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Stable Graphite Exfoliation by Fullerenol Intercalation via Aqueous Route

Rachana Kumar,^{*a} Pramod Kumar,^{*b} Samya Naqvi,^a Neha Gupta,^a Niharika Saxena,^a

Jitendra Gaur,^a Jitendra K. Maurya,^c and Suresh Chand^a

^a*Physics of Energy Harvesting Division, National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi, India-110012*

^b*Department of Physics, Indian Institute of Information Technology Allahabad, Uttar Pradesh, India-211012*

^c*Department of Chemistry, Delhi University, New Delhi, India-110007*

Address of corresponding authors:

^a*Dr. Rachana Kumar*

Physics of Energy Harvesting Division

National Physical Laboratory

Dr. K. S. Krishnan Marg

New Delhi, India-110012

Email: rachanak@nplindia.org

Phone Number: +91 11 4560 9353

Fax Number: +91 11 4560 9310

^b*Dr. Pramod Kumar*

Department of Physics

Indian Institute of Information Technology Allahabad

Uttar Pradesh, India-211012

Email: pkumar@iiita.ac.in

Phone Number: +91 532 2922 202

Fax Number:

Abstract

Graphene is a wonder material possessing unique properties. However, graphene prepared by exfoliation of graphite has property to restack because of van der Waals forces to form graphite. This restacking can be prevented by insertion of large molecules like fullerene, which not only exfoliate graphite layer but also prevent restacking of prepared graphene sheets. The present article also describes a mild method of graphite oxide synthesis (GO) for lower degree of oxidation resulting in less defected graphene sheets. Exfoliation is done by intercalation of large fullerene molecules by aqueous reaction of fullerene hydroxide (fullerenol) with the epoxy functionalities on graphite oxide to prepare fullerene intercalated graphite (G-Fol). Fullerene functionalization of GO to form G-Fol has been established by FTIR, UV-Vis, TGA and number of layers has been ascertained by Raman, XRD, and HRTEM. Stable exfoliation of G-Fol has been confirmed by change in absorbance with time. Photoluminescence property of the material is also evaluated by fluorescence emission and excitation measurement at different excitation and emission wavelengths respectively. The present article explains a new method of exfoliation of graphite to form stable functionalized graphene layers with fewer defects for future applications as buffer layer in electronic devices.

Key words: graphene chemistry, fullerene chemistry, fullerenol, organic solar cells, aqueous chemistry, graphite exfoliation

1. Introduction

Graphene is single layer graphite, composed of a honey comb arrangement of carbon atoms and finding applications in vast areas.¹⁻¹² Many efforts have been made to take advantage of these exceptional properties for the electronic and energy applications.¹³⁻¹⁷ Graphene is prepared from graphite by several methods,¹⁸⁻²⁰ among which, single layer graphene prepared by 'scotch-tape' method has shown promising electrical properties that could be useful for developing novel electronic devices.²¹⁻²⁴ To prepare graphene materials of different sheet size, functionalities and structures, chemical route through oxidation of graphite is being widely used.²⁵⁻²⁸ The rationale is the easy scalability of the process and the cost involved. Now a days, the most widely used method for preparation of graphite oxide and or graphene oxide is either Brodie's²⁵ or the Hummer's²⁶ method. These methods, involve reaction of graphite with strong oxidizing agents like, sulphuric acid, nitric acid in presence of salts like, potassium chlorate or potassium permanganate and lot of precautions are required during the addition of salts. Introduction of oxygen containing functional groups help in increasing the d-spacing of GO as well as change the hybridization from sp^2 to sp^3 . Further ultrasonication followed by ultra-centrifugation help in exfoliation of graphite oxide and formation of graphene layers. It is seen that the resulting graphene sheets have permanent defects, such as the partial cleavage of the hexagonal framework of planer carbon atoms which can not be healed and tend to reattach to form graphite through van der waals interactions.²⁸⁻²⁹

Recently a wet chemical approach has been introduced to prepare graphene from GO with the carbon skeleton preserved in the order of tens of nanometers.²⁹ There are also several other routes for graphite exfoliation by insertion of organic molecules to avoid such agglomeration and also to prepare less defected graphene sheets. Graphene has been functionalized with several types of molecules, like, polymers, small molecules, porphyrin, diazonium salts, alkyl isocyanates etc.³⁰⁻³⁷ Some research has also been carried out to attach bulky fullerene molecules in between the graphite layers to exfoliate it,

like, pyrrolidine fullerene,³⁸ methano fullerene etc.³⁹⁻⁴⁴ In some of the above cases fullerene molecules were only attached on the edges. Zhang et. al., reported the exfoliation of graphite to graphene monolayers by inserting fullerene molecules in between graphene layers of graphite and grafted on both sides of graphene.⁴⁰ The grafted fullerene exfoliate graphene sheets to higher extent and avoid the restacking and also help in maintaining the large surface area.

In the present article, we have further simplified the insertion of fullerene molecules between graphene layers by very simple aqueous route where, graphite oxide (GO) is prepared by oxidation with conc. Nitric acid.⁴⁵ Synthesis of graphite oxide without use of strong salts avoids the impurities of salt byproducts.⁴⁶ On the other hand, water soluble polyhydroxyl fullerene (fullerenol) was prepared by modified base method.⁴⁷⁻⁵⁰ Under basic condition, the strong electrophilic character of fullerene cage easily release protons to form fulleroxide anions, (Fol-O)⁻ⁿ, which is capable of undergoing several types of reactions. Fullerenol undergoes nucleophilic addition reactions on epoxy groups to form star-like macromolecules under mild basic condition.⁵⁰ Here also, we have exploited the strong nucleophilic character of the sodium salt of fullerenol to undergo nucleophilic addition reaction with epoxy groups on the surface of GO resulting in chemically bonded fullerene functionalized graphene sheets (G-Fol).

The resulting G-Fol was characterized for its optical properties and thermal stability, also the chemical attachment was established by FTIR. In contrast to the previous reports for edge functionalization of graphite oxide on reaction with fullerenol molecules, in the present case we have obtained stable exfoliation with formation of few layered graphene sheets.⁴³ The quality, exfoliation and number of layers of thus prepared graphene have been confirmed by XRD and Raman spectroscopy measurements. To confirm the stability of dispersion of the exfoliated graphite, optical studies have been performed with the stable supernatant of the dispersions in different solvents. Graphite exfoliation was further confirmed by high resolution transmission electron microscopy.

