Environmentally Benign Metal-Free Reduction of GO Using Molecular Hydrogen: A Mechanistic Insight

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ABSTRACT: A simple yet effective methodology to obtain high-quality reduced graphene oxide (RGO) using a tetrahydrofuran suspension of GO under hydrogen at moderate pressure has been demonstrated. The extent of reduction as a function of the pressure of hydrogen gas, temperature, and time was studied, where the abstraction of oxygen is achievable with least mutilation of C-sp² bonds, hence upholding the integrity of the graphene sheet. Herein, the formation of a short-lived species is proposed, which is possibly responsible for such reduction. A detailed theoretical calculation along with in situ UV–visible experiments reveals the existence of a transient solvated electron species in the reaction medium. The hydrogen RGO (HRGO) achieved a C/O atomic ratio of 11.3. The conductivity measurements show that HRGO reached as high as 934 S/m, which indicates a high quality of RGO. The process is hassle-free, environmentally benign, and can be scaled up effortlessly without compromising the quality of the material.

1. INTRODUCTION

Reduced graphene oxide (RGO) is one of the most intensively studied derivatives of graphene.1−3 Ever since the extraordinary properties of graphene (e.g., mechanical, electrical, thermal, and optical properties as well as their high specific surface areas) were discovered, graphene and its derivatives have been at the forefront of material research till today.4−5 RGO is one of the most promising materials used instead of graphene. The most common route used for the mass production of graphene is to reduce GO chemically into RGO. The process is well suited to versatile chemical functionalization and involves low material cost. Simplicity and suitability for large-scale production are among the few strong reasons for extensive use of this method.6−7 The challenges associated with the chemical route were inadequate reduction, nonreproducibility, and formation of undesired defects. Till date, the chemical reduction of GO has been performed with several reducing agents such as NaBH₄,8 hydrazine and its derivatives,9,10 hydroquinone,11 hydriodic acid (HI),12,13 sulfur-containing compounds,14 metal powders,15 and so forth. Among them, metal powders are the most powerful reducing agents achieving a high C/O atomic ratio of RGO. Nascent hydrogen, which is considered to be especially reactive and produced from the reaction of metals, such as Mg, Al, Fe, and Zn, with an acid or amphoteric metals (Al and Zn) and their alloys with the alkali solution, has been used by many groups for the reduction of GO.16−19 However, achieving a high C/O ratio does not ensure a better quality RGO.20

Herein, we have explored a new synthetic methodology and its mechanistic insights, which can reroute the procedure for the bulk production of RGO. Instances of mere diatomic hydrogen for the reduction of GO in tetrahydrofuran (THF) without a metal catalyst would be a new addition to the literature. Herein, we report a simple methodology to synthesize RGO under hydrogen in THF, which can be scaled up effortlessly without compromising the quality of the product. The procedure involves exposure of GO suspension in THF, to diatomic hydrogen at a moderate pressure and temperature. The extent of reduction reaches a maximum at a pressure of 40 bars at 180 °C. The reaction is carried out in a stainless steel pressure vessel, resulting in excellent quality RGO. The method of extraction is very facile and imparts zero impurity, and hence, no purification is needed after reduction. The hydrogen RGO (HRGO) using hydrogen achieves a C/O atomic ratio higher than 11.3 and the I_D/I_G ratio obtained higher than 1.6. It should be noted that a controlled experiment was carried out in the presence of argon keeping other reaction parameters intact. GO used in the reaction was not reduced under argon, confirming the role of hydrogen in such reduction (see Supporting Information S1). A detailed theoretical calculation reveals the possibility of formation of
solvated electrons in such reaction, which is shown for the first time.

