Facile synthesis of reduced graphene oxide films at the air–water interface and \textit{in situ} loading of noble metal nanoparticles

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Abstract

Transparent free-standing films of reduced graphene oxide (RGO) are obtained from graphene oxide solution at the air–water interface in a simple, rapid, one-step reduction process with tetrakis(hydroxymethyl)phosphonium chloride (THPC), a widely used reducing agent for synthesizing metal nanoparticles from metal salts. The thickness of the films depends on the initial concentration of graphene oxide (GO). The restoration of the aromatic basal plane network and the removal of oxygen groups are confirmed by UV-visible and infrared spectroscopies. Atomic force microscopy shows that the film consists of a self-assembled monolayer of RGO platelets that are continuous over micrometre scale areas. In the presence of noble metal ions, THPC reduces both GO and metal ions to form free-standing films of RGO decorated by noble metal nanoparticles. Compared to other reported methods, the THPC route offers a very rapid and one-step process to obtain ultra-thin films of RGO loaded with noble metal nanoparticles.

Keywords: chemical reduction, reduced graphene oxide film, tetrakis(hydroxymethyl) phosphonium chloride, self-assembly, metal nanoparticle

Classification numbers: 2.03, 5.00, 5.15

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1. Introduction

Graphene, a single layer of graphite, has emerged as a powerful platform for future nanoelectronics due to high carrier mobility, ballistic transport and excellent mechanical and thermal properties [1, 2]. Since its demonstration as a potential quantum electronic device, the scientific literature is enriched with various strategies to produce graphene on a large scale without compromising on its quality. Among several methods, defect-free graphene is prepared by micromechanical cleavage of graphite and chemical vapour deposition of hydrocarbons on catalyst-loaded substrates [3, 4]. Graphene has also been prepared by sonication-assisted exfoliation of graphite in surface-active solvents and molecules [5]. Chemical or thermal reduction of solution-processed and exfoliated single layer graphite oxide platelets is the popular method of producing graphene in laboratories owing to its inexpensive and simple methodology [6, 7], although reduced graphene oxide (RGO) may possess a fair amount of basal plane defects and oxygen functionalities [8]. Moreover, RGO has been demonstrated to be suitable for many applications such as field-effect transistors, electrodes in lithium batteries, solar cells, sensors for gases and organic molecules and substrates for surface enhanced Raman spectroscopy (SERS) [9, 10]. Self-assembly of graphene oxide (GO) platelets at the air–water interface and
Figure 1. (a) Photograph of a transparent thin RGO film floating on the water surface in a 100 ml beaker. (b) Photograph of a thicker RGO film on the water surface obtained using a higher concentration of GO. (c) RGO film transferred to a 2.5 × 2.5 cm\(^2\) quartz substrate. (d) UV-Vis absorption spectra of GO solution and RGO film. (e) FTIR spectra of GO and RGO.

advantages of performing chemical reduction of GO is the facilitation of \textit{in situ} reduction for grafting metal, semiconductor, and magnetic nanoparticle (NP) on RGO and also \textit{in situ} polymerization of conducting polymers along with reduction of GO forming composites [9, 16]. Metal NPs anchored on RGO also have potential applications as sensors, SERS substrates and catalysts [9, 17]. Metal NP–RGO dispersions have been prepared by \textit{in situ} reduction of the metal salt and GO by various reducing agents [16, 18]. Photochemical reduction of metal salts on RGO assisted by photoactive molecules has also been observed [19].

In this article we present a simple, fast and easy synthesis route for obtaining large-area, free-standing films of RGO at the air–water interface employing tetrakis(hydroxymethyl)phosphonium chloride (THPC) as the reducing agent. Though THPC is widely used as a reducing agent for metal salts to prepare metal NPs [20, 21], its ability to reduce GO has not been explored to our knowledge. The formation of RGO films readily by THPC prompted us to apply the method to obtain films of noble metal NPs supported on RGO at the air–water interface, in a one-step, \textit{in situ} reduction.

2. Experimental methods

2.1. Preparation of RGO and RGO–metal NP films

Exfoliated graphite oxide was prepared from highly oriented pyrolytic graphite flakes (ZYH grade, Momentive Performance) or graphite particles (–300 mesh, Alfa-Aesar) by adopting Hummers method (see the supplementary data for details available at stacks.iop.org/ANSN/3/045002/mmedia) [6, 22]. A standard solution of GO was prepared and sonicated for further use. For the preparation of RGO films, 10–20 \(\mu l\) of 80\% THPC in water (Sigma-Aldrich) was added to 0.2–0.5 mg ml\(^{-1}\) GO in 25 ml milli-Q water and heated to 100 °C in a 100 ml beaker for 1 h. After 1 h, a nearly transparent film was seen floating on the surface. Au and Ag NP-RGO films were prepared in one-step by adding 100–300 \(\mu l\) of 25 mM HAuCl\(_4\) (Alfa-Aesar) or AgNO\(_3\) (Aldrich) to 25 ml 6.25 mM NaOH solution containing 10–20 \(\mu l\) of 80\% THPC and 0.2–0.5 mg ml\(^{-1}\) GO and heated to 100 °C in a beaker for 1 h.