2. Experimental Section

Graphite oxide (GO) was prepared by refluxing micrometer sized-graphite in conc. Nitric acid (1mg/mL) for 24 hours (**scheme 1**). The resulting material was filtered and washed several times with deionized water to remove all acid impurities and dried in oven at 80 °C. Fullerenol (Fol) is prepared by the reaction of aqueous solution of sodium hydroxide (3 g) with toluene solution of fullerene (50 mg) in presence of phase transfer catalyst (tetra butyl ammonium bromide). The clear toluene layer is separated and brown aqueous layer is precipitated with addition of excess of methanol. The brown product is collected by centrifugation and washed several times with methanol/ water mixture (80:20) to remove the traces of sodium hydroxide. Thus prepared fullerenol is further reacted with GO following a simple aqueous route. Sodium salt solution of fullerenol (45 mg) is prepared in water is added to aqueous suspension of GO, stirred at room temperature for 24 hours followed by 50 °C for 12 hours. The resulting suspension is washed with cold water to remove unreacted fullerenol and the resulting material (G-Fol) is dried under vacuum at 60 °C for 12 hours.

Thus synthesized G-Fol was characterized by Fourier Transform Infrared spectroscopy (FTIR) using KBr pallets on Perkin Elmer FTIR Spectrum 2. FTIR spectra were collected over a range from 3500 to 500 cm^{-1} . A background in air was done before scanning the samples. UV-vis spectroscopy measurement was performed on a Shimadzu UV-vis spectrophotometer in solution. Emission and excitation fluorescence measurements were performed on Varian (CARY eclipse) Fluorescence Spectrophotometer in THF suspension. Horiba Jobin Yvon (Fluorohub) was used to record time resolved fluorescence. Thermal gravimetric analysis (TGA) was run under nitrogen flow of 20 mL/min using Perkin Elmer (Pyris 1) TGA instrument and mass loss was recorded as a function of temperature. The samples were heated from room temperature to 950 °C at a ramp rate of 10 °C/min. Raman spectrometry was done on Renishaw Raman Microscope in powder. GO and G-Fol were also characterized by XRD on Rigaku diffractometer with Cu-K radiation ($\lambda = 1.54056$) to estimate the

interlayer distances. Cyclic voltammetry measurements were performed using a three electrode standard configuration with a platinum wire as counter electrode and Ag/AgCl sat. as reference electrode in a 0.05 M TBAPF₆ (tetra-n-butylammonium hexafluorophosphate) and acetonitrile solution as electrolyte. A film of GO/G-Fol was prepared on working electrode (Pt disc) by drop casting. The solution was purged with N₂ for at least 30 min before measurements. Current vs Voltage was measured on an Autolab potentiostat. G-Fol was also characterized by HRTEM (Technai G² F30, HV= 300.0 KV) to observe the exfoliation and formation of graphene sheets.

3. Results and Discussions

In the present work graphite oxide (GO) is prepared by milder method and exfoliation has been done by fullerene functionalization following a very simple chemical route by nucleophilic addition of fulleroxide anion on the epoxy groups of GO. This is a facile and friendly route for graphite exfoliation by inserting fullerenol molecules to weaken the van der Waals forces between the neighbouring graphene sheets. The detailed reaction steps are shown in scheme 1. The resultant samples (Fol, GO & G-Fol) were characterized by FTIR for their chemical functionalization (figure 1). FTIR spectra of graphite oxide clearly showed the appearance of peaks at 878 cm⁻¹ (epoxy group), 1399 cm⁻¹ (C-OH), and small peak at 1723 cm⁻¹ for C=O of carboxylic acid group (figure 1a). Peak at 1630 cm⁻¹ can be assigned to adsorbed water molecules. On chemical attachment of Fullerenol molecules, typical epoxy was disappeared with appearance of broad O-H stretching peak appears at 3439 cm⁻¹ with a strong C=C stretching peak at 1611 cm⁻¹ (shifted from 1590 cm⁻¹ in fullerenol) and 1120 cm⁻¹ for C-O stretching with distinct peak of C=O stretching at 1743 cm⁻¹ in G-Fol samples (1b). Thus, the FTIR results clearly indicate the successful chemical attachment of fullerenol molecules on GO.

A comparative UV-vis analysis was done for the suspended samples of GO and G-Fol in THF (Figure 2). Both the samples were sonicated for an hour before recording the data. GO showed the characteristic absorption at 285, 300, 515 and 560 nm, while in G-Fol an additional absorption band

was observed at 336 nm characteristic of fullerene derivatives.⁵¹

TGA has been exploited as a tool to calculate the number of hydroxyl groups or addends attached exohedrally on fullerene ball.^{52,53} In the present work, the number of hydroxyl groups per fullerene has been calculated to be ~ 16 . TGA thermogram of G-Fol and its comparison with unreacted fullerenol and GO reveal several interesting observations. The analysis ascertains the chemical attachment of fullerenol molecules onto graphene sheets and also predicts its thermo-chemical behaviour. The typical thermogram of GO, fullerenol, and G-Fol are depicted in figure 3. No major weight loss was observed for GO ($\sim 4.2\%$) samples up to $950\text{ }^{\circ}\text{C}$ and only showed a small weight loss at $\sim 326\text{ }^{\circ}\text{C}$ for the decomposition of weak bonds like epoxide (3a). Compared to $\sim 50\%$ weight loss for graphite oxide prepared by Hummer's process, only 13% weight loss up to $950\text{ }^{\circ}\text{C}$ attributes to the lower degree of oxidation of graphite sheets in the present case.⁵⁴ On the other hand fullerene intercalated graphite sample (G-Fol) showed continuous weight loss up to $950\text{ }^{\circ}\text{C}$ (3b) as in the case of fullerenol. The dehydroxylation of fullerenol starts at $\sim 150\text{--}160\text{ }^{\circ}\text{C}$ and completes between the temperature range of $150\text{--}570\text{ }^{\circ}\text{C}$ before the structural degradation of fullerene core starts (3c). Similarly for G-Fol the first weight loss occurs between $163\text{--}550\text{ }^{\circ}\text{C}$ ($352\text{ }^{\circ}\text{C}$ crest temperature), which is for the loss of free hydroxyl groups of fullerenol. Another major loss starts from $680\text{ }^{\circ}\text{C}$ and only 66.8% residue is left after $950\text{ }^{\circ}\text{C}$ compared to 88.3% for GO. The second weight loss is due to the breakage of graphite-O-fullerene bonds of G-Fol. Because of high functionality of graphite on chemical attachment of fullerenol molecules, a continuous decomposition occurs in TGA of G-Fol, however, this material is also showing better thermal stability compared to previously reported data for fullerene modified graphite.⁵⁵ Thus TGA results further confirm the successful functionalization of graphite with fullerenol molecules.