2. RESULTS AND DISCUSSION

The progress of reduction of GO using diatomic hydrogen was monitored using UV–visible absorption, Fourier transform infrared (FTIR), and Raman measurements (Figure 1) as a function of time. GO shows an absorption maximum at 230 nm owing to the π−π* transitions of the aromatic C=C bonds along with a weak shoulder at 303 nm due to n−π* transitions of C=O bonds. A red shift of the characteristic peak at 270 nm was observed for C=C, once the reduction is over. During the process of reduction, the optical absorption of RGO should have increased as the intensity of UV–visible spectra is directly proportional to the concentration of the solute. However, owing to the hydrophobic nature of RGO, the intensity decreases as it shows minimum amount which can form a stable dispersion of RGO in water (Figure 1A).

Figure 1. (A) “a” shows the UV–vis spectrum of GO, whereas “b,” “c,” and “d” correspond to RGO at 30 min, RGO at 60 min, and RGO at 120 min formed in the reaction, respectively. (B) FTIR spectra of GO at different intervals of time showing the progress of the reaction. (C) Raman spectra of GO and RGO at 60 min reduction and RGO at 120 min reduction, respectively. (D) TGA profile of GO, RGO@20 bar of H2 (HRGO_1), and RGO @ 40 bar of H2 (HRGO_2).

Figure 2. (A) AFM images showing the height profile of HRGO. (B) IV plots of (----) GO and (——) HRGO samples. XPS spectra of (C) GO and (D) HRGO.
For all the FTIR and Raman measurements, shown in Figure 1B,C, reduction of GO was performed at 40 bar of H2 pressure. The peak (Figure 1B) showing oxygen functionality almost vanishes with time and a new peak generates at around 1578 cm$^{-1}$ for the formation of C=C bonds. The degree of removal of oxygen functionalities of GO at different intervals of time can be observed in the plots shown below (Figure 1B). The peak intensities corresponding to O–H stretching (3400 cm$^{-1}$) and the vibrations for O–H deformation (1410 cm$^{-1}$) were decreased gradually. The peak intensities corresponding to the stretching of oxygen functionalities such as >C=O (1720 cm$^{-1}$), epoxy >C=O (1226 cm$^{-1}$), carboxylic >C=O (1320–1210 cm$^{-1}$), and alkoxy C=O (1050 cm$^{-1}$) were also observed to decrease during the progress of the reaction, whereas C=C stretching vibration peaks for pristine GO were detected at ca. 1600 cm$^{-1}$, which is shifted to 1578 cm$^{-1}$ for RGOs as reported by Fang et al.

The Raman spectra showing the D band and G band of GO were shifted to 1336 cm$^{-1}$ and 1571 cm$^{-1}$, respectively, after the reduction. The intensity ratio of the D and G bands, $I_D/I_G$, increases with time as depicted in Figure 1C. Such enhancement in the intensity ratio is attributed to the increased sp$^2$ domains in the system.$^{22}$

Thermogravimetric analysis (TGA) (Figure 1D) did not show any significant weight loss for GO and RGO near 100 °C, as the samples were dried before measurements to eliminate the influence of absorbed moisture on the results. GO unveils a two-step downdrift; the first step starting at 175 °C owing to the loss of hydroxyl, epoxy functional groups, and remaining H2O molecules. The second step involves a decline in the range of 450–550 °C, which involves the pyrolysis of the remaining oxygen-containing groups and the burning of ring carbon. RGO shows a weight loss of only about 7–9 wt% at 250 °C, which is much lower than that of GO, indicating a significant decrease in the amount of oxygenated functional groups.$^{21}$ The height profile of RGO using atomic force microscopy (AFM) (Figure 2A) shows the thickness of the RGO sheet to be 1.05 nm, revealing that the sheet has a single layer of RGO and is consistent with the previous literature reports. The conductivity for GO was found to be 0.04 S/m and the same for RGO was 934 S/m, which validate the claim regarding the quality of HRGO obtained using the aforementioned technique (Figure 2B).