2.2. Characterization of the films

UV-visible (UV-Vis) spectroscopy was either performed on films collected on a quartz plate or an aqueous dispersion of the films obtained by filtration and sonication. A Perkin-Elmer Lambda 20 spectrophotometer was used for this purpose. Fourier transform infrared spectroscopy (FTIR) was done on pellets of KBr ground with vacuum-dried RGO powder employing a Perkin-Elmer spectrum 1000 spectrometer. A thick film was prepared using a higher concentration of GO and THPC in order to obtain sufficient sample for FTIR measurements. Scanning electron microscopy (SEM) was
performed on films collected on doped silicon substrates, employing a field-emission SEM (Nova NanoSEM600, FEI, The Netherlands) operating at 5 kV in high vacuum equipped with a through-lens detector. Energy dispersive x-ray spectra (EDS) were acquired at 20 kV using EDAX software. For atomic force microscopy (AFM) studies, the films were lifted on to doped Si or SiO$_2$/Si substrates, washed and dried by blowing Ar gas. Agilent 5500 AFM was operated either in contact mode or intermittent contact mode under ambient conditions to obtain the topography of the films.

3. Results and discussion

Partially hydrolyzed THPC in alkaline medium is an efficient reducing agent for metal salts and is generally used for preparing hydrosol of metal clusters and also metal nanocrystalline films at liquid–liquid interfaces [20, 21]. We observed that THPC reduces GO even at pH 6–6.5 (no alkali added) forming RGO films on the water surface. Signatures of film formation were observed on the water surface within 30 min when a dilute GO solution is heated at 100 °C with small amounts of THPC. After 1 h, films that are continuous over centimetre scale containing folds and tiny black particles are seen floating on the water surface. Larger black aggregates settle down to the bottom of the beaker. Figure 1(a) shows the photograph of a thin RGO film floating on the water surface. A higher concentration of GO (> 0.5 mg ml$^{-1}$ and THPC or a longer reaction time (> 3 hrs) causes more aggregation and forms thicker films, as shown in figure 1(b). With large excess of THPC in the medium, film formation is not favoured and the particles aggregate and settle down. Temperatures between 80 and 100 °C are found to be suitable for easy film formation. These free-standing films could be transferred to any substrates and figure 1(c) shows the film on a quartz substrate that appears nearly transparent. A comparison of the UV-Vis spectra given in figure 1(d) acquired from the GO solution and the film after reaction with THPC reveals a red shift of the $\pi$–$\pi^*$ transition peak of C≡C from 227 to 265 nm indicating reduction of GO.
Figure 3. UV-Vis spectra showing the plasmon absorption from RGO-Au NP and RGO-Ag NP suspensions.

and restoration of aromatic network [23]. Also, the shoulder at \( \sim 305 \) nm arising from \( \pi-\pi^* \) transition of C=O in GO disappears in the case of RGO film. The peak position of the \( \pi-\pi^* \) transition indicates that the extent of reduction by THPC is comparable to the case of hydrazine hydrate [13]. The presence of oxygen-containing functional groups in RGO film is evaluated using IR spectroscopy. The FTIR spectra in figure 1(e) show that the absorption due to major oxygen functionalities such as C=O (carbonyl) at \( \sim 1730 \) cm\(^{-1}\), C–O (alkoxy) at \( \sim 1060 \) cm\(^{-1}\) and O–H bending of carboxyl at \( \sim 1380 \) cm\(^{-1}\) observed in GO vanishes in the case of RGO [8, 24]. The absorption in the region 1620–1570 cm\(^{-1}\) corresponds to O–H bending of water and C=C stretching and is observed in the case of both GO and RGO. The absorption at \( \sim 3430 \) cm\(^{-1}\) indicates the presence of C–OH groups [24]. Raman spectra (see the supplementary data available at stacks.iop.org/ANSN/3/045002/mmedia) exhibit prominent D and G bands at 1327 and 1596 cm\(^{-1}\) consistent with previous reports of RGO by chemical reduction [7, 13]. A strong D band suggests the presence of sp\(^3\) hybridized edge states in RGO.

The surface of the RGO films has been examined by SEM and AFM. SEM image of a thin RGO film in figure 2(a) reveals that it is composed of very thin regions of graphene platelets, appearing as black regions and also thicker regions that are folded and wrinkled, appearing as bright portions. Higher magnification views of the thin and thick regions are given in figures 2(b) and (c). The thin regions show smooth areas while thick regions show folded mass and aggregates. AFM images given in figures 2(d)–(f) present the finer details of the surface. The thin regions are indeed composed of single layer RGO sheets (figure 2(d)) continuous over micrometre scale. The cross-section analysis along the black line in figure 2(d) is given in figure 2(g) and gives the thickness of the flat area to be 1 nm and folded edges have a higher thickness (4 nm). A zoomed-in view of the flat area (figure 2(e)) shows that the RGO platelets are tightly packed and continuous. An AFM image of the thicker region (figure 2(f)) shows a cobweb-type pattern formed by the folded and wrinkled RGO sheets, continuous over a large area. A height variation of 8–10 nm is seen across the film (figure 2(h)). However, the edges of the thicker region consist of monolayer RGO. For a thick film obtained by larger concentration of GO (around 0.5–1 mg ml\(^{-1}\)), the roughness of the film increases due to the presence of aggregated particles. The morphology of RGO films obtained by THPC reduction bears a close resemblance to RGO films obtained by hydrazine hydrate reduction of a dilute GO solution [25]. However, film formation in the latter case is achieved in a longer reaction period of 12 h while our method requires only an hour.