Graphite oxides prepared by other methods are highly oxidized material with high hydrophilic nature and readily exfoliate in water to yield stable dispersions consisting mostly of single layered graphene

oxide sheets. Paredes et. al.,⁵⁴ have reported the dispersion behaviour of graphite oxide in different solvents and identified that graphite oxide is exfoliated into individual graphene oxide sheets or few layers sheets with long term stability in several solvents. The stability of dispersion of GO and G-fol samples in different polarity solvents were studied to find out the significance of such chemical modification of GO in exfoliation and dispersion stability in different solvents. GO was dispersed in five solvents (0.5mg/mL in water, DMF, THF, Ethanol, ethylene glycol) by ultrasonication. Figure 4 shows the dispersed GO sample in different solvents. The supernatants after two weeks of dispersion were used to record the UV-vis spectra to compare the dispersion stability. Absorption spectra of the supernatant of GO and G-Fol in water are shown in figure 5a where, GO shows the onset at ~ 425 nm, however, G-Fol had extended absorption in the visible region which is the characteristic of the fullerene containing materials.⁵¹ G-Fol in water also showed the structured absorption bands at 273 nm for graphene and 356 nm for fullerene moieties respectively. G-Fol showed higher absorption intensity in water showing better and stable dispersion compared to GO on attachment of fullerenol molecules with free hydroxyl groups helping in better dispersion. Similarly, G-Fol also showed better dispersion stability in THF than GO. On comparing the dispersion stability among the five solvents, DMF, Ethanol and THF showed the highest and comparable stability for GO (Figure 5c). Thus GO and G-Fol samples dispersion with long term stability can be prepared in THF and water with best exfoliation. To further analyze the long term stability the absorbance of supernatant of G-Fol in water was measured at different intervals, i.e., after three weeks, one month and two months of dispersion respectively without any further sonication (5d). Only 25% absorbance loss was seen even after two months showing stability of the suspended graphene sheets avoiding the restacking.

To further confirm the graphite layer exfoliation by insertion of fullerenol molecules, Raman analysis was carried out (figure 6). Graphite oxide showed the characteristic D-band at 1360 cm^{-1} , G-band at 1580 cm^{-1} and 2D-band at 2729 cm^{-1} . On incorporation of fullerenol molecules by chemical

bonding the overall sp^3 carbon content has been increased (on the site of $-OH$ groups in hydroxyl fullerene) in the material resulting in more intense D-band (at 1355 cm^{-1}) with appearance of additional peaks of fullerenol at 1261 cm^{-1} and 1399 cm^{-1} . For proper comparison, Raman spectra of fullerenol was also recorded, showing three characteristic bands at 1387 cm^{-1} (sp^3 hybridization), 1456 cm^{-1} , and 1574 cm^{-1} (sp^2 hybridization). In G-Fol, the 1456 cm^{-1} band of fullerenol is shifted to lower energy and appears at 1399 cm^{-1} which is because of the plausible charge transfer from fullerenol moiety to graphite sheets as fullerene-oxide is strong nucleophile. Still the I_D/I_G ratio is very small providing evidence of low degree of functionalization of graphene sheets conserving its defect free nature. On analyzing the 2D peak, the relative intensity of G/2D peak is found to be ~ 0.7 in G-Fol, indicating the formation of few layer graphene (2-4 layers).⁵⁶ Also, the width of 2D peak is splitting into four sub-peaks on fitting as shown in figure 6 (inset) which directly reflects the double layered graphene formation.^{56, 57}

The lattice expansion of graphite on oxidation is one of the indications for the degree of oxidation. An XRD analysis has been performed on GO and G-Fol samples at ambient conditions to confirm the functionalization of graphene sheets and also the degree of functionalization. Figure 7 shows the XRD pattern of powder sample of GO and G-Fol. As expected, the characteristic [001] diffraction peak of GO appears at 12.88° (2θ), corresponding to an inter-layer distance of 6.88 \AA which is comparatively lower than the highly oxidized graphite oxide ($\sim 8\text{ \AA}$)⁵⁸ because of the lower degree of oxidation corroborating with the Raman results. On functionalization with fullerenol molecules, the interlayer distance is further increased to 8.1 \AA indicating the exfoliation to few layers graphene. The larger interlayer distance results in less ordered packing of sheets, which is evidenced by the significantly broader [001] peak in G-Fol. No peak appeared at $\sim 25^\circ$ (2θ) which also excludes the formation of any chemically converted graphite in unfunctionalized areas on the surface of graphene sheets.

Fluorescence spectra of GO and G-Fol were recorded in THF with the same sample prepared in

absorption measurement experiment and are shown in figure 8. On excitation with 350 nm wavelength, GO shows three emission bands at 406, 572 and 618 nm for the three corresponding absorption bands at 308, 515 and 560 nm respectively. On the other hand, G-Fol sample shows four emission bands at 405, 415 nm and highly blue shifted bands at 560 and 605 nm compared to GO samples (~12 nm blue shift). Emission peak at 415 nm corresponds to absorption peak at 360 nm for the fullerene moiety in G-Fol sample. Because of the chemical modification of graphite oxide with fullerene, the intensity of graphite emission peaks at 560 and 605 nm are highly quenched and shifted to higher energy due to effective charge transfer in G-Fol.

Emission spectra of G-Fol was also recorded at different excitation wavelength in THF to study the effect of excitation energy on intensity of emission bands corresponding to fullerene and graphite moieties in 400 nm and 500-600 nm range respectively. As shown in figure 9, on excitation with energy lower than 3.5 eV (350 nm), very weak emission was observed in both the regions. Emission peak intensity at 415 nm was highest with 350 nm excitation due to the highest absorption by fullerene in this range ($\lambda_{\text{max}} = 336$ nm). On further lowering the excitation energy, the intensity of emission bands at 560 and 605 nm increases with the quenching of the 415 nm peak intensity which also shows a red shift. Excitation with 2.47 eV (500 nm) shows the highest emission intensity for 560 & 605 nm bands corresponding to graphite sheet absorption in these regions. Thus, the emission fluorescence study of G-Fol sample gives good understanding of electron transfer processes on excitation with different energies and at the same time emission color tuning by controlling the excitation energy.

