Rate and Mechanistic Investigation of Eu(OTf)$_2$-Mediated Reduction of Graphene Oxide at Room Temperature

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Abstract

We have developed a fast and efficient method for reduction of graphene oxide (GO) at room temperature. A divalent europium complex {Eu(OTf)$_2$} has been used as reducing agent. The product {reduced graphene oxide (rGO)} was characterized by various spectroscopic (FT-IR, UV-visible absorption and Raman), microscopic (TEM and AFM) and powder X-ray diffraction (XRD) techniques. Kinetic investigations suggest that, bimolecular rate constants for the reduction are 13.7±0.7 M^{-1}s^{-1} and 5.3±0.1 M^{-1}s^{-1} in tetrahydrofuran-water and acetonitrile-water mixtures, respectively. We have also determined the rate orders for every components to understand the mechanism of the reduction reaction.

Introduction

Graphene, a two dimensional arrangement of sp^2-hybridized carbon atoms, has received considerable attention in recent past due to its unique physical properties.[1] While various methods are reported for the reduction of GO to rGO, a fast and efficient method is essential for bulk scale production of graphene.[2] Moreover, determination of the rate and explaining the reaction mechanism is crucial to understand the fundamentals of the reduction process.[3] Herein, we described a divalent europium {Eu(OTf)$_2$} mediated reduction of GO and analyzed the rate and mechanistic aspects of the reaction.[4]

Results and Discussion

Eu(OTf)$_2$-Mediated Reduction of GO

A tetrahydrofuran (THF) {or acetonitrile (ACN)} solution of Eu(OTf)$_2$ was added to an aqueous solution of GO at room temperature.

Time progress of reduction
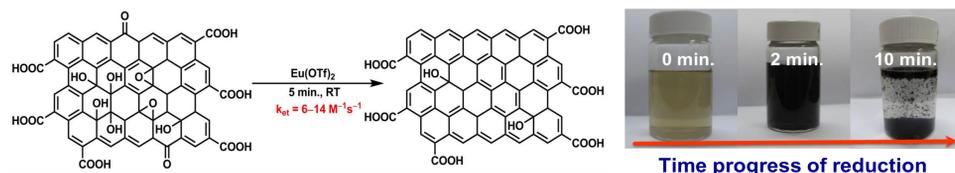
Scheme 1. Schematic presentation of possible reduction of GO by Eu(OTf)$_2$.
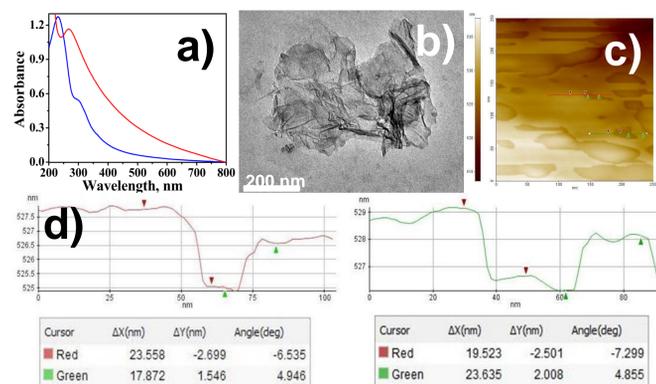
Characterization of rGO

Figure 1. (a) UV-visible absorption spectra of GO (blue) and rGO (red). (b) TEM image of rGO sheets. (c) AFM image of rGO sheets. (d) The height profile of the AFM image.

Determination of Rate Constants

The absorbance growth at 600 nm was plotted versus time for the determination of rate constant of Eu(OTf)$_2$-mediated reduction of GO.
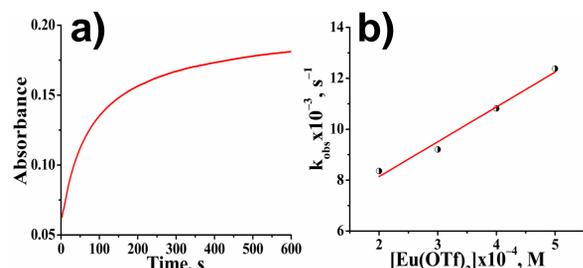

Figure 2. (a) Plot of growth of absorbance at 600 nm vs. time. (b) Plot of observed rate constant (k$_{obs}$) vs. [Eu(OTf)$_2$].

Acknowledgements

Table 1. Comparison of the measured bimolecular rate constants for the reduction of GO by various reducing agents

Sl. No.	Reducing Agent	Solvent	Temperature (°C)	Time	Bimolecular Rate Constant (M^{-1}s^{-1})	Reference
1	Hydrazine + Ammonia	H$_2$O	95	1 h	17×10^{-1}	_Nat. Nanotechnol._ 2008, _3_, 101
2	Sodium Borohydride	H$_2$O	125	3 h	3.3×10^{-1}	_Chem. Mater._ 2009, _21_, 3514
3	Glucose + Ammonia	H$_2$O	95	1 h	1.3×10^{-1}	_ACS Nano_ 2010, _4_, 2429
4	Eu(OTf)$_2$	ACN-H$_2$O	RT	5 m	5.3	Present work
		THF-H$_2$O	RT	5 m	13.7	

Free-energy change of electron transfer

$$\Delta G_{et} = 23.06 \times [E_{ox} - E_{red}](kcal/mol)$$
$$\Delta G_{et} = -7.85 \ kcal/mol$$

Determination of Rate Orders

Rate orders for each components have been determined to understand the mechanism of the reduction, using reaction progress kinetic analysis (RPKA) method.
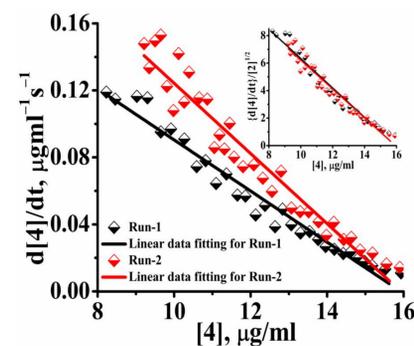

Figure 3. Plot of rate vs. [4] for determination of rate order of Eu(OTf)$_2$. Inset shows the plot of normalized rate vs. [4].

Table 2. Observed rate orders for various components

| Solvents | Rate orders with respect to various components | | |
	GO (1)	Eu(OTf)$_2$ (2)	H$_2$O (3)
THF	−1.03±0.1	0.46±0.05	0.76±0.05
ACN	−0.68±0.05	0.44±0.05	0.89±0.05

Conclusion

Eu(OTf)$_2$ has been introduced as an efficient reagent for the reduction of graphene oxide. Details kinetic studies have been performed which suggests that, the method is more efficient compared to that of other commonly used reduction methods.

References

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[2] Gao, X.; Jang, J.; Nagase, S. _J. Phys. Chem. C_ 2010, _114_, 832.
[3] McDonald _et al._, _Nano Lett._ 2013, _13_, 5777.
[4] Ghosh, T.; Maity, S.; Prasad, E. _J. Phys. Chem. B_ 2014, _118_, 5524.