The reducing action of THPC is associated with its dissociation products in aqueous medium. In excess of NaOH, pH > 9, THPC dissociates to tris(hydroxymethyl)phosphine oxide (THPO), formaldehyde and hydrogen gas that are responsible for reduction [26, 27]. It is noteworthy that THPC reduces GO and forms films on the water surface during heating in the presence and absence of NaOH. At pH \( \leq 9 \), only tris(hydroxymethyl)phosphine (THP) and formaldehyde are formed [27]. As the graphene oxide platelets get reduced to graphene, they self-assemble on the water surface due to hydrophobic interaction and attractive capillary forces.
similar to the case of RGO suspension spread on the water surface \cite{28}.

Optical transmittance of the RGO films, at 550 nm, prepared by THPC reduction of GO solution with an initial concentration of 0.2–0.5 mg ml\(^{-1}\) is in the range 80–85\% (see the supplementary data available at stacks.iop.org/ANSN/3/045002/mmedia). As a further step, we have employed THPC reducing agent to decorate RGO films with metal NPs at the air–water interface, in a rapid, one-step synthesis. Previously, THPC reduction has been performed to decorate the surface of CNTs with metal NPs \cite{29}. In our method, GO and metal salts such as HAuCl\(_4\) and AgNO\(_3\) were added to THPC in NaOH solution and heated. The onset of reduction of metal salts is indicated by a change in the colour of the aqueous solution, pink for Au and reddish brown for Ag. After 30 min, a film is seen floating on the surface. In contrast to the transparent, continuous films observed during GO reduction by THPC, the films formed in the presence of metal salts are not very continuous and slightly aggregated. However, they are stable and float on the surface for weeks without settling down and extend to mm scale area. Metal NPs are also formed in the aqueous medium during the reduction reaction.

Figure 3 gives the UV-Vis spectra of RGO-Au and RGO-Ag dispersions obtained by sonication of the filtered films in water. The characteristic surface plasmon absorptions of Au and Ag are observed at 528 and 400 nm, respectively, along with RGO absorption at 265 nm, indicating that Au and Ag NPs have been formed on RGO. SEM and AFM images of the RGO-Au NP films in figures 4(a) and (b) show that the RGO film is covered with Au NPs appearing as bright dots. EDS data obtained from a portion of the film (inset of figure 4(a)) confirm the presence of Au. The AFM image and the cross-section analysis (figures 4(b) and (c)) also indicate the presence of aggregates of small Au NPs covering the folds and wrinkles of RGO adding up to a height of 120 nm. The SEM image in figure 5(a) and the inset EDS support the presence of Ag NPs on RGO film. A high-magnification view of the film is given in figure 5(b) which reveals that the Ag NPs form aggregated assemblies and some larger particles are also seen. The observed shoulder at 500 nm in the UV-Vis spectra of RGO-Ag probably arises from the

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**Figure 5.** (a) SEM image of RGO-Ag NP film showing particles attached to RGO sheet. EDS data in the inset show Ag line. (b) High-magnification SEM image of Ag NP aggregates and larger particles. (c) AFM topography of the RGO-Ag NP films. (d) Cross-section analysis across the black line in (c).

**Figure 6.** SEM image of RGO-Pd NP film on Si substrate and the inset shows the EDS data.
inter-particle interaction in these assemblies. The AFM image and cross-section analysis along the marked line (figures 5(c) and (d)) show features of size 60–100 nm on the film which further supports the presence of NPs on RGO film.

Our preliminary investigations show that RGO films can also be loaded with Pd NPs by using H$_2$PdCl$_6$ as the precursor metal salt. Figure 6 shows the SEM image of the surface morphology of RGO-Pd NP film obtained after THPC reaction. Highly aggregated films with very small particles attached to the RGO sheet can be seen. EDS acquired data show the presence of Pd. Further investigations are in progress.

4. Conclusions

We have demonstrated the ability of THPC in aqueous medium to reduce GO forming ultra-thin RGO films at the air–water interface. The transparent free-standing RGO films consisting of tightly packed graphene platelets are continuous over centimetre scales and transferable to any substrate. Simultaneous reduction of GO and noble metal salts could be achieved by THPC forming RGO films decorated by noble metal nanoparticles, at the air–water interface in a one-step process. Our method provides a direct, quick and easy route to obtain ultra-thin films of RGO and RGO-noble metal nanoparticle materials. We envisage potential applications for these materials as solid phase catalysts and SERS substrates, which are the subject of future studies.

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