To further analyze these data, excitation at different emission wavelengths were recorded (figure 10). For 350 and 400 nm emission wavelength, the highest excitation intensity was observed in 300-400 nm range (corresponding to fullerene moiety). On further lowering the emission energy, excitation intensity in 500-600 nm goes up which is very well understood as graphite moiety is having absorption in this range of wavelengths. Overall, we found a good dependency of both emission spectra vs λ_{ex} and

excitation spectra vs λ_{em} and such behaviour has been reported in multiple chromophore / fluorophore systems having aromatic and oxidation groups.⁵⁹

Time resolved fluorescence measurements of G-Fol samples in THF were done and showed the multiexponential decay kinetics. As reported by Shang et. al.,⁶⁰ the origin of fluorescence in graphite oxide material is the recombination of electron-hole from the bottom of the conduction band and near by localized states to wide-range valence band and also GO emission is predominantly suggested to originate from the electron transition among/between the non-oxidized carbon region and boundary of oxidized carbon atom region. Fullerene intercalated G-Fol sample is also showing similar behaviour. Figure 11a-c show the TRF decay curves for G-Fol samples at $\lambda_{ext}=280$ nm by time correlated single photon counting (TCSPC) system for $\lambda_{em}=403, 413$ and 560 nm. The kinetic curves show multiexponential decay with three time constants to fit the curves as given in table 1. Huge improvement in emission lifetimes has been observed compared to previously reported data for graphene oxide.⁶⁰

The electrochemical properties of the hybrid compound G-Fol were also investigated by cyclic voltammetry (CV). For comparison, electrochemical behaviour of GO was also recorded. All experiments were performed in films at room temperature using acetonitrile as solvent and tetrabutyl ammonium hexafluorophosphate (TBABF₄) as supporting electrolyte. The first reduction potential for GO was observed at -0.91 V which is also reversible. On the other hand, G-Fol shows two reversible reduction potentials at -0.97 and -1.1 V. The chemical modification by attachment of fullerenol molecules on graphene sheet is causing cathodic shift of first reduction potential of GO suggesting the existence of electronic interaction between the two moieties (Figure 12).³⁸ Also huge shift in reduction onset is observed on functionalization of GO ($red_{onset} = -0.38$ V) with fullerenol to form G-Fol ($red_{onset} = -0.67$ V) which clearly indicate effective change in energy levels of resulting material G-Fol and required for device applications.⁶¹

HRTEM was done to characterize the exfoliation of graphite interlayer due to intercalation of fullerene molecules (figure 13) and formation of stable functionalized graphene sheets. Figure 13A shows the exfoliated graphene sheets by fullerenol intercalation. The high quality of the sheets with high crystallinity was clearly demonstrated by the perfect crystal lattice in HRTEM image (inset) and the corresponding Fast Fourier Transform (FFT) with a typical six fold symmetry pattern. Figure 13B clearly shows the formation of few layer graphene flakes. Thus, G-Fol makes stable exfoliated graphite avoiding the restacking of graphene sheets.

4. Conclusions

A promising and mild methodology for the preparation of stable exfoliated graphite has been demonstrated by insertion of water soluble fullerenol molecules, providing less chemically defected few layered graphene. We also identified that fullerenol intercalated graphene sheets form long term stable dispersions, i.e., avoiding restacking, in THF and water which is currently required for preparation of good quality films in devices as buffer layer. Further work is being carried out to test these materials as buffer layers and also for attachment of different photoactive fullerene derivatives on graphite sheets to explore their application in organic photovoltaic.

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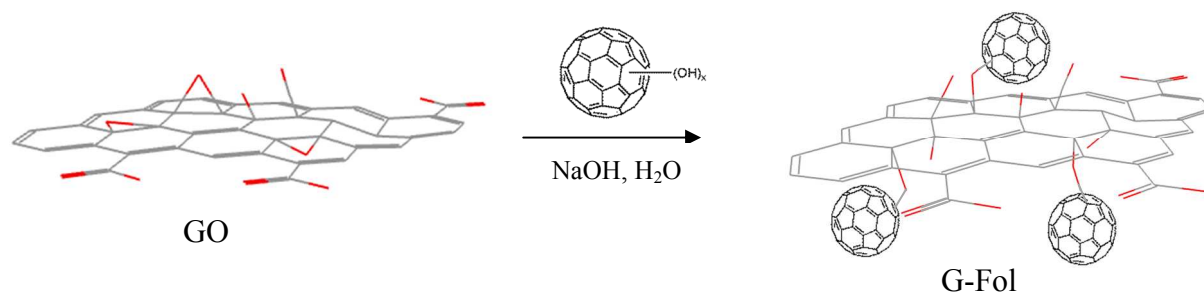
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Scheme 1. Synthesis of fullerene intercalated graphene by reaction of GO with NaOH solution of Fullerene.

