

DISPERSION BEHAVIOR OF CATIONIC SURFACTANT TREATED REDUCED GRAPHENE OXIDE IN DIFFERENT SOLVENTS

K.N. Amba Sankar¹, P. Nandakumar^{1,✉}, C. Sathishkumar², R. Deepa³
and Kallol Mohanta⁴

¹Department of Electronics, PSG College of Arts & Science, Coimbatore-641014, Tamilnadu.

²Department of Chemistry, Sardar Vallabhbhai Patel International School of Textiles and Management, Coimbatore-641004, Tamil Nadu, India

³Department of Information Technology, PSG College of Arts & Science, Coimbatore-641014.

⁴Nanotech Research Innovation and Incubation Centre (NRIIC), PSG Institute of Advanced Studies, Coimbatore- 641004, Tamil Nadu, India

✉Corresponding Author: nandacjb@gmail.com

ABSTRACT

The dispersion behavior of chemically modified reduced graphene oxide (CRGO) has been investigated in five different solvents. Herein, we used cationic surfactant CTAB as a dispersing agent to prevent the agglomeration of graphene layers. The main role of the surfactant is to create dangling bonds on graphene layers and those help to exfoliate. In the physical process, ultra-sonication is used to break the π bonds whereas, in the chemical process, surfactant molecules occupy the space between the graphene layers. The dispersion behavior of CRGO in different liquid media has been observed for over a month. The chemically reduced graphene oxide was characterized by Transmission electron microscopy (TEM) analysis and current-voltage (I-V) measurement.

Keywords: CRGO, Organic Solvents, Dispersion Stability, TEM, I-V Characterization

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INTRODUCTION

In recent decades conductive inks are widely investigated due to potential applications in flexible and printed electronics.¹⁻⁹ Generally, conductive coatings are used to cover dielectric substrate and increase electron mobility in less conductive films.^{10, 11} Conductive metallic nanomaterials¹² and carbon-based 0D, 1D, and 2D materials¹³ ensure potential applications in growing scientific areas. These kinds of nanomaterials have good transparency and conducting behavior and are used in advanced electronic device applications such as transparent electrodes¹⁴⁻¹⁸, electromagnetic interference shielding¹⁹, solar cell, liquid crystal display, supercapacitor, lubricant systems²⁰, and smart textiles.²¹⁻²³

Graphene is a 2D nanostructured carbon allotrope with a high surface area. It has unique electrical, strong mechanical, and good thermal properties. Graphene cleaves to immense assure for fabricating a choice of electronic devices, for example, energy production and storage, conducting reinforcing addition materials, sensors, transparent electrodes, and so on. The unique properties of graphene come from the individually separated layers, but isolated graphene layers tend to agglomerate together as a result of van der Waals force exhibited from π - π hoarding; then it forms the graphitic structure. These appearances create graphene mainly beneficial in energy expertise. In addition, graphene can be shifted to substrates for clear electronic applications that permit the production of crystal clear or semi-transparent energy-producing and storage devices. To avoid the agglomeration of graphene layers, various approaches like surface modification through ultrasonic and microwave processes which come under physical dispersion and chemical modifications using polymer composites and organic coatings have been executed. These techniques offer a capable slant for the fabrication of new electronic devices.²⁴⁻²⁹

For graphene synthesis mainly two approaches such as wet chemical and non-wet chemical methods are followed. The non-wet chemical method gives high quality but has a low yield, on the other hand, the wet

chemical method is a scalable process as the yield is high. In wet chemical processes, chemical modification and non-covalent functionalization play important roles in surface modification at edges and on graphene layers. It improves the solubility or dispersion stability in organic solvents.³⁰

Generally, surface modifications on graphene have been employed to make stable dispersion in an aqueous medium and different organic solvents or surfactants.^{31, 32} The surface modification is created by chemical modification and non-covalent functionalization. In the chemical modification process, the CTAB creates bonding on graphene layers.³³

The three main stages to make perfect graphene layers through the wet chemical method are oxidation, intercalation, and reduction process. In the oxidation process, chemical exfoliation is done via a strong oxidation agent to split the π bond, and the force of this method to the carboxyl and hydroxyl functional groups are founded around the exfoliated graphite coatings to modify the structural arrangement of the layers transformed it to graphene oxide.^{34, 35} The intercalation process helps to prevent agglomeration in reduced graphene oxide and finally reduction process is carried out to remove the 'oxide' components to gives few-layer graphene; but due to electrostatic force, it may possible that re-agglomeration can happen. On the other side, in non-covalent functionalization, sulphonate groups create modifications on graphene layers. Non-covalent functionalized graphene prevents stacking in π conjugated systems and makes them isolated. But the chemical modification of graphene layers or embedding them into polymer matrix affects its electrical property due to the attachment of organic radicals.

