Facile Synthesis and Characterization of Reduced Graphene Oxide Produced with Green and Conventional Reductants

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Graphene oxide (GO) has been studied as a material of broad interest because of its extraordinary properties, such as high surface area and tunable electric conductivity. The surface of GO mainly contains different oxygen-containing functional groups, such as GO epoxide, hydroxyl, and carboxyl which make GO hydrophilic and insulating in nature. Most of the epoxide groups are removed during the oxidation. There are several methods and routes that can efficiently provide reduced graphene oxide (rGO), such as chemical reduction, thermal reduction, electrochemical reduction and photocatalytic reduction of GO. Among all these processes, chemical reduction of GO is considered as the fastest way to produce rGO. Reduction by chemical reagents is based on their chemical reactions with GO. On the other hand, the reduction can make a great change in the microstructure and properties of GO by removing functional groups like oxygen-containing groups. This can result in a highly conductive sheet electrode. The chemical reduction method is a cheaper and more convenient way for the mass production of rGO with high efficiency, especially when compared with other methods like thermal reduction. In addition, the requirements for equipment and laboratory environment are not as critical as that for thermal annealing treatment. For example, the chemical reduction can be performed at room temperature, which makes chemical reduction one of the favorite and most effective methods of GO reduction.

In many cases, strong reducing agents such as hydrazine monohydrate, hydroxylamine, hydroquinone, phenylenediamine, sodium borohydride, and hydrohalic acid have been used as reducing agents to increase the efficiency of reduced GO and improve the final properties. Many studies, including this one, confirmed that the hydroiodic (HI) has a reducing ability much higher than that provided by other reduction materials and techniques, in terms of conductivity and mechanical properties. For that, we used HI to modify a high-performance flexible electrode for electrocatalysis production simultaneously in fabricating many samples to investigate the efficiency of these materials when used together. Considering the result from this reduction work by HI and EGCG, we can see that the electrical conductivity for rGO sheet, which is obtained from HI treatment, is higher and shows a very good flexibility with a much higher tensile strength than the samples created with the presence of EGCG.

In this work, environmental friendly reductant, EGCG, was used as reductive for GO sheet and for deposition of Pt nanoparticles (Pt NPs) on sheets of rGO. Combination of rGO sheet and metal nanoparticles will give a variety of applications, specifically in electrocatalytic activity area.

This study shows the recent advances in properties of rGO sheets by combining EGCG with HI in two separate steps which provides the conductivity of the sheets and introduces active sites. The aim of this work is using these rGO sheets with active sites for further modification of rGO with metal nano particles and obtaining high active electrocatalysis. There are many applications nanomaterial deposition onto electrode surfaces in catalysis, photocatalysis, and electrochemical areas such as electronic and optical devices, energy generation and storage, chemical sensors, catalysis, and even biological materials.

Methods and Characterization

Materials and reagents.—Graphite nanoplatelets obtained from XG Sciences, Lansing, MI, were used as the main precursor for the synthesis of graphene oxide. ACS reagent grade chemicals such as sulfuric acid (H₂SO₄), sodium nitrate (NaNO₃), potassium permanganate (KMnO₄), and hydrogen peroxide (H₂O₂) used in the synthesis of GO.
were purchased from Sigma-Aldrich. Hydroiodic acid (HI), and epigallocatechin gallate (EGCG) utilized to reduce GO were purchased also from Sigma-Aldrich.

Preparing GO sheet electrode.—Graphene oxide had been synthesized by a modified Hummers’ method. In brief, graphite nanoplatelets (1 g) and NaNO₃ (1 g) were mixed with 46 mL of concentrated H₂SO₄ in a beaker cooled in an ice bath, followed by the addition of 6 g of KMnO₄. The mixture was stirred at 35 °C for 1 h followed by 80 mL of deionized water which was added dropwise, and the reaction mixture was maintained in the water bath at 90 °C for 30 min. Subsequently, 200 mL of deionized water was slowly added, followed by addition of 6 mL of H₂O₂ to the resultant dispersions, and the solution was left to cool at room temperature. The GO dispersion was centrifuged to remove most of the ionic impurities followed by more washing with DI water and centrifugation. The GO was dispersed in DI water to form a hydrosol, ultrasonicated, and dried to form a GO sheet.

Chemical reduction of GO sheet electrode.—Preparation of GO–(EGCG) modified sheet electrode.—The required amount of EGCG was first dissolved in 10 mL of DI water and treated with sonication for 30 min. Then, the GO sheet was immersed in an aqueous solution of EGCG for two days to obtain GO–(EGCG) sheet. The GO–(EGCG) was washed with DI water for several times and dried at room temperature. Preparation of RGO–HI sheet electrode.—The GO sheet was directly immersed into hydroiodic acid (HI) solution in a sealed cuvette at room temperature for 1 h. Then, the RGO–HI sheet was washed with DI water for several times and dried also at room temperature to obtain the final sheet electrode.