X-ray photoelectron spectroscopy (XPS) analysis was carried out to provide direct evidence of reduction through the removal of oxygen functionality in GO. The C/O ratio of GO was calculated by taking the ratio of peak areas of C 1s to O 1s in XPS spectra (see Supporting Information S.8.) increased from 2.5 to 11.3 after the reduction. The raw data of carbon 1s XPS spectrum of GO was deconvoluted into four peaks, which were assigned to four types of carbon (as shown in Figure 2C), with different chemical valences, including nonoxygenuated ring carbon, C–C (284.8 eV), carbon in C=O (286.5 eV), C–O–C (287.4 eV), and O–C=O (288.9 eV), respectively. After reduction, the decrease in the intensity of all C 1s peaks corresponding to the oxygenated carbon and the corresponding increase in the intensity of sp$^2$ carbon confirm the efficacy of this methodology in restoring the conjugated graphene network and removal of functional groups (Figure 2D).

Capacitive behavior of as-synthesized HRGO samples was evaluated using several electrochemical measurements. Cyclic voltammetry (CV) measurements were done in the potential window of 0–1 V, at various scan rates as shown in Figure 3A. Capacitive performance was indicated by an increase in current response with increasing scan rate. The galvanostatic charge–discharge (GCD) curve at various current densities is shown in Figure 3B. Charge–discharge curves are almost symmetrical in nature, indicating the contribution of both double-layer capacitance and pseudocapacitance. At a current density of 0.5 A/g, HRGO showed a capacitance of 179 F/g. As the current density increases to 6 A/g, the HRGO retains only...
48% of initial capacitance (Figure 3B inset), which is due to low penetration of ions in the inner pore induced by the fast potential changes.23 In general, the capacitance is primarily proportional to the surface area of the electrode materials. Graphene has a very high electrical conductivity and an exceptionally large specific surface area (theoretical value, ~2650 m²/g).24 It was reported that such a high theoretical surface area can provide a gravimetric capacitance of a supercapacitor (SC) as high as 550 F/g.25 Despite this promising interpretation, when prepared in the form of RGO using established solution processes (via Hummer’s method), typical graphene SCs exhibit only 100 to 120 F/g in organic electrolytes26 and around 135 F/g with aqueous electrolytes.27 These smaller specific capacitances are attributed to irreversible restacking of the individual RGO sheets during the reduction and drying processes.28 Graphene SCs are largely dependent on the detailed characteristics of graphene such as its functional groups, size, pore structure, and surface accessibility.29 Lack of porosity in RGO makes substantial surfaces unavailable for charge storage. Nyquist plots at various amplitudes are shown in Figure 3C. The plot exhibited two distinct regions, that is, a semicircle in the high-frequency region and a slope line in the low-frequency region. Appropriate fitting of the obtained electrochemical impedance spectroscopy (EIS) spectra with the equivalent circuit diagram is shown in the inset, and the charge transfer resistance appears to be 7 Ω, which reveals superior quality of HRGO. Furthermore, the cyclic rate performance of specific capacitance from charge–discharge measurements was evaluated. At a current density of 6 A/g, HRGO retained 93% of capacitance after 2000 cycles as shown in Figure 3D. The GCD curves are almost symmetrical in shape even after prolonged cycling as depicted in the inset (Figure 3D).

A two-way approach was attempted to understand and detect the reactive intermediate responsible for such GO to RGO reduction. The first approach involved the use of a probe substrate in the same reaction condition. The second approach was to monitor the reaction mixture during the progress of the reaction using a UV–visible spectrophotometer connected to the reactor (experimental details are shown in Supporting Information S2) (see Scheme 1).

In the first study, styrene oxide was used as the probe substrate in the same reaction condition to see the fate of the epoxide functionality that actually exists in the graphitic lattice of GO. Interestingly, peaks of all the products are clearly visible in the spectra obtained from gas chromatography (GC) and GC–mass spectrometry and are very much aligned with the products formed using traditional reducing agents reported in the previous literature30 (see Supporting Information S3). This evidence strongly supports the possibility of the formation of a transient reducing species responsible for such reaction. A possible mechanism for such reduction is shown in Scheme 2. Kindly note that the reactive intermediate proposed in the reaction involving the probe substrate is purely based on the products obtained, and no claim has been made on the proof of formation of the organic reactive intermediate.