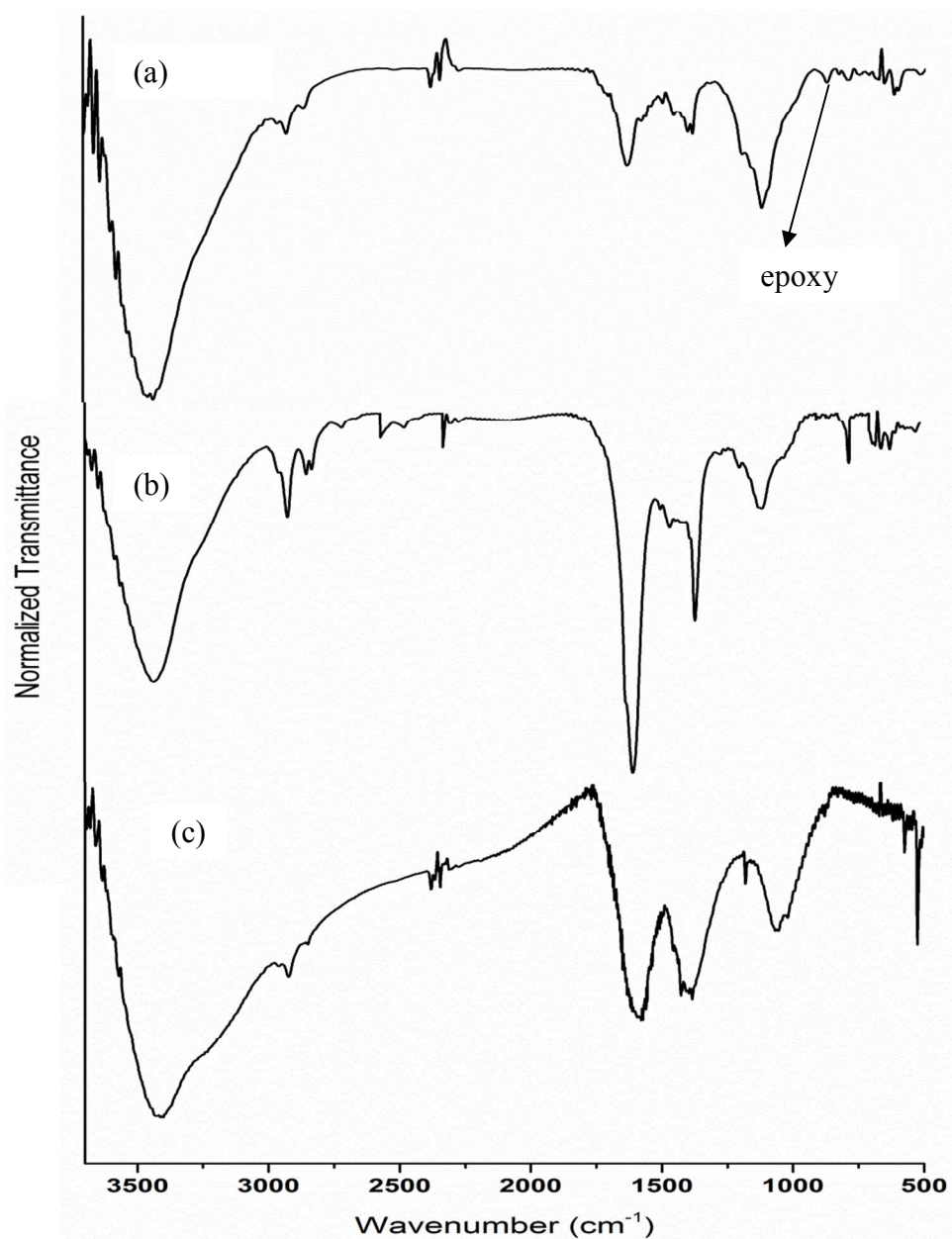


Figure 1. FTIR spectra of (a) GO, (b) G-Fol and (c) Fullerenol.

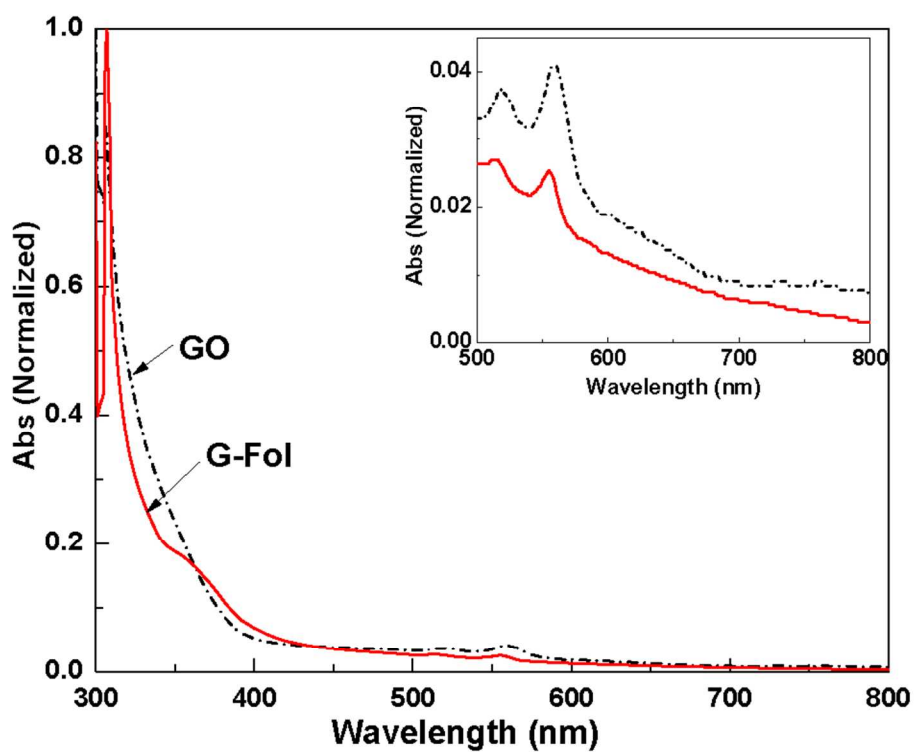


Figure 2. UV-vis absorption spectra of GO and G-Fol samples in THF. Inset shows the 10x view of 500-800 nm region.