In this work, we explained the synthesis process of cationic surfactant treated reduced graphene oxide and compare the dispersion behavior in five different solvents i.e. DI water, acetone, ethanol, chloroform, and methanol. The cationic surfactant plays an important role in stable dispersion behavior via surface modification around the graphene layer. It prevents the agglomeration of graphene layers due to steric force.

EXPERIMENTAL

Material and Methods

Natural graphite powder of 60 mesh size, methanol, acetone, hydrochloric acid (HCl), Hydrogen peroxide (H_2O_2), and Sulfuric acid (H_2SO_4) was purchased from Loba Chem, Potassium permanganate ($KMnO_4$) was purchased from Merck, Sodium nitrate ($NaNO_3$) was purchased from SDFCL, CTAB and chloroform were purchased from Sigma Aldrich. Ethanol was purchased from Changshu Longsheng Fine Chemical Co. Ltd. Millipore water was used for all the experiments, and Current-Voltage (I-V) curve was taken by Keithley Source Meter 2450.

General Procedure

Graphene oxide (GO) be prepared via the adapted Hummer's method.³⁶ The synthesis process of GO and CRGO was reported elsewhere. The chemical oxidation process was used to synthesize graphene oxide from natural graphite powder. In this process, concentrated H_2SO_4 , $KMnO_4$, and $NaNO_3$ were used for oxidizing the graphite flakes. After the chemical exfoliation process, we get a mixture of graphene and few graphite oxide flakes in the form of a homogeneous solution. In the filtering process - low-speed centrifugation at around 900 rpm separates graphite oxide and it settles at bottom of the centrifuge tube, and at high-speed centrifugation around 6000 rpm removes the unwanted molecular ingredients. In CRGO synthesis, we used cationic surfactant CTAB to modify the surface of graphene layers through chemical techniques instead of the ultrasonication and reduction process.³⁷

Synthesis of Surface Modification in Graphene Sheets Via Ionic Interaction

In the chemical reduction process, centrifugation takes the main role in the filtering process to get the few layers CRGO - at low-speed centrifugation around 900 rpm to separate the large graphite particles and after that high speed 8000 rpm centrifugation of the supernatant to remove the excess surfactant and reducing compounds from CRGO.³⁸

Characterization

The morphology study was conceded out throughout High-Resolution Transmission Electron Microscope (HRTEM) by JEOL JEM 2100 as well as the electrical description of CRGO thin-film conceded out by Keithley Source Meter 2450 utilizing two probe techniques.

