

Reduction of graphene oxide *via* L-ascorbic acid†

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We demonstrated that the individual graphene oxide sheets can be readily reduced under a mild condition using L-ascorbic acid (L-AA). This simple approach should find practical applications in large scale production of water soluble graphene.

Ever since the discovery of the advantageous properties of graphene, the challenge has been to produce individual graphene sheets in a bulk quantity.^{1–5} In the last few years, several approaches, such as micromechanical exfoliation of graphite,¹ chemical vapor deposition,^{2–6} and solution-based chemical reduction of graphene oxide (GO) to graphene,^{7–10} have been developed. Among these methods, one may mention the solution-based chemical reduction of GO because it has advantages of low-cost and bulk-scale production. However, the low solubilities of the chemically reduced graphene oxide (CR-GO) sheets in water and most organic solvents, and the strong π - π stacking tendency between CR-GO sheets lead to the formation of irreversible agglomerates unless the capping reagents (polymers or surfactants) are used. On the other hand, the capping reagents may affect the properties of the graphene sheets, accordingly limited their practical applications. Additionally, in the most successful cases, the chemical reduction of the GO was conducted using hydrazine or hydrazine hydrate as the reducing agent. However, because hydrazine and hydrazine hydrate are highly poisonous and explosive,¹¹ precautions must be taken when large quantities of hydrazine or hydrazine hydrate are used. Consequently, a new approach for effectively converting GO into stable graphene sheets under mild conditions needs to be explored.^{12,13}

L-Ascorbic acid (L-AA), having a mild reductive ability and nontoxic property, is naturally employed as a reducing agent in living things,^{14–16} and has also been used as a primary reductant in the laboratory.^{17–20} Herein, we present a facile approach for reducing GO sheets using L-AA as a reductant in an aqueous solution at room temperature. As will be shown, besides the pronounced reduction capability to GO, the oxidized products of L-AA may also play a role as a capping

reagent to stabilize as-reduced GO sheets simultaneously, avoiding the usage of additional capping reagents. More significantly, in comparison with the conventional reductants used in GO reduction, such as hydrazine and hydrazine hydrate, L-AA itself and the oxidized products are environmentally friendly.

The aqueous dispersion of GO sheets was prepared following the literature procedure.^{21,22} Briefly, the graphite powder was first oxidized into graphite oxide using $\text{KMnO}_4/\text{H}_2\text{SO}_4$, and then the graphite oxide was exfoliated into GO sheets by ultrasonication in water. Fig. 1a and c depict the typical atomic force microscopy (AFM) and transmission electron microscopy (TEM) images of the GO sheets we obtained. The thickness, measured from the height profile of the AFM image, Fig. 1b, is about 1.2 nm, which is consistent with the data reported in the literature, indicating that the formation of the single layered GO.⁸ The reduction of the GO using L-AA was performed in water at room temperature ($\sim 23^\circ\text{C}$). In a typical experiment, 50 mg of L-AA was added to 50 mL (0.1 mg mL^{-1}) of an aqueous dispersion of the GO under vigorous stirring. The reduction progress was monitored by UV-vis spectroscopy. As shown in Fig. 1d, with the reduction progressing, the intensities of two UV-vis absorption peaks centered at 230 and 300 nm, which are caused by the GO, decayed gradually with the increase of reduction time, and disappeared after 24 h. Meanwhile, a new absorption peak showed up around 264 nm, and red-shifted with the reduction time. The absorption intensity of the entire spectrum, especially in the region above 300 nm, increased dramatically, providing a first hint that the GO might be reduced and the aromatic structure might be restored gradually.⁷ The reduction of the oxygen-containing groups in GO by L-AA was also confirmed by FT-IR spectroscopy. As shown in Fig. 2a, after 48 h reduction of the GO with L-AA, the intensities of the FT-IR peaks corresponding to the oxygen functionalities, such as the $\text{C}=\text{O}$ stretching vibration peak at 1726 cm^{-1} , the vibration and deformation peaks of $\text{O}-\text{H}$ groups at 3395 cm^{-1} and 1410 cm^{-1} , respectively, the $\text{C}-\text{O}$ (epoxy) stretching vibration peak at 1226 cm^{-1} , and the $\text{C}-\text{O}$ (alkoxy) stretching peak at 1052 cm^{-1} decreased dramatically, and some of them disappeared entirely. These observations confirmed that most oxygen functionalities in the GO were removed. The variation of the relative intensities of G (the E_{2g} mode of sp^2 carbon atoms) and D (the symmetry A_{1g} mode) bands in the Raman spectra of the GO during the reduction usually reveals the change of the electronic conjugation state.^{9,23} As depicted in Fig. 2b, with the reduction, the ratio of D/G increased significantly. This agrees well with the Raman spectrum of the GO reduced by hydrazine that was