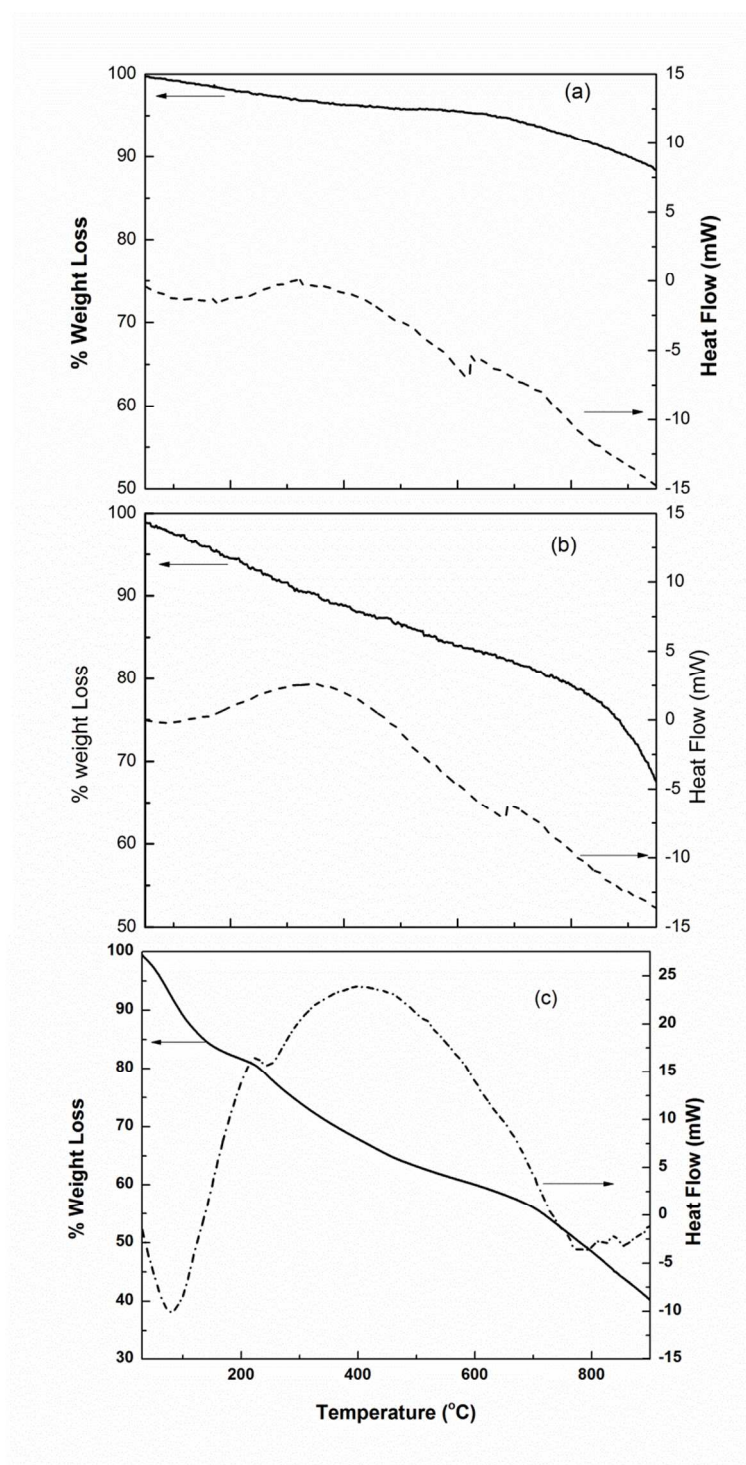


Figure 3. TGA graph of (a) GO, and (b) G-fol and (c) Fullerenol under N_2 .

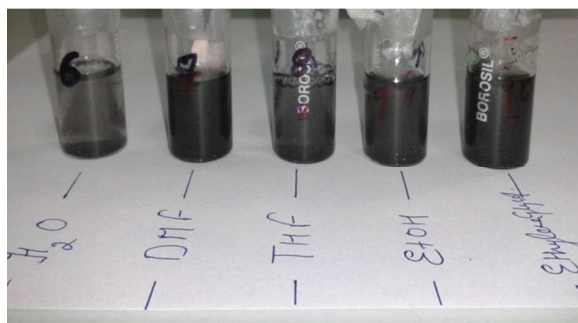


Figure 4. Camera picture of suspension in different solvents for GO.

