



Synergistic effect of UV and L-ascorbic acid on the reduction of graphene oxide: Reduction kinetics and quantum chemical simulations

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ABSTRACT

A photochemical strategy for eco-friendly reduction of graphene oxide (GO) was developed by using L-ascorbic acid (L-AA) as a photosensitive reducing agent. L-AA was excited and oxidized with deprotonation by UV irradiation (254 nm) and the proton coupled electron transfer induces chemical reduction of GO. This photochemical process is quite eco-friendly and scalable, and the reduction kinetics and degree of GO were highly enhanced. To understand the improved reduction power by UV light, the redox properties of L-AA in the ground and excited states were characterized by using quantum chemical simulations. Based on the results, we clearly demonstrated the mechanism how UV irradiation considerably enhances the reducing power of L-AA for the reduction of GO.

1. Introduction

Graphene has attracted much research interest for various applications including biosensors [1], catalysts [2], electronic devices [3], transparent electrodes [4] and nanocomposites [5] based on its unique and excellent physicochemical properties. For its commercial applications, the large scale production is a prerequisite and thus numerous effects have been devoted to develop an appropriate synthetic procedure for high quality graphene [6]. One of the most promising synthetic strategies for graphene is a chemical reduction of graphene oxide (GO), oxidized version of graphene presenting oxygen containing functional groups [7], but this strategy has been suffered from the toxicity and dangerousness of chemical reducing agents including hydrazine [7], hydroiodic acid [8], etc. In this regard, it is an important issue to discover an eco-friendly reducing agent, and thus many eco-friendly reducing agents have been discovered such as amino acids [9], L-ascorbic acid (L-AA) [10], glucose [11], dextran [12], etc.

Despite of their eco-friendly properties, those eco-friendly reducing agents have been not widely utilized owing to their relatively low efficiency compared to conventional toxic and dangerous reducing agents. If the activity of eco-friendly reducing agents is further enhanced, it can greatly aid the scalable and eco-friendly production of

reduced GO (RGO) and graphene analogues. Herein, we demonstrate UV irradiation (254 nm) improves the activity of L-AA, one of the most efficient eco-friendly reducing agents, for the chemical reduction of GO based on its UV sensitive oxidation property (Fig. 1) [13]. The enhanced reduction kinetics and degree of reduction of GO with L-AA under UV irradiation was confirmed by using UV-Vis, Fourier transform infrared (FT-IR), Raman and X-ray photoelectron (XPS) spectroscopy. In addition, the enhancement mechanism of reduction power was explained by quantum chemical simulations of L-AA based on its redox properties in ground and excited states, respectively.

2. Experimental section

2.1. Materials

Natural graphite (FP 99.95%) was purchased from Graphit Kropfmühl AG (Hauzenberg, Germany). Potassium permanganate, Sodium nitrate, sodium hydroxide, ethanol, hydrochloric acid, sulfuric acid, ammonium hydroxide (25%) and hydrogen peroxide (30%) were purchased from Daejung Chemicals (Siheung, Korea). L-AA, ACS, 99+ % was purchased from Alfa Aesar (Ward Hill, Massachusetts, USA).

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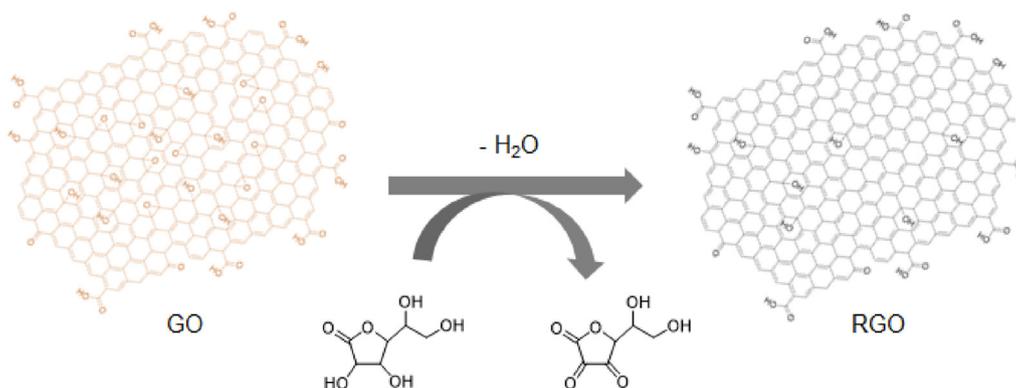


Fig. 1. Schematic diagram of UV assisted oxidation of L-AA accompanied with generating two protons and the subsequent reduction of GO by the proton coupled electron transfer.

2.2. UV irradiation to GO

GO was synthesized by our previously reported method [12]. The detailed protocol was reported in our previous research. For the synthesis of RGO, GO was suspended in 25 mL of water at 0.1 mg mL^{-1} and then pH of the GO suspension was adjusted to 10 by adding NH_4OH . UV was irradiated for 24 h with stirring at room temperature. After the reaction, the reaction mixture was cooled to room temperature, centrifuged at 15770 rcf, washed with water and re-suspended in water. RGO was obtained by repeating centrifugation and washing processes three time.

