

A Study of Stable Graphene Oxide Dispersions in Various Solvents

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(Received on 28th May 2013, accepted in revised form 4th Feb 2014)

Summary: The work on processibility and practical use of Graphene is expanding, so the need for stable dispersion of Graphene in different solvents is ever increasing. The dispersion behavior of Graphene oxide (GO) prepared by modified Hummer's method was studied in ten different solvents namely Water, Tetrahydrofuran(THF), Dimethyl formamide(DMF), Ethylene Glycol, Acetone, Pyridine, 2-Propanol, Methanol, Ethanol, and Dimethyl sulfoxide (DMSO). The effect of sonication and addition of surfactant (Sodium Cholate) on dispersion behavior was also investigated. Homogeneous dispersions were found in all freshly prepared GO solutions but they were short lived. The dispersions were then left as such for three weeks and after three weeks they were observed again. It was found that stable dispersions were left only in some solvents like Water, THF, DMF, Ethylene Glycol and Pyridine. Finally in a separate set of experiment we treated the GO solutions in all these solvents with surfactant (Sodium Cholate) and sonication (400 Hrs) to see the dispersion behavior. It was observed that stable dispersion remained only in few solvents like Water, DMF, Ethylene Glycol and Pyridine. These were most stable and showed no sedimentation or settling down of GO even after three weeks. These solvents are easily available and can be effectively used for dispersion formation and further processing of Graphene.

Key words: Graphene Oxide, Stable dispersion, Water, THF, DMF, Ethylene Glycol, Acetone, Pyridine, 2-Propanol, Methanol, Ethanol, DMSO, Sodium cholate.

Introduction

Graphene has become the material in recent years which gained attention of scientist and researchers. It is a novel material having prospects of wide application in gas sensors [1], nanoelectronic devices [2, 3] and composite materials [4].

The production of dispersed Graphene in large quantities by cheap, workable and easy method has become a top priority. There are some methods proposed by various workers in this regard like the micromechanical cleavage of bulk graphite [5] and chemical conversion of graphite to graphitic oxide [6, 7]. The first method *i.e.* micromechanical cleavage was found good for low productivity, while the conversion method has been found to be reliable for adequate quantities. The graphite oxide is layered structured material which in water yields dispersion that are mostly single layered sheets known's as graphite oxide sheets [8]. The graphite oxide sheets are highly exfoliated and very stable when dispersed in aqueous environment. The dispersion has been used to prepare polymer- Graphene composites [9], Graphene thin films [10, 11] and so on [12]. However there are several drawbacks in GO, like presence of oxides, their removal [13], structure defects introduced by the oxidation process [3] and poor conduction of GO.

In order to prepare stable dispersions of GO and to remove above mentioned defects, for practical

application, several studies are reported and various techniques have been developed which are, dispersion of graphene in solvents [14, 15], using surfactants [16, 17], Colloidal suspension in organic solvents [18], Chemical conversion of graphite [19] and others. Dispersion has been reported in both aqueous and non aqueous solvents which are volatile and non volatile also. Arlene O, Neill [15] have shown dispersion of graphene in three low boiling point solvents *i.e.* chloroform, isopropanol and acetone while J.I. Parades *et al.*[20] have given detail about dispersion in fourteen different solvents (both aqueous and non aqueous).The surfactant stabilized Graphene dispersion in water by the large sonication has also been termed to produce stable dispersion [16].

All these have led to different suggestion about best possible solvent for application, but there is some controversy regarding stable suspension formation in different solvents. We have tried twelve different solvents for dispersion preparation with sonication and also with surfactant and found some different results from the previous studies. We have identified some new solvents which give stable dispersion even after three weeks. These results can be effectively used and helpful in future Graphene based materials.