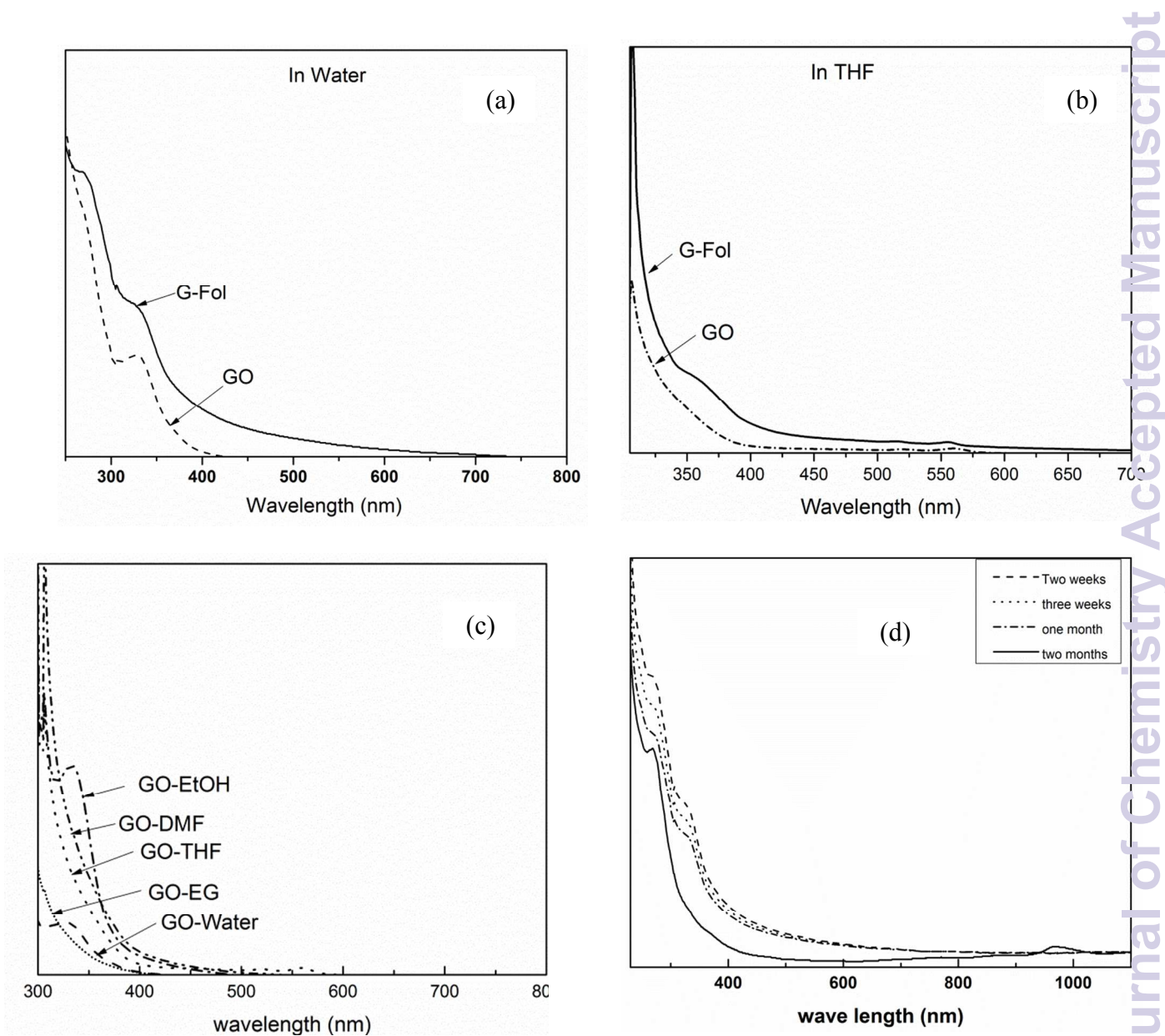


Figure 5. Absorption spectra of stable suspension (a) of GO and G-Fol in water and (b) of GO and G-Fol in THF and, (c) GO in different solvents and (d) absorbance vs. time for G-Fol in water.

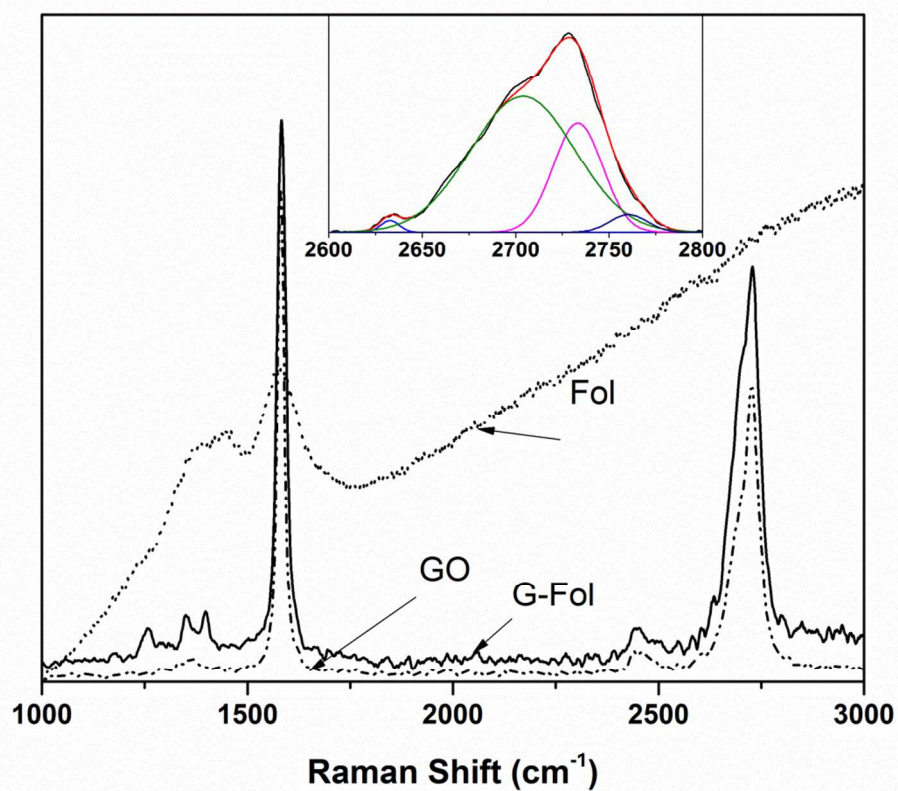


Figure 6. Raman spectra of GO, Fulleranol and G-Fol in solid state. The inset shows the Lorentzian fit for 2D peak of G-Fol into four sub-peaks.

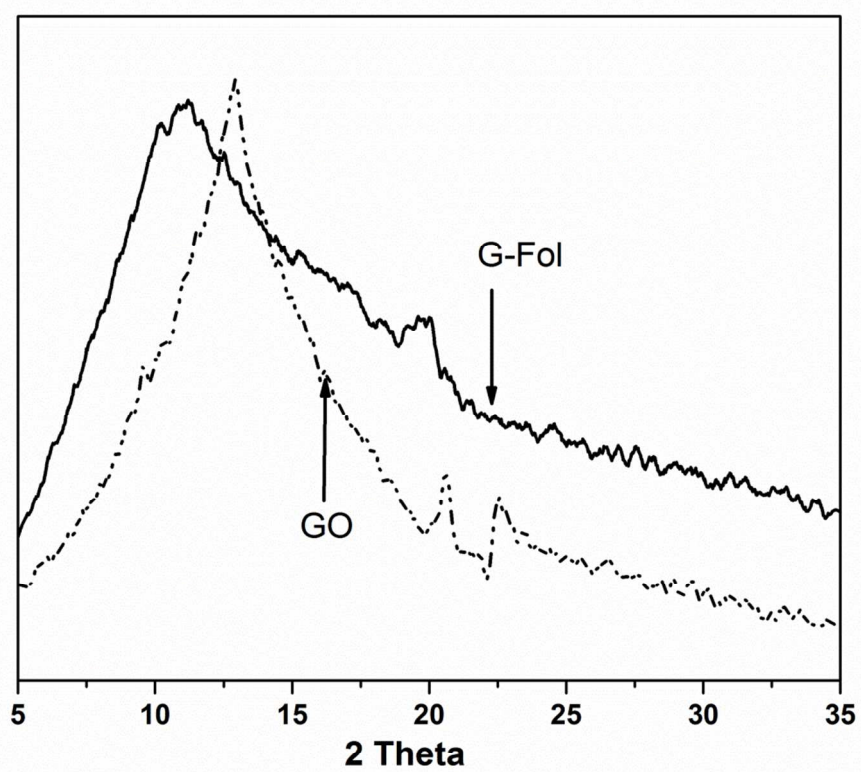


Figure 7. Powder XRD of GO and G-Fol.