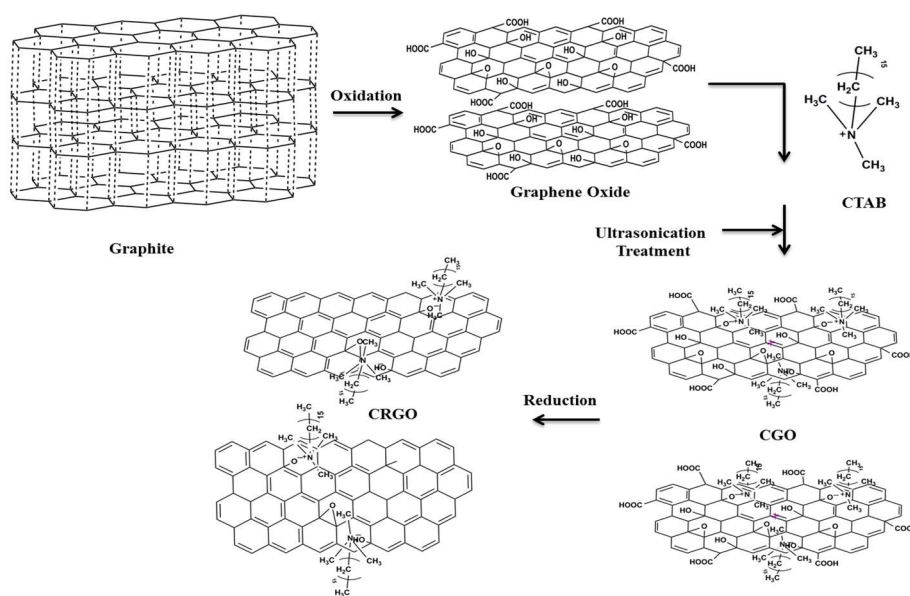


Fig.-1: Schematic Representation of CRGO Synthesis Process

RESULTS AND DISCUSSION

In our preceding paper, we conversed the synthesis procedure of CRGO and inveterate it with Fourier Transformed Infra-Red spectra, X-Ray Diffraction patterns and Transmission Electron Microscope images and dispersion stability in an aqueous medium. In this effort, we clarified the dispersion stability of CRGO in dissimilar solvents such as deionized water (H_2O), methanol (CH_3OH), acetone (C_3H_6O), ethanol (C_2H_5OH), and chloroform (CH_3Cl) were employed as dispersion media.

Graphene is an n-type material. It has localized quasi-free electrons on specific moieties of individual sheets. These moieties share their electrons with the moieties of another graphene sheet when they are stacked on each other and try to create aggregations. This is called π - π stacking interaction also a weak van der Waals force comes into play due to shifting electronic charge density.

The electrostatic force and van der Waals force (steric forces) are strong enough to agglomerate the layers of the graphene oxide again and again unless the layers are well separated and functionalized with cationic groups provided by CTAB. Thus, a long (~ 8h with breaks in between) sonication is necessary (a) to break the weak van der Waals force by using the liquid exfoliation method and (b) to make a stable supernatant suspension homogeneous CRGO solution via long time sonication process

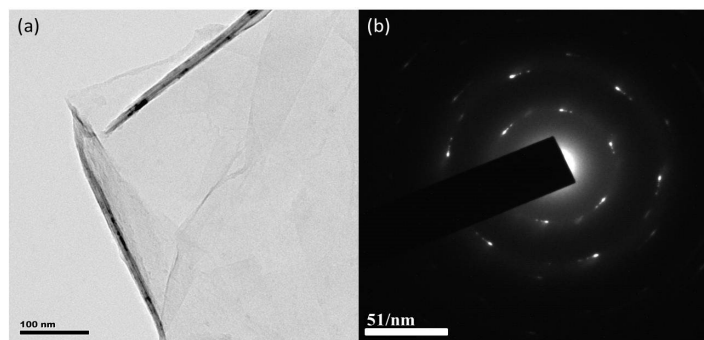


Fig.-2: Picture of (a) HRTEM and (b) Selected Area Electron Diffraction Pattern of CRGO

Figure-2 shows that the morphological results of CRGO carried out by HRTEM characterizations. The thin CRGO layers with large magnification (100 nm) could be seen in the HRTEM image. In Figure 2(b), the selected area energy dispersion (SAED) patterns clearly show the hexagonal spots which reveal the crystallinity of the CRGO.

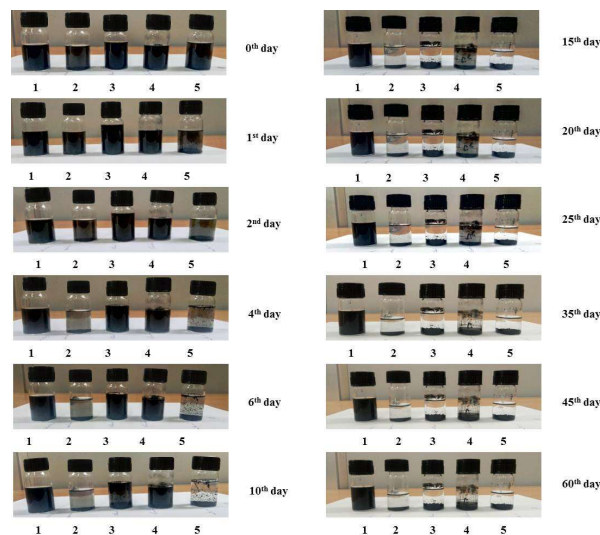


Fig.-3: Dispersion Stability of Synthesized CRGO dispersed in Different Solvents (1- DI water, 2- acetone, 3- ethanol, 4- chloroform, and 5- methanol) and the Digital Picture was taken Different Time Durations.