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Experimental

Materials and Preparation

Graphene oxide (GO) was prepared by modified Hummers method from Graphite powder (99% Pure) supplied by Scharlau, Spain. For the preparation of dispersion of GO in different solvent, the ground product was added to the solvent and after stirring of one hour, it was placed in sonicator and sonicated for about 400hrs in an ultrasound sonicator Model Powerasonic 410, Seoul Korea. For Comparison purposes, a fixed amount *i.e.* 5g of GO was added to 100mL of solvent. The solvents used for dispersion preparation were water, THF (reagent grade, 99% extra pure), DMF (reagent grade, 99% extra pure), Ethylene Glycol (99% reagent grade extra pure), Acetone (99% reagent grade extra pure), *n*-Hexane (reagent grade, 96% extra pure), Methanol (reagent grade, 99% pure), Ethanol (reagent grade 99% pure), DMSO (reagent grade, 96% pure) and Dichloromethane (reagent grade, 99% pure). These were taken from Scharlau, Spain while Pyridine (reagent grade, 98% pure) was from BDH, England and 2-Propanol (reagent grade, 99% pure) was from Merck, Germany. Sodium Cholate was added as in these solvent-Graphene systems for studies.

Characterization

Prepared Graphene Oxide powder was characterized by means of XRD, FTIR, TGA and UV-Visible spectroscopy.

Fourier Transform Infrared Spectrometer (FTIR)

FTIR analysis was carried out by using Shimadzu (IR Prestige-21) spectrometer (Japan).

Thermo Gravimetric Analysis (TGA)

Thermo gravimetric analysis was carried out by using Diamond TG/DTA (Perkin Elmer USA) analyzer. The samples were analyzed at a heating rate of 10 °C/min in N₂ atmosphere.

X-Ray Diffraction Analysis (XRD)

The XRD patterns were studied by JDX-3532 (JOEL JAPAN) X-ray diffractometer having a fixed radiation wavelength of λ -1.54 Å radiation at 35 kV and 40mA.

Scanning Electron Microscopy (SEM)

A JOEL Scanning Electron Microscope Model JSM-5910 (Japan) was used for the analysis of surface morphology of IGO.

UV-Vis Spectroscopy

UV/Visible spectroscopy was done using Perkin Elmer UV/Visible spectrophotometer (USA). A double beam system with a scan rate of 650nm/min was used.

Results and Discussion

The prepared GO was first characterized in order to check whether it is correctly prepared or not. The TG, FTIR, XRD and SEM were done on our prepared materials before using it for solvent dispersion studies.

The TG plot of our prepared GO (Graphene) is shown in Fig. 1. It can be seen that the major loss take place around (200 °C) due to oxygen functional group decomposition [21]. The weight loss below 100 °C is due to the evaporation of adsorbed water.

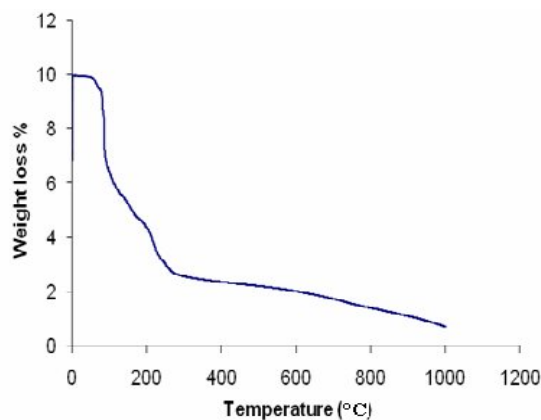


Fig. 1: TGA of GO.

Fig. 2 shows a typical FTIR spectrum of our Graphene material. It can be seen from this that the characteristic bands are at 3430 cm⁻¹ (OH stretch vib), 1726 cm⁻¹ (C=O stretching of carbonyl and carboxylic groups), 1588 cm⁻¹ (vibration from unoxidized graphite), 1266 cm⁻¹ (C-OH stretching vibration) and 1103 cm⁻¹ (C-O stretching vibration). These bands are in agreement to the literature reports on Graphite oxide FTIR [22, 23].

The XRD of our prepared GO is shown in Fig 3. It has a strong peak at approx $2\theta = 11-12^\circ$. This is in agreement to the literature reported spectra [24].