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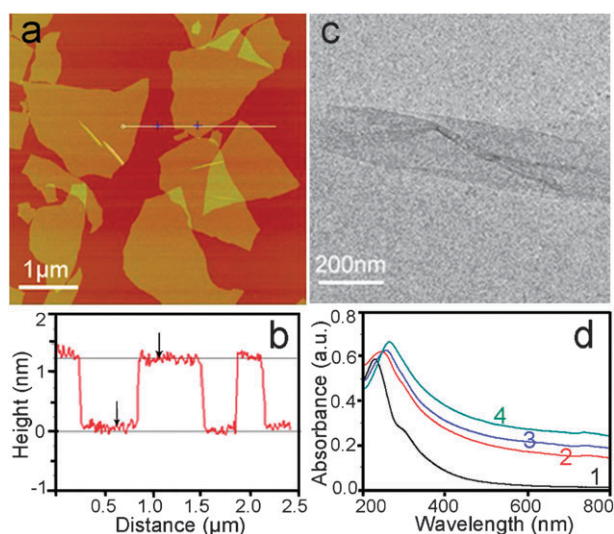


Fig. 1 (a) A tapping mode AFM image of graphene oxide (GO) sheets on mica surface, (b) the height profile of the AFM image, (c) TEM image of the GO, and (d) UV-vis spectra of GO aqueous dispersions before (1) and after being reduced *via* L-AA for 12 (2), 24 (3), and 48 (4) hours.

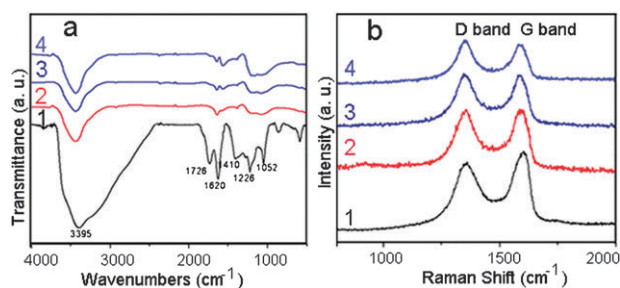


Fig. 2 FT-IR (a) and Raman (b) spectra of GO before (1) and after being reduced *via* L-AA for 12 (2), 24 (3), and 48 (4) hours.

reported by Stankovich *et al.*,⁹ indicating the reduction did take place.

The reduction of GO with L-AA was also characterized using X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRD). Fig. 3 shows the C 1s XPS spectra of GO before and after the reduction with L-AA for 48 h. Before reduction (Fig. 3a), four different peaks centered at 284.5, 286.4, 287.8, and 289.0 eV, corresponding to C=C/C-C in aromatic rings, C-O (epoxy and alkoxy), C=O, and COOH groups, respectively, were detected. After the reduction for 48 h (Fig. 3b), the intensities of all C 1s peaks of the carbons binding to oxygen, especially the peak of C-O (epoxy and alkoxy), decreased dramatically, revealing that most oxygen containing functional groups were removed after the reduction. As shown in Fig. S1†, after the reduction, the sharp XRD peak of GO (d-spacing 7.94 Å at $2\theta = 11.1^\circ$) disappeared, but a new broad diffraction peak (d-spacing 3.7 Å at $2\theta = 24.0^\circ$) appeared, which is closer to the typical (002) diffraction peak of graphite (d-spacing 3.35 Å at $2\theta = 26.6^\circ$). This result further supports the reduction of GO by L-AA.

Generally, electrical conductivity of reduced GO could reflect both the extent of the reduction and the restoration

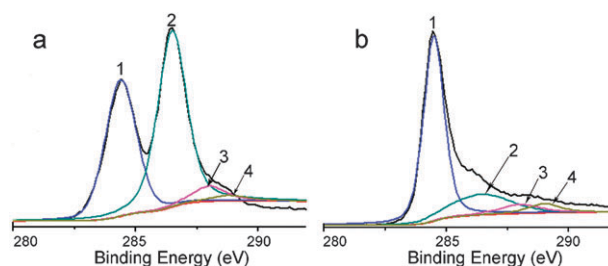


Fig. 3 XPS spectra of C 1s of GO before (a), and after (b) the reduction with L-AA for 48 h. The peaks 1, 2, 3, and 4 correspond to C=C/C-C in aromatic rings, C-O (epoxy and alkoxy), C=O, and COOH groups, respectively.

