Q600 from TA instruments under nitrogen atmosphere. X-Ray photoelectron spectroscopic (XPS) measurements were performed on an XPS unit with a K-alpha X-ray source. Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 spectrometer using KBr Pellet.

2.2 Sample preparations

For the preparation of RD–rGO complex (RD–rGO), 70 mg of RD and 30 mg of rGO were mixed in 70 ml of water. The mixture was sonicated for 1 hour in a sonication bath and filtered through a 0.45 μm cellulose acetate membrane to remove free RD. The collected solids were re-dispersed in water, filtered and washed repeatedly until the filtrate showed negligible PL signals originating from RD. Then the final RD–rGO was used for the subsequent study. For UV-vis and photoluminescence measurements, an aqueous solution of RD–rGO (2 ml) was placed in a UV cuvette with a magnetic stirrer bar. Thereafter the spectra were consecutively measured each time after a small portion of SDBS or lysophospholipids (LPC 18:0) was added with vigorous stirring for 3 minutes each time. For the preparation of SDBS–rGO complexes (SDBS–rGO), the pre-formed RD–rGO was re-dispersed in a 1 wt% SDBS solution in water and sonicated for 30 minutes to replace RD. The mixture was then filtered and washed following the above-mentioned procedure for three times to remove free SDBS. The orange colour from detached RD appeared during the purification of SDBS–rGO, an indication of a successful reaction. The resultant SDBS–rGO was then used for further analyses.

3. Results and discussion

3.1 The enhanced dispersion of rGO in aqueous medium with RD

Fig. 2a (right) shows rGO aggregates in an aqueous medium even after sonication for 1 hour. Upon mixing the rGO with RD, it was found that rGO was dispersed well in the presence of RD by simple sonication (Fig. 2a, middle). The RD-induced enhancement in the rGO dispersibility was reflected by colour change of the dendrimer solution from orange (Fig. 2a, left) to deep-brown (Fig. 2a, middle). In addition to the hydrophobic–hydrophilic interactions, the π–π stacking and van der Waals force have been known to dominate the interactions between rGO and RD.14 As schematically shown in Fig. 1, it can be envisioned that the hydrophobic core of RD adsorbed on the basal plane of rGO while its hydrophilic poly(ethylene oxide) shell dangled into the aqueous medium. Fig. 2b shows UV-vis spectra of RD, rGO, and RD–rGO. While RD–rGO shows similar features as RD over the whole wavelength range, the absorption of RD–rGO that is even stronger than the addition of absorbance from both RD and rGO reveals that RD has brought an extra amount of rGO into the solution, i.e. exfoliated and/or dispersed rGO in this case. Thus, the enhanced dispersibility of rGO with adsorption of RD was evident not only from the colour change visualized by the naked eye (Fig. 2a) but also from the enhanced absorbance seen

Fig. 2 (a) Photograph of pure RD (left), RD–rGO composites (middle) and the pristine rGO (right) in an aqueous medium, (b) UV-vis spectra of the pure RD, RD–rGO and pristine rGO and (c) photoluminescent spectra of pure RD, RD–rGO and pristine rGO with 330 nm excitation wavelength. The concentrations of RD and rGO are 0.25 mg ml⁻¹ for (a) and 0.1 mg ml⁻¹ for (b) and (c).
in UV-vis spectra. On the other hand, the photoluminescence (PL) emission from RD was almost quenched after dispersing with rGO due to possible energy and/or electron transfer between RD and rGO (Fig. 2c). As expected, no detectable PL emission was observed from the pristine rGO at the same experimental condition (Fig. 2c). The optimized ratio between RD and rGO for the efficient dispersion of rGO is 2 : 1 (w/w) and the deep-brown solution of RD–rGO complex, shown in Fig. 2a, was stable for more than 3 months without noticeable aggregations. It should be noted that the maximum dispersibility of rGO with RD (<0.05 mg ml\(^{-1}\)) is much lower than that of SWNTs (<0.25 mg ml\(^{-1}\)). This lower dispersibility is probably due to the big clusters of rGO used as the starting material in this study. During the rGO preparation, big clusters (up to several millimetres wide) of rGO can be easily formed because of the strong hydrogen bonding and van der Waals force between graphitic layers. Once the big clusters are formed, it is very difficult to delaminate them into single or few-layered structures again. The smaller or less aggregated rGO is used (e.g. through filtration), the better dispersibility of rGO is expected.