The reduction of THF-suspended GO at high (H₂) pressure indicates the formation of H⁺ + e⁻ from H₂, which might lead to the formation of solvated electron in THF. The role of THF in these reactions is extremely significant. An important structural aspect of THF is that it is a polar molecule which, we believe, may induce polarity in hydrogen molecules at that temperature and pressure.

Apprehending the possibilities of the formation of such species, a DFT calculation directly correlating with the experimental results were performed to evaluate the electronic structure and properties of solvated electrons for anionic, solvated, and neutral form of THF. We hypothesized that the transient species is the solvated electron in THF. In the presence of suspended GO in THF at high pressure, H₂ generates H⁺ and e⁻. The generated e⁻ undergoes through a different nonequilibrium relaxation process. It could reduce neutral THF to [THF]⁻. The other possibility is that the generated electron could be solvated by THF solvent molecules. Here, we would like to emphasize that the electron is a fundamental quantum particle and thus any classical picture of solvation (e.g., ions solvated in water) will certainly not hold. Rather, it is an additional electron that loosely bounds with multiple THF molecules and none of these solvent (THF) molecules that form the solvation shell can have exclusive access to that additional electron. Such special sharing of an electron between the THF molecules provides additional stability to be detected as the transient species. We speculate that over the time period, such a solvation picture starts to diminish as the one that THF molecules start to get the exclusive access of the electron and turns into [THF]⁻ (anion) from the solvated electron [e⁻·][THF]⁻ picture.

As a proof of concept, we have investigated the single anionic dimer, that is, [e⁻·][THF]₂, that clearly indicated that the additional electron gets trapped between the two [THF] species as the highest occupied molecular orbital (HOMO) is localized in between the spatial region (see Figure 4). The time-dependent (TD)-DFT spectra also confirm a prominent peak at 262 nm that is originated from HOMO to lowest unoccupied molecular orbital (LUMO) + 16 (52%) electronic transition (shown in the Supporting Information, Table S3). This commensurate with the transient peak observed in the experiments. We further observed that the neutral THF and anionic [THF]⁻ have dipole moments opposite to each other (see Figure 4). Thus, the solvent dynamics will play a crucial role in stabilizing the “solvated electron”; however, the detailed studies of dynamics are in the process and will be communicated soon.

### 3. CONCLUSIONS

Herein, we have developed a new environment-friendly synthetic methodology to effectively reduce GO using molecular hydrogen at a moderate pressure and temperature. Mechanistic studies with a two-way approach, along with theoretical analysis, reveal the possibility of the formation of
transient species, hypothesized as "solvated electron". The RGO so formed has achieved a C/O atomic ratio greater than 11.3 and a bulk electrical conductivity of as high as 934 S m\(^{-1}\).

The combination of XPS and TGA analyses suggested that most of the labile oxygen functional groups were removed during hydrogen reduction. Compared to other methods using reducing agents, such as hydrazine, NaBH\(_4\), HI, and so forth, this process is less time consuming and hassle free as postpurification of the product is not required. There is a huge possibility to explore and optimize the procedure for industrial applications.

4. EXPERIMENTAL SECTION

4.1. Materials. Major chemicals such as THF, hydrogen peroxide (\(\text{H}_2\text{O}_2\)), potassium permanganate (KMnO\(_4\)), sulfuric acid (\(\text{H}_2\text{SO}_4\)), and hydrochloric acid were purchased from Merck Chemicals unless mentioned otherwise and used as received without further purification. Graphite powder (<20 \(\mu\)m) was purchased from Sigma Aldrich.