of the electronic conjugation state.^{10,24} To check the electrical conductivity of the reduced GO, thin circular “papers” (1 cm in diameter, 0.3 mm in thickness, see Fig. S2†) of the reduced GO were prepared by filtration, and were dried under vacuum at 80 °C for 12 h. To get reliable electrical conductivity data, a four-point probe was carefully placed on the reduced GO “papers”, and three different sites of each sample were chosen to be measured. We found the average conductivity of the reduced GO (reduced for 48 h with L-AA) is $\sim 800 \text{ S m}^{-1}$, which is comparable to the conductivity of the GO reduced using hydrazine and other reductants.⁸ This result showed unambiguously that the GO was reduced by L-AA, and the electronic conjugation was re-established after the reduction. To optimize the reduction capability of L-AA to GO, we changed the ratio of L-AA to GO in the reduction experiments. As expected, increasing the ratio of L-AA to GO can certainly speed up the reduction. For instance, the UV-vis spectra, Fig. S3†, showed that the decaying rate of the prominent UV absorption peaks of the GO at 230 and 300 nm increased with the increase of the ratio of L-AA to GO from 2 to 20 (by weight).

The formation of irreversible graphene agglomerates has been a key problem in the preparation of individual graphene sheets through aqueous solution based chemical reduction of GO.^{7,8} To overcome this obstacle, appropriate polymers or surfactants were usually added as capping reagents in most cases.^{25,26} In this work, we found that the reduced GO sheets can be suspended stably in water at room temperature for several days without adding any capping reagent. Fig. 4a shows the photograph of the aqueous suspensions (0.1 mg mL^{-1}) of the GO (left) and the L-AA reduced GO (right) sheets that were kept at room temperature for four days. The AFM image and the height profile, Fig. 4b and c, illustrates that the individual sheet motif was still preserved. The thickness of the L-AA reduced GO sheets ranges of $\sim 0.8 \text{ nm}$ (Fig. 4c). Fig. 4d depicts a typical high-resolution transmission electron microscopy (HRTEM) image and a selected area electron diffraction (SAED) pattern (inset) of the L-AA reduced GO sheet. The well-defined diffraction spots in SAED illustrates that the crystalline state of the reduced GO was re-established, although the discontinued fringes in the HRTEM image indicate that there are defects in the L-AA reduced GO sheets. The stabilization mechanism of the reduced GO aqueous suspension might originate from the oxidized products of L-AA. It is well known that each L-AA molecule can release two protons (deprotonation) to form

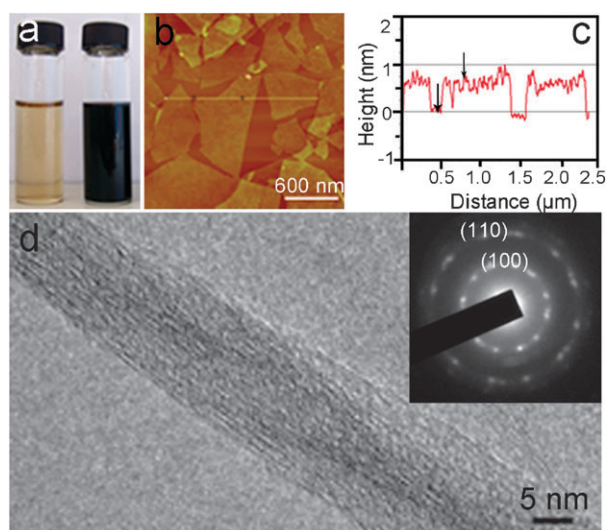


Fig. 4 (a) Photographs of aqueous dispersions (0.1 mg mL^{-1}) of GO before (left) and after (right) the reduction with L-AA, which were kept at room temperature over 4 days, (b) tapping mode AFM image of the L-AA reduced GO sheets on mica substrate, (c) the height profile of the AFM image, and (d) HRTEM image of the reduced GO sheets. The inset in (d) is a typical SAED pattern of the reduced GO.

dehydroascorbic acid.¹⁶ The protons have commonly high binding affinity to the oxygen-containing groups, such as hydroxyl and epoxide groups forming water molecules. The dehydroascorbic acid can be converted further into oxalic and guluronic acids.^{14,15} The reduced GO may also have some residual oxygen functionalities, such as the periphery carboxylic groups as shown in Fig. 2a. Thus, guluronic acid or oxalic acids might form hydrogen bonds with the residual oxygen functionalities on the reduced GO surfaces. Such interactions can disrupt the π - π stacking between the reduced GO sheets, and further prevent the formation of the agglomerates.

In summary, we have demonstrated that the reduction of GO with L-AA results in a substantial removal of oxygen functionalities of the GO and the noteworthy restoration of the electronic conjugation state of the reduced GO. This method avoids the usage of harmful chemical reductants and any additional capping agents (polymers or surfactants) that are undesirable for most applications of graphene. Given these advantages, the strategy described in this study can be developed as a simple and environmentally friendly route to water soluble graphene.

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