### 3.2 Thermal gravimetric analysis (TGA)

As shown in Fig. 3, RD started to decompose around 300 °C, while rGO was relatively stable up to 800 °C under nitrogen. In contrast, a stepwise weight loss was observed for RD–rGO and SDBS–rGO. From the TGA results, the amounts of adsorbed RD and SDBS onto the rGO were estimated to be 8 and 10 wt%, respectively. This result shows that a larger amount of SDBS was adsorbed on rGO than RD. This is probably due to the higher affinity of SDBS than RD to the basal plane of rGO and the excess amount of SDBS being used in the preparation of SDBS–rGO.

### 3.3 Photoluminescence studies for substitution phenomena of RD–rGO with SDBS and LPC (18 : 0)

It was found that the pre-adsorbed RD on the surface of rGO can be readily replaced by small amphiphiles, including SDBS and lysophospholipid (LPC 18 : 0). These amphiphiles are expected to show stronger interactions with rGO in respect to RD. Recently, SDBS was used as a stabilizer for both GO and rGO to improve dispersibility during processing. To demonstrate the surface replacement of adsorbed RD, we completely removed free RD in RD–rGO solution by filtering it through a 0.45 μm cellulose acetate membrane and subsequent washing until there was no PL signal from RD observed in the filtrated liquid. The fast replacement of the pre-adsorbed RD by SDBS was then easily monitored by the PL recovery from the newly released RD.

As shown in Fig. 4a, the PL of an aqueous solution of RD–rGO gradually increased with increasing SDBS concentration. The changes in the PL intensity were relatively small at low
SDBS concentrations. However, PL started to increase significantly above a certain concentration (0.40 wt%) and levelled off above 0.70 wt% (Fig. 4b). The concentration level of SDBS, which could cause detectable PL changes, was as low as 0.01 wt%. Three RD–rGO solutions of different concentrations were used for PL measurements in the presence of SDBS. Similar PL enhancement patterns were observed for all of the concentrations, which implied that the replacement reaction was independent of the concentration of RD–rGO over the concentration range (0.1–0.5 mg ml\(^{-1}\)) used in this study (Fig. 4b). In a controlled experiment, two more samples were prepared and analyzed. Firstly, rGO was used directly for PL measurement with SDBS. As expected, there was no detectable PL observed even at higher concentration SDBS (Fig. 4c). Fig. 4c also shows the emission plots of RD–rGO before and after filtration. Upon filtration, RD–rGO was removed from the solution. The filtered solution was separately collected and used for PL measurements with addition of SDBS showing no observable PL either (Fig. 4c). Therefore, the increase in PL emission with the addition of SDBS seen in Fig. 4a is indeed due to the replacement of pre-adsorbed RD in RD–rGO by SDBS to produce SDBS–rGO.

The utilization of biomolecules, instead of commercial surfactants, is an interesting challenge for the development of biosensors. It was well known that lipids or lysophospholipids are the major structural components in the cell membrane.\(^{17}\) We, along with others, have previously demonstrated that lysophospholipid (LPC 18 : 0) shows strong interactions with SWNTs.\(^{10,18}\) On this basis, it is anticipated that there are also strong interactions between lysophospholipid and rGO. Indeed, the similar sharp PL enhancements to those for surfactants (see Fig. 4a) were also observed upon gradual addition of lysophospholipid (LPC 18 : 0) into the RD–rGO solution (see Fig. 5a).

As can be seen in Fig. 5b, PL increased with the lipid concentration initially, and then levelled off above 0.012 wt%. The PL response was sensitive to the lipid at a concentration as low as 0.001 wt%. Thus, this result suggested that RD–rGO can be useful for the biosensor applications. The higher sensitivity for lysophospholipid than that of commercial surfactant SDBS could be attributable to the stronger interactions between lysophospholipid and rGO.