Preparation of (rGO–EGCG), (rGO–2EGCG), and (rGO–2EGCG)–HI modified sheet electrodes.—EGCG (12.5 wt% relative to GO) was added to a GO suspension for fabricating (rGO–EGCG) sheet electrode and (25 wt% relative to GO) for (rGO–2EGCG) sheet electrode. The mixture was sonicated for 1 h, and then dried at 40 °C. In order to obtain (rGO–2EGCG)–HI sheet electrode, (rGO–2EGCG) sheet was reduced again by immersing this one directly into hydroiodic acid (HI) solution in a sealed cuvette at room temperature for 1 h. The (rGO–2EGCG)–HI sheet was washed with DI water for several times then dried also at room temperature.

Single step of chemical deposition in decorating reduced graphene oxide with metal nanoparticles.—Preparation of (rGO–EGCG)–Pt and (rGO–2EGCG)–Pt sheet electrodes.—To prepare Pt salt, 8.75 mg Pt salt was dissolved in 25 mL of DI water and sonicated for 30 min. The (rGO–EGCG) and (rGO–2EGCG) sheets immersed in the solution of Pt salt for 5 h, then these sheets were washed several times with DI water and dried at room temperature.

Characterization and electrochemical measurement.—Scanning Electron Microscopy (SEM) images were obtained using FEI Quanta 600 FEG Environmental Scanning Electron Microscope (ESEM), equipped to perform elemental chemical composition analysis by Energy Dispersive X-ray Spectrometry (EDS/EDX). The electrical conductivities of all modified electrodes (GO, rGO–EGCG), and rGO–HI) were tested by a cyclic voltammetry (CV) experiment which was performed with a Single Potentiostats / Galvanostats / EIS SP – 300 (Bio Logic since instruments). The working electrode was any one of the sheet electrodes which was set in cell device. The auxiliary and reference electrodes were Pt wire, and Ag/AgCl, respectively. Cyclic voltammetry CV analysis was used in the investigation of all sample electrodes behaviors in 0.1 M H₂SO₄ solutions at different Scan Rates of (mV/s).

Results and Discussion

Synthesis and characterization of reduced graphene oxide sheet by EGCG (polyphenol); (GO–(EGCG)), (rGO–EGCG) and (rGO–2EGCG) sheets.—EGCG was employed as a kind of reducing agent and an efficient stabilizer for GO (see Figure 1). Moreover, many characteristics of oxidized EGCG have been reported in the literature. Corresponding EDX analysis was conducted to determine the atomic percent (at %) of the elements present in the samples of this research. In EDX investigation, the change of C/O atomic ratio of all rGO samples suggests the reduction degree of GO. The reduction behavior of EGCG was used to prepare a different modification of rGO sheets. As shown in Table I, the C/O ratio of GO sheet was ∼1.6. Although the GO sheet was immersed in EGCG solution for two days to produce (GO–(EGCG)) sheet, the C/O ratio was only ∼2.7. However, mixing of EGCG (12.5 wt% of graphene oxide weight percentage) with a GO suspension to modify (rGO–EGCG) sheet showed a clear increase of the C/O ratio ∼3.1. Consistently, doubling of EGCG amount (25 wt% of graphene oxide weight percentage) to utilize (rGO–2EGCG) sheet led to double the C/O ratio ∼6.3. This significance is expressed by the sonication of EGCG with GO suspension which contributed in a more uniform distribution for EGCG and more effective reduction for GO. As a schematically structured of EGCG in Figure 1A, the ability of EGCG in reducing GO resulted from the conversion of phenols on the gallic acid units (rings B and C) into galloyl-derived orthoquinon through the nucleophlic addition of epoxide on GO[29]. The stability caused from oxidized EGCG strongly absorbed on rGO samples leading to π–π interactions.[39,50]

SEM images were taken of all samples; feature surfaces of the composites are shown in Figure 2. As compared to GO sheet (Figure 2A), there is no significant morphology for distributing EGCG clearly seen in composite described earlier. For (GO–(EGCG)) sheet in Figure 2B, non-uniform size distribution particles in the solution of EGCG with its aggregation caused non-stable reduction. The aggregation prevented the EGCG interaction with GO within the GO sheet which made the reduction limited to the surface of GO sheet. However, the significance of mixing EGCG with GO suspension to obtain a sheet consisted of GO and EGCG together implied more reduction stability with less aggregation, Figures (2C and 2D).