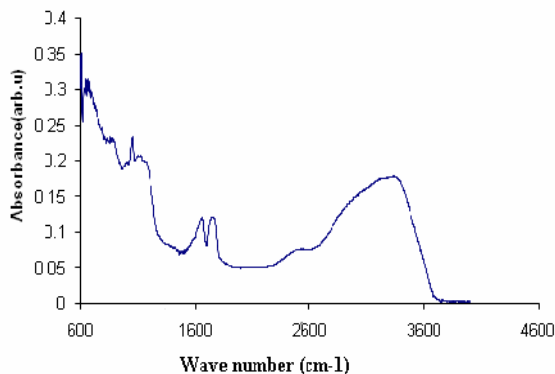


Fig. 2 FTIR of GO

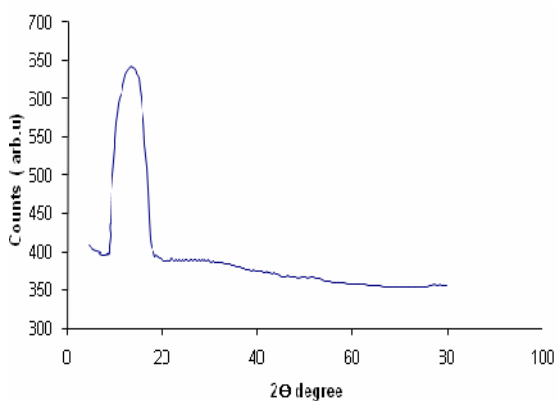


Fig. 3: XRD of GO.

SEM of graphene oxide is given in Fig .4 which is a kind layered structure or somewhat crumpled paper like morphology.

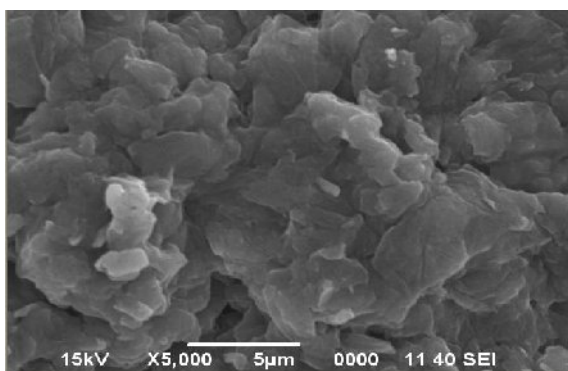


Fig. 4: SEM of GO.

Graphite Oxide Dispersion

As mentioned in the introduction, the solubilization of Graphene is of immediate concern as pure Graphene is hydrophobic and has no

appreciable solubility in most of the solvents [25]. In order to look at this and to prepare stable dispersion, as mentioned in experimental section, we have dispersed our as prepared graphite oxide material in water and nine other organic solvents namely Tetrahydrofuran (THF) , Dimethyl Formamide (DMF), Ethylene Glycol (EG) , Dimethyl Sulphonate (DMSO) , Pyridine (Py) , Acetone (Ac), Methanol (Me), Ethanol (Et) and 2-Propanol (Prop). The dispersion was monitored and their settlement was noticed for just prepared and after several weeks settlement time.

Fig 5 shows the pictures of all the dispersions *i.e.* immediate (Top), after sonication for 3 weeks (middle) and with addition of surfactant (Sodium Cholate). It can be seen from this Fig, that the degree of dispersion is variable. After just preparation the dispersion is seen in almost all solvents. These dispersions were short lived and precipitated in some of the solvents like DMSO, Acetone, Methanol, Ethanol and 2-propanol although the sonication was more than 400 hrs. Then the effect of addition of surfactants Sodium Cholate was seen and even after several weeks (three), we obtained stable dispersion in solvents like water, THF, EG, DMSO, PY and DMF. The surfactant treated long term stable dispersions were not reported previously in some of the solvents like pyridine and DMSO [20]. We have found them to be forming homogeneous and sustainable dispersions. This adds to the list of available solvents for such purpose.