3.4 X-Ray photoelectron spectroscopy (XPS) study

To further assure the replacement of pre-adsorbed RD onto the surface of rGO with amphiphiles, XPS measurements were performed on the pristine rGO, purified RD–rGO, and SDBS–rGO. High resolution XPS spectra are shown in Fig. 6. Compared to rGO, RD–rGO shows significant changes in the C 1s (Fig. 6a) and S 2p (Fig. 6c) spectra but little change in the N 1s spectrum (Fig. 6b), indicating the successful adsorption of RD onto rGO. On the other hand, SDBS–rGO clearly shows a new S 2p peak at different positions than that of RD–rGO (Fig. 6c), which is strong evidence for the replacement from RD to SDBS. As expected, the main C–C peak at 284.5 eV from the highly oriented pyrolytic graphitic (HOPG) structure clearly appears in all three samples (Fig. 6a).\(^{19}\) However, an additional C component at a higher binding energy of 286.1 eV, attributable to the C–O bond, becomes prominent in RD–rGO. This peak is mainly originated from poly(ethylene oxide) groups located at...
Fig. 7 FT-IR spectra of rGO, RD, RD-rGO, SDBS and SDBS-rGO.

the periphery of the adsorbed RD. After replacement of RD with SDBS, this characteristic peak was diminished due to the absence of –C–O bond in SDBS (Fig. 6a). Distinct from our previous study with SWNTs, no detectable change in N 1s peaks was observed in all samples (Fig. 6b). The main reason for this negligible change is due to the existence of N atoms in rGO incorporated during the hydrazine-mediated reduction. For all three samples, the curve fitting of N 1s shows three component peaks at 399.0, 400.0 and 401.9 eV, which correspond to pyridinic, pyrrolic and quaternary N, respectively. They are originated from surface bound SDBS.

SDBS–rGO shows a shifted peak at 169 eV for oxidized sulfur atoms from benzothiadiazole units in RD (Fig. 6c). In contrast, with SDBS, which also reveals the consecutive adsorption of RD and its replacement with SDBS, this characteristic peak was diminished due to the periphery of the adsorbed RD. After replacement of RD with SDBS, this characteristic peak was diminished due to the absence of –C–O bond in SDBS (Fig. 6a). Distinct from our previous study with SWNTs, no detectable change in N 1s peaks was observed in all samples (Fig. 6b). The main reason for this negligible change is due to the existence of N atoms in rGO incorporated during the hydrazine-mediated reduction. For all three samples, the curve fitting of N 1s shows three component peaks at 399.0, 400.0 and 401.9 eV, which correspond to pyridinic, pyrrolic and quaternary N, respectively. They are introduced by the chemical reduction with hydrazine. The positions of pyridinic N 1s is from rGO and benzothiadiazole units in RD overlap near 399.3 eV. On the other hand, the atomic composition of N is increased from 2.93% to 3.34% after adsorption of RD and then reduced to 2.81% after treatment with SDBS, which also reveals the consecutive adsorption of RD and its replacement with SDBS onto rGO. Furthermore, RD–rGO shows S 2p peaks at 165 eV, a characteristic peak of sulfur atoms from benzothiadiazole units in RD (Fig. 6c). In contrast, SDBS–rGO shows a shifted peak at 169 eV for oxidized sulfur originated from surface bound SDBS. These XPS results clearly indicate that the adsorbed RD onto the surface of rGO has been successfully replaced by SDBS.

3.5. FT-IR spectroscopy study

Fig. 7 shows the FT-IR spectra of rGO, RD, RD–rGO, SDBS and SDBS–rGO. For rGO, the dominant peak of C=C bonds located at 1630 cm⁻¹ is from the skeletal vibrations of the graphitic domain. After adsorption of RD, a new peak at 1100 cm⁻¹, originated from C–O stretching vibration of ethylene oxide in RD, becomes prominent and it agrees quite well with the spectrum of pure RD. Finally, new peaks at 1180 and 1040 cm⁻¹, originated from the asymmetric vibration of the SO₃ group and in-plane skeleton vibrations of the benzene ring in SDBS, respectively, appeared. The disappearance of pre-existing C–O bonds at 1100 cm⁻¹ is observed after replacement of RD with SDBS. These results also clearly reveal the adsorption of RD and the replacement of pre-adsorbed RD with SDBS onto rGO.

4. Conclusions

We have demonstrated that fluorescent amphiphilic dendrimer (RD) could adsorb onto rGO to enhance the dispersibility of rGO in aqueous medium. More interestingly, the surface bound RD can be efficiently replaced by small amphiphiles, such as SDBS and lysoospholipid (LPC 18 : 0). This fascinating replacement was investigated and confirmed by photoluminescent, X-ray photoelectron and FT-IR spectroscopic measurements. These unique features can lead to the development of novel fluorescence turn-on biosensors based on the newly developed smart RD–rGO complexes.

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References