2.3. Reduction of GO by using L-AA

GO was suspended in 25 mL of water at 0.1 mg mL^{-1} and then pH of the GO suspension was adjusted to 10 by adding NH_4OH . 5 mg of L-AA was added to the GO suspension for 24 h with stirring in an water jacket to maintain room temperature. After the reaction, the reaction mixture was centrifuged at 15770 rcf, washed with water and re-suspended in water. L-AA-RGO (no UV) was obtained by repeating centrifugation and washing processes three time.

2.4. UV assisted reduction of GO by using L-AA

GO was suspended in 25 mL of water at 0.1 mg mL^{-1} and then pH of the GO suspension was adjusted to 10 by adding NH_4OH . 5 mg of L-AA was added to the GO suspension and UV light (254 nm) was irradiated at 2 mW/cm^2 power for 24 h with stirring in an water jacket to maintain room temperature. After the reaction, the reaction mixture was centrifuged at 15770 rcf, washed with water and re-suspended in water. L-AA-RGO (UV) was obtained by repeating centrifugation and washing process three times.

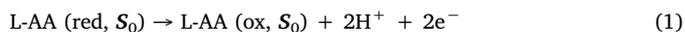
2.5. Characterization

UV-Vis-NIR spectra were recorded with a J670 (Jasco, Japan). Their lateral size was observed by using a NOVA NanoSEM 450 (FEI company, Netherlands). Fourier transform infrared (FT-IR) analysis was performed by using a Nicolet iN10 microscope (Thermo Scientefic, USA) under a reflective mode. Raman analysis was achieved by using a HORIBA LabRAM (jobin Yvon, France) using an air-cooled He/Ne laser (514 nm) focused through an integral microscope (Olympus BX 41) with a $50\times$ objective lens. X-ray photoelectron spectroscopy (XPS) spectra were obtained by using a Thermo Scientific K-alpha (Thermo VG, USA) using monochromated Al $K\alpha$ (1486.6 eV). The zetapotential of GO and all RGOs were analyzed by using a Nano ZS (Malvern, UK). UV was irradiated by using a UVGL -58 Handheld UV lamp (UVP, Upland, CA, USA).

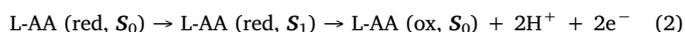
2.6. Quantum chemical simulation details

While the chemical properties of the ground state L-AA are well understood [14], the excited state properties remain elusive. There has been no experimental approach to measure the redox properties of L-AA in the excited state. Having established the good agreement between theory and experiment for the ground state properties, we described the oxidation potential of L-AA in the excited state using a quantum chemical three-state model. The following notations would be used to describe the electronic and oxidation state. A ground (first excited) state is denoted as S_0 (S_1), respectively, and the redox state is given in the parenthesis (ox/red for an oxidized/reduced form of L-AA, respectively).

The oxidation potential of L-AA (red, S_0) can be obtained from the two-species chemical equation (Eq (1)).



If one is interested in redox properties of L-AA (red, S_1), then the chemical equation needs to be rewritten to include this excited state.



A three-state model incorporates following two chemical events. The first arrow entails the population increase in the first excited state by external light source. The reduced form of L-AA in the ground state, L-AA (red, S_0), is promoted to excited states (S_n , $n \geq 1$) by external light source ($\sim 254 \text{ nm}$, 4.88 eV). The molecules excited above S_1 state decay into the first excited state via ultrafast internal conversion. (10^{-11} – 10^{-14} s) Therefore, treating only the first excited state is a reasonable assumption to understand the redox properties of excited species (Blue arrow in Fig. 5a). The second arrow shows the two-electron two-proton oxidation, which is the same process occurring in the Eq (1) (Green arrow in Fig. 5a).

The ground state geometry of L-AA (ox) and L-AA (red) was optimized using density functional theory (DFT), BLYP functional and 6-31G* basis sets. The excited state geometry was obtained using time dependent DFT (TD-DFT) theory with the same level of calculations used for the ground state geometry optimization. Single point energy was obtained based on the optimized geometry with the solvent medium effect considered through polarizable continuum model. Dielectric constant of 78.39 for water was used. Oxidation potential was calculated based on the thermodynamic cycles (Fig. 5b) [15,16], where ΔG_g (ΔG_{aq}) denotes Gibbs free energy change in gas (aqueous) phase, respectively, ΔG_{solv} corresponds to solvation energy in aqueous solution. Solvation energy of proton of -0.424 eV is used, and the potential of normal hydrogen electrode (NHE) in aqueous solution is -4.24 V as a reference electrode value [17]. All oxidation potential value reported in this study is referenced to NHE value. Absorption energy and oxidation potential of L-AA (red, S_0) are compared to available

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