4.2. GO Synthesis. GO was synthesized using an improved method as reported in the previous literature.\(^3\) Reduction of GO was carried out in a pressure reactor autoclave using hydrogen gas under various pressures and temperatures to optimize the reaction condition. In brief, 50 mg of GO was dispersed in 35 mL of THF. The above dispersion was then transferred to a 50 mL reactor vessel equipped with pressure and temperature sensors and heated to 180 °C under H\(_2\) (40 bar) for 2 h. The obtained reaction mixture was then centrifuged at 7000 rpm and washed with distilled water and acetone. The dispersion was then filtered using 0.47 \(\mu\)m poly(tetrafluoroethylene) membrane, and the resulting solid was vacuum dried for 24 h and characterized further.

4.3. Characterization. Powder X-ray diffraction (PXRD) of the resulting GO and RGO was carried out with Bruker Eco D8 advance with Cu K\(\alpha\) radiation (\(\lambda = 1.54056\) Å; see Supporting Information S5); morphological studies and Brunauer–Emmett–Teller (BET) surface area analysis are shown in Supporting Information S6 and S7, respectively; UV–vis absorption spectra were recorded using a UV-2600 spectrophotometer (Shimadzu); TGA (Figure 1D) was carried using STA-8000 (Perkin Elmer) under nitrogen atmosphere at a scan rate of 5 °C/min. AFM was performed with a Bruker Multimode 8 AFM using tapping mode; XPS (EscaLab: 220-IXL) measurements were performed with a Mg-K\(\alpha\) non-monochromated X-ray beam having a photon energy of 1253.6 eV (chamber pressure 6 · 10\(^{-10}\) torr, Supporting Information S8). The progress of reactions was monitored using a Carry...
Electrochemical measurements were performed with an Autolab multichannel PGSTAT 204M electrochemical workstation using a three-electrode configuration involving platinum and Ag/AgCl as counter and reference electrodes, respectively. A glassy carbon electrode (3 mm diameter) coated with HRGO ink was used as a working electrode. A homogeneous ink was prepared by dispersing HRGO in dimethylformamide (1 mg/mL) by ultrasonication for 2 hours and 10 μL of the above ink was drop cast on the glassy carbon electrode. It was vacuum dried and 5 μL of 5% Nafion solution was drop cast on the electrode surface, followed by further drying for 12 h. CV measurements were done in the potential window of (0 to 1 V) at various scan rates. GCD tests were also done in a similar potential window at various current densities ranging from 0.5, 1, 2, 4, and 6 A/g. All the measurements were done in an Argon purged system containing 1 M Na2SO4 as an electrolyte. The specific capacitance, C (F g−1), of the electrode material was calculated from the following equation:

\[ C = \frac{I \Delta t}{m \Delta V} \]

where \( I \) (A) is the discharge current, \( \Delta t \) is the discharge time, \( \Delta V \) is the potential window, and \( m \) (g) is the active mass. EIS was performed over a frequency range from 0.01 Hz to 100 kHz at an open-circuit potential with an ac perturbation of 5 mV.

4.5. Computation Details. DFT-based AIMD simulations were performed at a finite pressure and temperature (1 atm & 400 K), and a 1 ps AIMD trajectory was generated to investigate the formation of the transient species. The molecular geometries were optimized using a hybrid B3LYP functional and def2-TZVP basis sets. The TD-DFT calculations were performed to obtain electronic spectra by applying a long-range correction including a hybrid exchange–correlation functional using the Coulomb-attenuating (CAM-B3LYP) method. An implicit solvent model was also adopted to incorporate the solvation effect in electronic spectra calculations (see Supporting Information S4). All the calculations were performed using VASP and ORCA quantum chemical codes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00848.

Control experiment, PXRD, scanning electron microscopy, transmission electron microscopy, BET analysis, XPS spectra, in situ TD UV–vis spectral analysis, mechanistic studies, GC analysis of the reaction of styrene oxide as a probe substrate in THF, mass spectra of products, and computational details (PDF)

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R.R. and Z.A. contributed equally. The manuscript was written through contributions from all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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