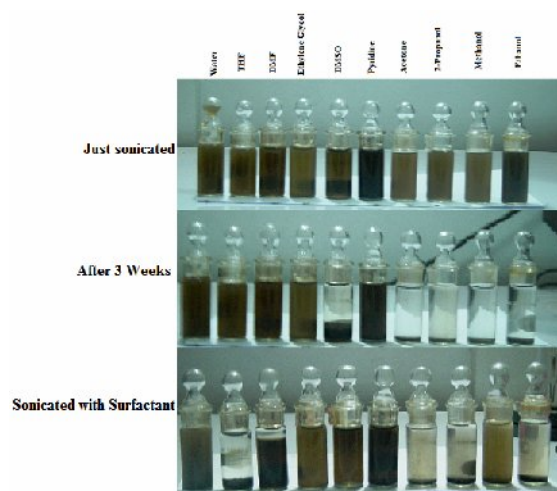


Fig. 5: Graphene oxide dispersions in various solvents.

UV-Vis spectroscopy of all these dispersions were undertaken to see the dispersion capability of these solvents. UV –Vis Spectra of GO is shown in Fig. 6. It is showing absorption Maxima

at around 260-270 nm. This is also in agreement to the literature reported values for reduced GO [24]. The UV-Vis spectra of just sonicated, after three weeks of sonication and with surfactant is given in Fig. 7 and 8. The spectra were obtained under similar conditions. Fig. 7 shows spectrum of just sonicated samples while for Fig. 8 is for the dispersion after 3 weeks times. The UV-Vis spectrum of this Graphene dispersion in different solvents show two characteristic peaks, a maximum absorption peak at around 231nm and a small shoulder at around 300nm. The first one may be π - π^* transition of C-C bonds (aromatic) while the second one may be C=O bond N-Pi star transition [26].

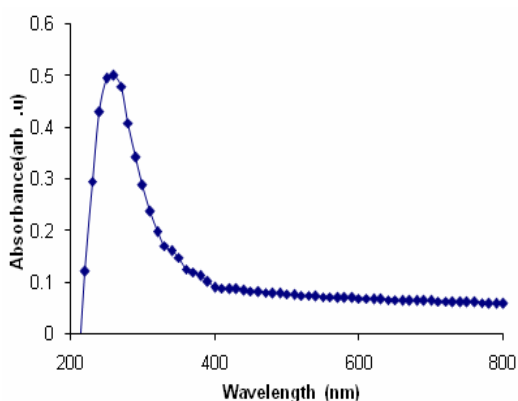


Fig.6 UV/Vis Spectra of GO

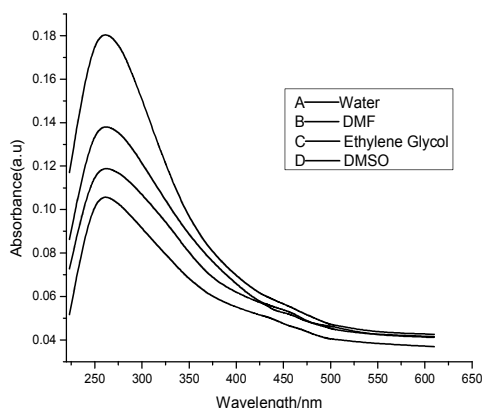


Fig. 7: UV- Vis absorption spectra of as prepared graphene oxide dispersed in different four solvents by means of bath sonication .The spectra were recorded for stabilized dispersion without surfactant Sodium Cholate.

The two spectra reveal that the absorbance values in surfactant treated dispersion are higher than the spectra without surfactant. No absorption was

detected in Et, ME, 2- Prop showing that the dispersion in these is not stable. Pyridine shows stable dispersion which was previously not reported. Fig. 8 shows the UV- spectra of surfactant added dispersion. It can be seen that the dispersion in water, DMF, Et-Glycol, Py, DMSO, are stable dispersion. This is the effect of surfactants which makes dispersions more stable than the sonication.

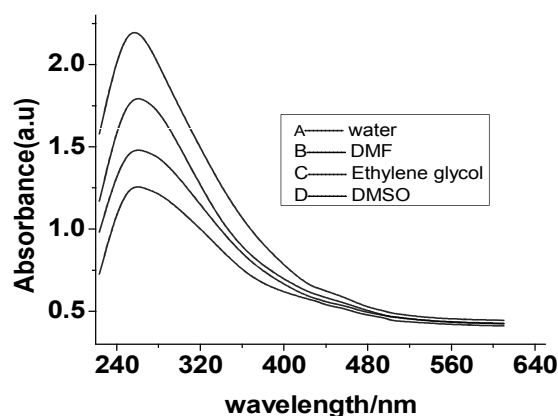


Fig. 8: UV- Vis absorption spectra of as prepared graphene oxide dispersed in different four solvents by means of bath sonication .The spectra were recorded for stabilized dispersion with surfactant Sodium Cholate.