Synthesis and characterization of reduced graphene oxide sheet by HI; (RGO) sheet.—In this study, we tried to efficiently remove functional groups - like epoxy, carboxyl, carbonyl, and hydroxyl groups - which are the key for the reduction of GO to produce a highly conductive rGO electrode. Halogenation agents, including concentrated hydroiodic acid (HI), are strong reducing agents. The RGO sheet resulted from the immersion of the GO sheet in HI showed an extremely high reduction degree (see Figure 3B). The optical observation shows the change in color of the GO sheet from black and lackluster to shining metallic luster after the reduction caused by HI, which indicates a reduced GO sheet. As shown in Table I, the surface atomic C/O ratio of RGO sheet was ∼12.5 with HI reduction.

Nevertheless, the hydrohalic acid has a corrosivity and toxicity effect. For all priority samples of rGO with EGCG reducing modification, the C/O atomic ratios were lower than those of rGOs reduced by hydrologic acid. Table I shows that the adsorbed of EGCG may contribute to oxygen groups. The rGO samples reduced by EGCG revealed a small wrinkle and intrinsic defect in sheets that was in contrast with the rest of samples. The presence of the defect may be induced by remaining of some residual oxygen groups (see Figures 2 and 3 and Table I). Remaining oxygen groups on the surface of GO reduced by EGCG could be a benefit for our next stages. In summarizing electrical conductivities from some recent reports (see Table II), the conductivity value of rGO sheet after being reduced by EGCG was lower than reduced sheet by HI.[39,31] Wang et al.[19] believed the adsorption of heavy EGCG molecules on the GO surface caused this limitation in the conductivity.
Figure 1. Schematic illustration of preparation of reduce graphene oxide. A) GO – (EGCG), B) RGO, C) (rGO – EGCG) or (rGO – 2EGCG), D) R(rGO – 2EGCG) – HI, sheets.

### Table I. EDX elementals analysis of GO, GO – (EGCG), rGO – EGCG, rGO – 2EGCG, RGO, R(rGO – 2EGCG) – HI, sheets, L-AA RGO-I,2, D-GLC RGO-I,2, N RGO, TP RGO, reported in the literature.28

| Samples                        | C% Atomic | O% Atomic | C/O   | Ref.  |
|--------------------------------|-----------|-----------|-------|-------|
| GO                             | 58.94     | 36.25     | ~1.6  | Our work |
| GO – (EGCG)                    | 73.27     | 26.73     | ~2.7  | Our work |
| rGO – EGCG                     | 74.04     | 23.96     | ~3.1  | Our work |
| rGO – 2EGCG                    | 83.79     | 13.28     | ~6.3  | Our work |
| RGO                            | 83.98     | 6.7       | ~12.5 | Our work |
| R(rGO – 2EGCG) – HI            | 71.23     | 6.94      | ~10.26| Our work |
| L-AA RGO-I                     | -         | -         | 5.15  | 28    |
| L-AA RGO-2                     | -         | -         | 4.87  | 28    |
| D-GLC RGO-I                    | -         | -         | 2.89  | 28    |
| D-GLC RGO-2                    | -         | -         | 2.67  | 28    |
| N RGO                          | -         | -         | 3.60  | 28    |
| TP RGO                         | -         | -         | 3.44  | 28    |

**Synthesis and characterization of reduced (rGO – 2EGCG) sheet by HI; R(rGO – 2EGCG) – HI sheet.**—Previous investigations have been conducted to evaluate the chemical reduction of GO sheet for improving the typical disadvantages of EGCG such as low conductivity. In trying of maximizing the reduction of GO sheet with EGCG based composite, the (rGO – 2EGCG) sheet was further reduced by HI to produce R(rGO – 2EGCG) – HI sheet. The second chemical reduction with HI, C/O ratio was ~ (10.26) (see Table I). The C/O atomic ratio of R(rGO – 2EGCG) – HI was a little lower than that of its corresponding RGO. However, C/O atomic ratio of (rGO – 2EGCG) was lower than R(rGO – 2EGCG) – HI and RGO after being reduced by HI. Most importantly, obviously all the rGO samples in the presence of EGCG might be suggested to have the C/O content contribution from EGCG (check Table I). However, reducing GO sheet by only HI recorded the highest C/O ratio and the lowest oxygen content. Additionally, the acidic environment for treating (rGO – 2EGCG) by HI to fabricate R(rGO – 2EGCG) – HI could be the reason of releasing free EGCG and limiting the effect of these reducing agents.52 After treating with HI as in Figure 3, R(rGO – 2EGCG) – HI sheet displays the characteristic of clear wrinkled morphology (light lines). Briefly, it is worth noting that all rGO samples with an EGCG reduction were showed to have a possibility of easily cracking while working as an electrode sheet. Although treating with HI displays improvement in texture properties, R(rGO – 2EGCG) – HI sheet showed no stability in working.