The dispersion behavior of CRGO has been investigated at a concentration of 0.2 mg ml⁻¹ in different solvents. Digital pictures were taken to display the dispersion quality of CRGO in five different solvents without any disturbance from 0 to 60 days' time duration at room temperature.

After one week, CRGO showed a stable dispersion in water, ethanol, and chloroform. In other solvents, CRGO flakes were started to sediment. From the 2nd day onwards dispersed CRGO particles in methanol solvent had started to settle slowly and on the 10th day, nearly all the particles had settled at the bottom of the vial. In acetone, dispersed particles had been agglomerated and started settle on day 2. Furthermore, all CRGO particles had settled at the bottom on day 15 but the other three different solvents, flakes remained dispersed for up to a week. But from the 10th day onwards particles were started to settle in ethanol solvent and on day 15th particles were completely settled at the bottom. In chloroform, most of the particles were settled within day 20. But in the water, there was no sedimentation and flocculation even after storing the vial for more than 60 days. Thus, CRGO dispersion in water exhibited long term stability

Current-Voltage (I-V) Characterization of CRGO Film

The synthesized CRGO solution was applied on the substrate via drop-casting technique and current-voltage (I-V) characterizations were measured. The CRGO conductive ink was obtained with 20 mg ml⁻¹ of CRGO and 10 wt% of PVA in ethanol. The mixture solution was applied on 1x1cm Al₂O₃ substrate using the drop-casting technique and the aluminum electrodes were cleanly deposited with thermal evaporation technique. The electrical properties were analyzed using two probe electrode methods.

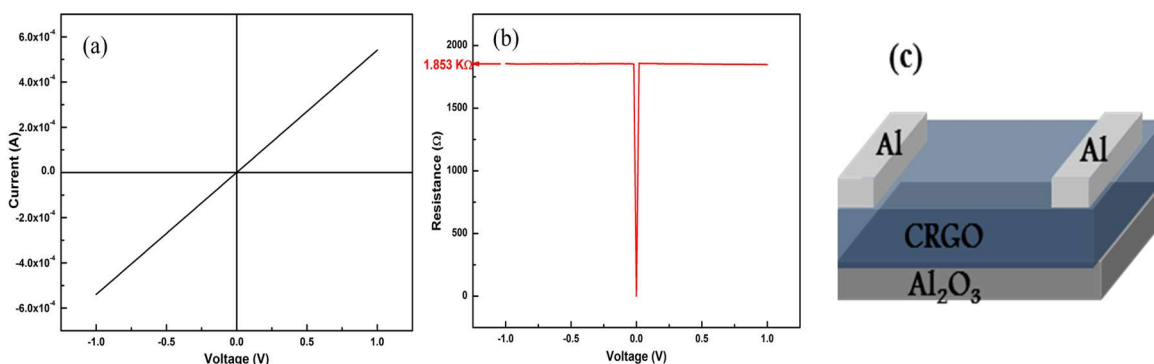


Fig.-4: (a) Current-voltage (I-V) Characteristics, (b) Resistance Value of CRGO Film and (c) Schematic of CRGO Film with Contact Electrodes

Figure 4 (a) shows the I-V graph of drop-casted CRGO coated films 1 cm² size taken from a voltage range of -1 to +1 V. The current measure shows a maximum of 0.53 mA at 1 V and (b) shows the resistance value CRGO film value around 1853 Ω. We painted a line on a paper sheet with concentrated CRGO ink, it showed a sheet resistance value around 1.329 MΩ cm⁻¹.

CONCLUSION

In summary, the dispersion behaviors of CRGO in five different solvents were compared. The H₂O solvent showed excellent dispersion stability and homogeneous solution for more than a month of period compare to the other four solvents. Surface modification and sonication were the main roles played in the dispersion behavior of CRGO. The surface modification created by two main factors was the ultrasonication process to break the weak van der Waals and surfactant creates steric force it prevents agglomeration. The CRGO film resistance value 1834 Ω was obtained.

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