The surfactant molecules are colloidal particles which are in constant Brownian motion in dispersion medium. Due to this motion, collisions between particles occur frequently. The stability is thus determined by the interactions between the particles during such a collision. When attraction dominates, the system will remain in dispersed state. The colloidal surfactant molecules seem to minimize repulsion between particles (may be due to electrical repulsion stabilization and steric stabilization) and hence producing more stable dispersion.

As far as the mechanism and reasons of the stable dispersion formation is concerned, it is not yet clear but here we put forward some points which help in stable dispersion formation.

- a. Polarity of the solvents: Polarity of the solvents seems to be playing a vital role in dispersion stability. The solvents with good dipole moments values are making good dispersions. It is also evident from Table-1. All these solvents used in our study show good dispersion, dipole or polarity can be one of the reason.

Table-1: Dipole moment values.

Solvents	Dipole moments
H ₂ O	1.82 D
THF	1.75 D
Et.Gly	2.31 D
DMF	3.24 D
Pyridine	2.20 D
DMSO	4.09 D

- b. Solubility parameter values of solvents: It is suggested that good solvents are those whose Hansen solubility parameters match reasonably well to the values suggested for Graphene [27]. The dispersion quality is particularly sensitive to dispersive Hansen parameter (δ_d) and successful dispersion can only be achieved for solvents with δ_d range of 15 – 20 (MPa^{1/2}). The δ_d values for the solvents used in present study are given below (Table-2). It can be seen that all those solvents which show stable dispersions have δ_d values in the range (15-20), so the solubility parameter can be another parameter to predict the stable dispersion.

Table-2: Hansen Parameters.

Solvents	HansenParameter (δ_d) MPa ^{1/2}
H ₂ O	15.6
DMSO	18.4
Pyridine	19.0
Et. Gly	17.0
DMF	17.4
Graphene	18.0

- c. Zeta potential values: ASTM defines colloids with Zeta potential (ξ) value higher than 40 mV (-Ve or +Ve) to have good stability. The range 60 – 70 mV is found to be ideal for stabilizing conventional colloid particles [28]. For electrostatic reasons, colloidal particles with $\xi > 15$ mV are expected to be stable. It has been reported that sodium cholate has ξ potential value in the range of -20 mV to -48.8 mV in dispersions of single walled carbon nanotubes [29]. Graphene is also carbon atom and we have added sodium cholate in that, so the ξ values can easily be assumed to be in this range for our system also. The mechanism of stabilization of surfactant-coated colloids is believed to be electrostatic repulsion between surfactant ions coating the carbon. The stabilizing effect can be gauged from the surface charge on the carbon (Graphene) atom. This charge can be measured in the form of the zeta potential, the electrical potential at the edge of the coated colloid. Sodium cholate is believed to be stabilizing the Graphene dispersion via this mechanism. The surfactant treated, well dispersed and highly stable dispersion can be due to the colloidal

particles of Surfactant *i.e.*, Sodium Cholate added in our systems.

The stable dispersions can be result of all of the above or some of the above reasons. Further it can be seen that in case of water, ethylene glycol and DMF, Oxygen atom is present in their structure which we think is interacting with Carbon of Graphene oxide to add stability to dispersions. In case of pyridine the presence of Pi (π) bonds may have strong affinity with Graphene via π - π interaction which is stabilizing the dispersion.

Conclusions

We have studied the dispersion behavior of Graphene in ten different solvents namely Water, THF, DMF, Ethylene Glycol, Acetone, Pyridine, 2-Propanol, Methanol, Ethanol, and DMSO. There was stable dispersion formation in all just prepared solutions which was short lived. The Dispersions were sonicated for 400hrs and also in separate solutions sonicated and Surfactant (with Sodium Cholate) treated. The long term stable dispersions were found only in Water, DMF, Ethylene Glycol and Pyridine with this treatment.

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