The top-section SEM images (Fig. 3A, 3B, and 3C) reveal that (rGO – 2EGCG) and R(rGO – 2EGCG) – HI sheets exhibit a rough corrugated surface feature, where the EGCG exhibits a wrinkled texture. The top surface of purer RGO paper is much smoother, associated with a flexible nature of graphene nanosheets, than that of (rGO – 2EGCG) and R(rGO – 2EGCG) – HI sheets.

**Electroless deposition of Pt nanoparticles on the (rGO – EGCG & rGO – 2EGCG) sheets from Pt salt; (rGO – EGCG) – Pt and (rGO – 2EGCG) – Pt.**

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Figure 2. SEM images for A) GO, B) GO – (EGCG), C) rGO – EGCG, D) rGO – 2EGCG, sheets.

Figure 3. SEM images A) (rGO – 2EGCG), B) RGO, and C) R(rGO – 2EGCG) – HI, sheets.
As shown before, GO sheet can be easily converted by using EGCG as chemical reduction agent to rGO, which offers better electrical conductivity. In this part, it introduces active sites in modifying rGO sheet with Pt NPs. Morphologies of Pt NPs deposited on rGO sheets have been characterized by SEM images in Figure 4 which shows the small size of Pt NPs with good dispersal and very few aggregations (as in (rGO – EGCG) – Pt sheet) on the surface of the sheet electrodes. As EDX recorded, the mean Pt NPs loading was increased from (∼9.9 wt% Pt) on (rGO – EGCG) – Pt sheet to (∼20.03 wt% Pt) on (rGO – 2EGCG) – Pt sheet.

The comparison of the reduction effects on GO sheet with HI and EGCG is shown in Figures 2 and 3 and Tables I and II. The GO sheet is reduced by HI that has improved conductivity and even texture, while all the GO sheets reduced by EGCG exhibited poor mechanical properties because of remaining oxygen groups. Besides, the GO sheets reduced by EGCG broke up into pieces. These results show that HI not only has a better reducing effect than EGCG but is also suitable for the reduction of GO sheet and might be a better choice as an electrode for our next step.

Thus, by choosing EGCG as a reductive agent for both GO sheet and Pt NPs, we can control the reduction effectiveness of graphite oxide and modify rGO sheets by metal nanoparticles. Therefore, the simple preparation process of Pt/rGO sheets will have promising applications in the future especially in catalytic activity area.

**Electrochemical characterizations of GO and rGO electrodes:**

**CVs of GO vs. (rGO – 2EGCG) and RGO sheets.**—Figure 5 displays the performance of some rGO sheets by cyclic voltammograms. CVs obtained on GO, (rGO – 2EGCG) and rGO sheets in 0.1 M H₂SO₄ solution as an electrolyte at a scan rate of 100 mV/s. The voltammograms show that the current density obtained in GO at the whole potential range is much lower than the two other electrodes related to the high resistivity of GO. The slightly higher current density obtained in GO treated with EGCG agrees with the conductivity value (see Table II). The highest current density obtained in GO after treatment by HI (RGO) shows that HI is obviously more effective in reducing GO functional groups and provides a faster electron transfer rate and a larger effective surface area than EGCG. The higher current density in the RGO electrode is significant due to the improved electrical conductivity behavior after GO sheet reduction with HI and the formation of more nucleation sites on the surface of an RGO sheet electrode. This statement is in a good agreement with previous investigation’s sections.

Figure 6 displays the cyclic voltammograms of GO, (rGO – 2EGCG) and (GO – 2EGCG) – Pt electrodes at a scan rate of 100 mV/s. (rGO – 2EGCG) – Pt sheet exhibited a much higher current density than...
that of the pure (rGO – 2EGCG) or GO. The sheet of (GO – 2EGCG) – Pt still has a very high resistance when compared with RGO sheet (as in Figures 5 and 6), because this sheet has low reduction of oxygen functional groups which contrasted with RGO sheet.

Conclusions

In this research, chemical reduction of GO was investigated with two main reducing agents: HI as a toxic chemical and very strong reducibility of green reductant EGCG was shown to have low C/O ratio ∼ 8.43 and low electrical conductivity which could be related to the heavily reducibility of green reductant EGCG was shown to have low C/O ratio which contrasted with RGO sheet.

Two steps reducing GO, first with EGCG and preparing rGO sheet and then treating it with HI acid showed high C/O ratio of about 10.26 which is slightly lower than rGO with only HI. This slightly lower C/O ratio might be related to the contribution of C and O content from EGCG.

This study shows that combining EGCG with HI in two separate steps, not only provides rGO with good conductivity but also the EGCG embedded in the rGO sheet introduces active sites for further modification of GO with metal nano particles and obtaining high active electrocatalysis.

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