Voltammetric Analysis of Graphene Oxide Modified Glassy Carbon Electrodes

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Reduced Graphene Oxide Derivatives

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Graphene and Graphene Oxide Applications

Potential New Products and Applications - *Flexible, transparent, small*

<http://www.cellphonebeat.com/transparent-cellphone-concepts-fun>
<http://news.cnet.com/coming-to-a-printer-near-you-electronics-manufacturing>
<http://arstechnica.com/science/2016/a-graphene-patch-that-monitors-and-possibly-treats-diabetes>.
<https://doi.org/10.1016/j.mattod.2019.01.007>

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Great interest in Graphene and Graphene Oxide

Contemporary and prospective Applications of GO and rGO. Size of blocks gives estimation of number of research publications areas.

According to the Web of Science.

Comparing Graphene to Graphene Oxide

- Graphene

- Graphene Oxide

Reduced Graphene Oxide (rGO) Derivatives

Reduced graphene oxide (rGO) is prepared by removing oxygen from the graphene oxide (GO) lattice.

Increase the C/O

rGO derivatives are intermediation forms of rGO reduction, C/O varies

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Focus of Study

Questions:

- 1. Are there “greener” ways to reduce graphene oxide?*
- 2. Can rGO derivatives (varying C/O GO) be stabilized?*
- 3. How do the properties of rGO derivatives, particularly electrical performance, compare to graphene and graphene oxide?*

UV-Vis spectroscopy, an easy way to track GO reduction

Graphene oxide red shifts from 230 $\rightarrow$ 270 nm upon reduction

Ascorbic Acid as a Replacement for Hydrazine

“Vitamin C is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions”

Fernandez-Merino et al.

TABLE 1: UV-vis Absorption Peak Position of 0.1 mg mL⁻¹ Aqueous Graphene Oxide Suspensions after Completion of Deoxygenation with Different Concentrations of Reductants (Sodium Borohydride, Pyrogallol, Vitamin C, and Hydrazine) and Bases (Ammonia and Potassium Hydroxide), with Indication of the Sample Acronyms Used Throughout the Text

reductant or base	sample acronym	concentration of reductant or base (mM)	absorption peak position (nm)	time to reaction completion (min)
none (unreduced graphene oxide)	GO		231 ± 2	
ammonia	N1	26	257 ± 2	240
	N2	51	260 ± 2	240
	N3	103	256 ± 2	240
	N4	206	257 ± 2	240
potassium hydroxide	K1	0.8	252 ± 2	240
	K2	4	258 ± 2	180
	K3	20	258 ± 2	120
	K4	100	251 ± 2	60
sodium borohydride	B1	0.5	251 ± 2	180
	B2	2	246 ± 2	45
	B3	8	253 ± 2	45
	B4	10	263 ± 2	15
	B5	31	266 ± 2	15
pyrogallol	P1	0.3	262 ± 2	120
	P2	0.5	266 ± 2	60
	P3	1	266 ± 2	60
	P4	2	266 ± 2	60
vitamin C	V1	0.3	263 ± 2	240
	V2	0.5	268 ± 2	180
	V3	1	268 ± 2	30
	V4	2	268 ± 2	15
hydrazine monohydrate	H1	1	268 ± 2	15
	H2	2	268 ± 2	15
	H3	10	268 ± 2	15
	H4	21	268 ± 2	15

Big Picture → Can rGO derivatives be stabilized and studied in a “greener” way?

Purpose of this study: Use the reducing agent, ascorbic acid to generate rGO derivatives and use simple methods to study stability and electrical performance.

Methods

1. UV-Vis max peak shift 230-270nm
2. Modified a glassy carbon electrodes and look at performance with a test sample

Graphene Oxide Source

This GO is prepared by the Hummers Method.

Specifications:

- Composition Carbon (79%) and Oxygen (20%)
- Flake size 0.5-5 microns
- Thickness – 1 atomic layer at least (60%)

Highly Concentrated
Graphene Oxide
Dispersion in Water

*from data sheet

First Method - UV-Vis Procedure and Controls

Procedure

- Test tubes were prepared with increasing concentrations of ascorbic acid and a fixed volume of graphene oxide
- Samples were heated for 90 minutes in a 90°C water bath and then cooled to room temperature
- λ_{max} was monitored using a UV-VIS spectrometer following careful ascorbic acid spectral subtraction

UV-Vis Controls

1. GO + Ascorbic Acid $\rightarrow$ no peak shift $\rightarrow$ no reduction
heat (or some catalyst) is required for the reduction
2. rGO derivatives $\rightarrow$ no peak shift for 48 hour
rGO derivatives are stable

Minutes	λ_{max}
15	246
30	246
45	243
60	246
75	247
90	245
105	244
120	247
1440 (24 Hours)	246
2880 (48 Hours)	247

Table 2. The Effect of Time on Wavelength Maximum for 0.0625 mM Ascorbic Acid and 20 μL Graphene Oxide Sample

Figure 1: GO + Ascorbic Acid, no heat

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Figure 2: Titration of graphene oxide with ascorbic acid. The different colors represent varying mM concentration of ascorbic acid. Inset, extent of reduction, λ_{max} versus mM ascorbic acid added to a constant volume of graphene oxide with heat.

UV-Vis Findings

- rGO derivatives were created
- UV-vis spectra were collected
- λ_{max} increases with increased concentration of ascorbic acid (mM)

Data collected on a Cary100BioUV-Vis spectrometer

Depositing rGO Derivatives on Glassy Carbon Electrodes

- A simple drop-casting method was used, Castro et al., but results were not reproducible.
- Deposition Method was adapted Chen et al.
 - 1.5 – 0.6 V for 15 cycles at 25mV/sec scan rate under N₂ after 10 min N₂ purge using Bioanalytical Systems, Incorporated (BASi) Epsilon Eclipse 3-electrode potentiostat/electrochemical workstation.

1. Castro, K. L. S. et al., Electrochemical response of glassy carbon electrodes modified using graphene sheets of different sizes. E. *Int. J. Electrochem. Sci.*, **2018**, *13*, 71-87, doi: 10.20964/2018.01.02.

2. Chen, L. et al., Direct electrodeposition of reduced graphene oxide on glassy carbon electrode and its electrochemical application. *Electrochemistry Communications*, **2011**, *13*, 133-137, doi: 10.1016/j.elecom.2010.11.033.

Proposed Deposition Mechanism

Electrodeposition Mechanism:

Figure 3: Electrodeposition of rGO

Figure 3: Deposition Mechanism for rGO

rGO Deposition and Testing of Electrochemical Properties

- Deposit stable rGO derivatives on a glassy carbon electrode
- Use linear sweep voltammetry to monitor current produced in a potassium hexacyanoferrate (III) test solution in 1.0M KNO₃. Current, I , is related to conductivity, σ , via the following equations.

Equation 1 $V = IR$

Equation 2 $R = L\Omega / \sigma A$

Experimental Parameters for a Trial

- Trial included variable concentrations of ascorbic acid (0.01-0.20 mM) with fixed volume of GO (20 μ L) diluted to 10 ml with type 1 water heated to 90°C for 90 minutes and then cooled to room temperature for 45 minutes.
- Same glassy carbon electrode used for trial
Glassy carbon electrode was polished with 1.0 μ m diamond followed by alumina slurry $\rightarrow$ sonicate 45 minutes $\rightarrow$ 0.10M sulfuric acid cycling (-1500 mV – 800 mV) between experiments in a trial.
- Deposition Method
-1.5 – 0.6 V for 15 cycles at 25mV/sec scan rate under N_2 after 10 min N_2 purge.
- Linear sweep experiment
Ag/AgCl reference electrode and Pt wire auxiliary electrode. Potassium hexacyanoferrate (III) test solution.

Trends from Linear Sweep Study of rGO Derivatives

Figure 4: rGO modified glassy carbon electrode used in linear sweep voltammetry study of 8mM potassium hexacyanoferrate (III) test solution in 1.0M KNO_3 .

Graphene Oxide Reduction Models

From Lerf et al.

Figure 5: Lerf-Klinowski GO model.

From Dideikin et al.

Figure 6: Schematic evolution of GO domain structure at reduction. Left – GO, Right – rGO. Dark green sp² graphene regions, light green sp³ oxygen containing areas.

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Next Steps

- Further investigate the kinetics/thermodynamics of the GO reduction using simple methods.
- Investigate other ways to prepare stable rGO derivatives.
- Study the function and performance characteristics of rGO modified glassy carbon electrodes (stability, reproducibility, etc).

Conclusions

1. Stable rGO derivatives can be prepared using the benign reducing agent, ascorbic acid.
2. The extent of reduction can be followed by UV-Vis spectroscopy by following the λ_{max} peak shift.
3. rGO derivatives where deposited on glassy carbon electrodes and current produced in linear sweep voltammetry can be measured using a test solution.
4. The current produced has two phases, possibly explained by the percolation threshold of the material.

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Project Co-Authors

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