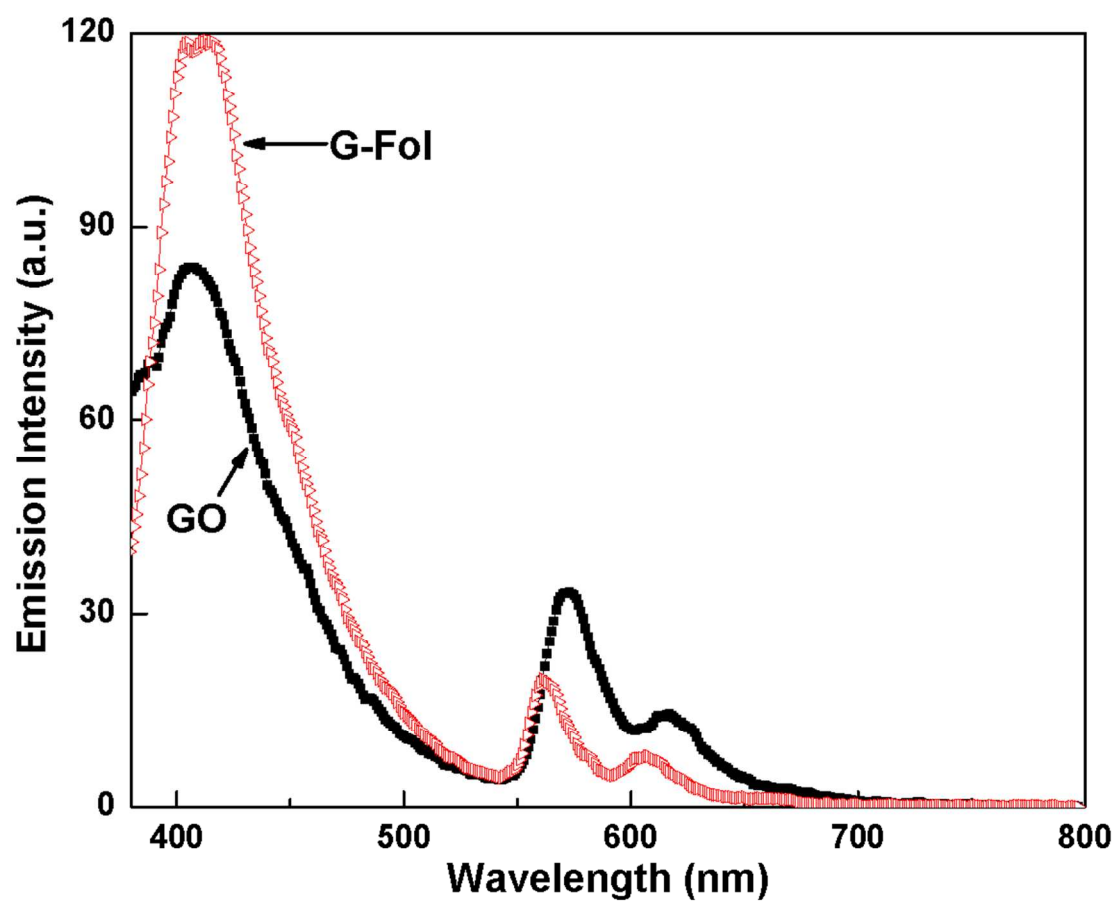


Figure 8. Emission fluorescence spectra of GO, and G-Fol in THF with 350 nm excitation.

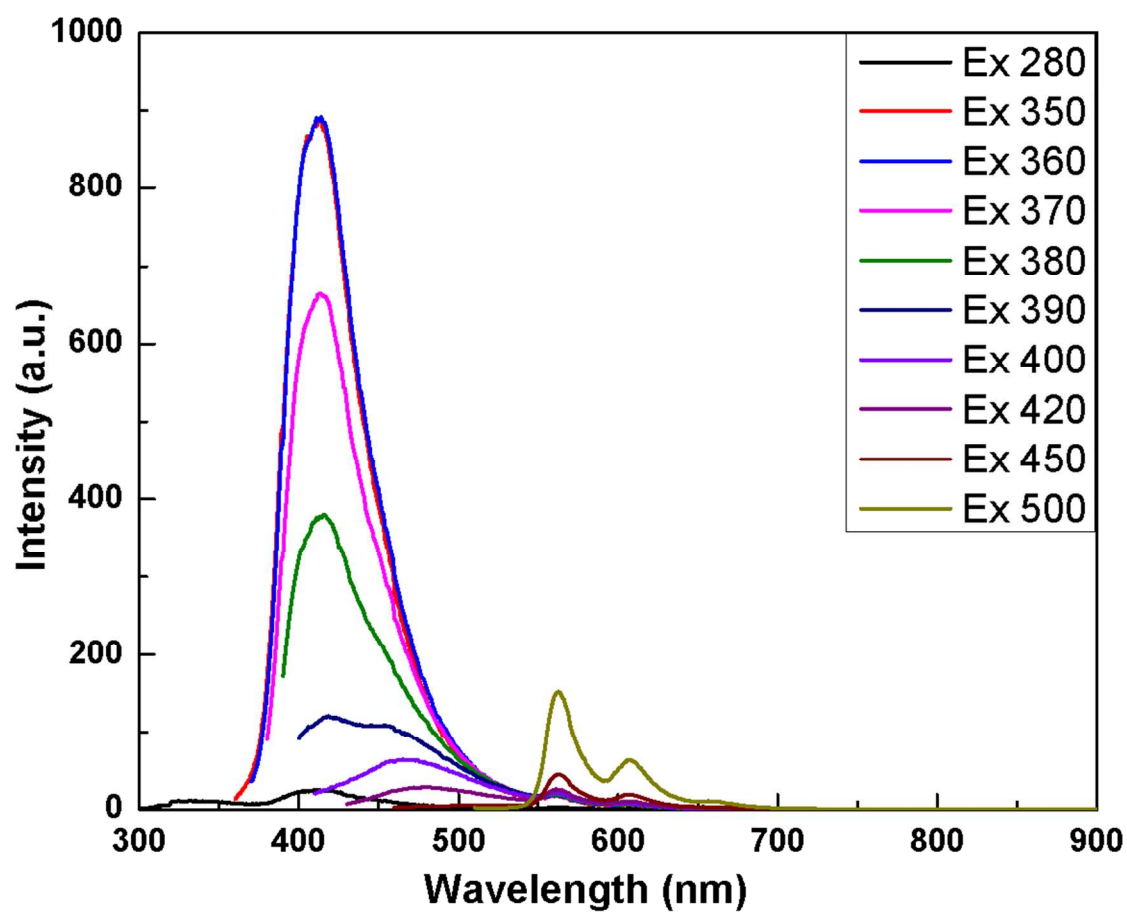


Figure 9. Emission fluorescence spectra of G-Fol in THF at different excitation wavelengths.

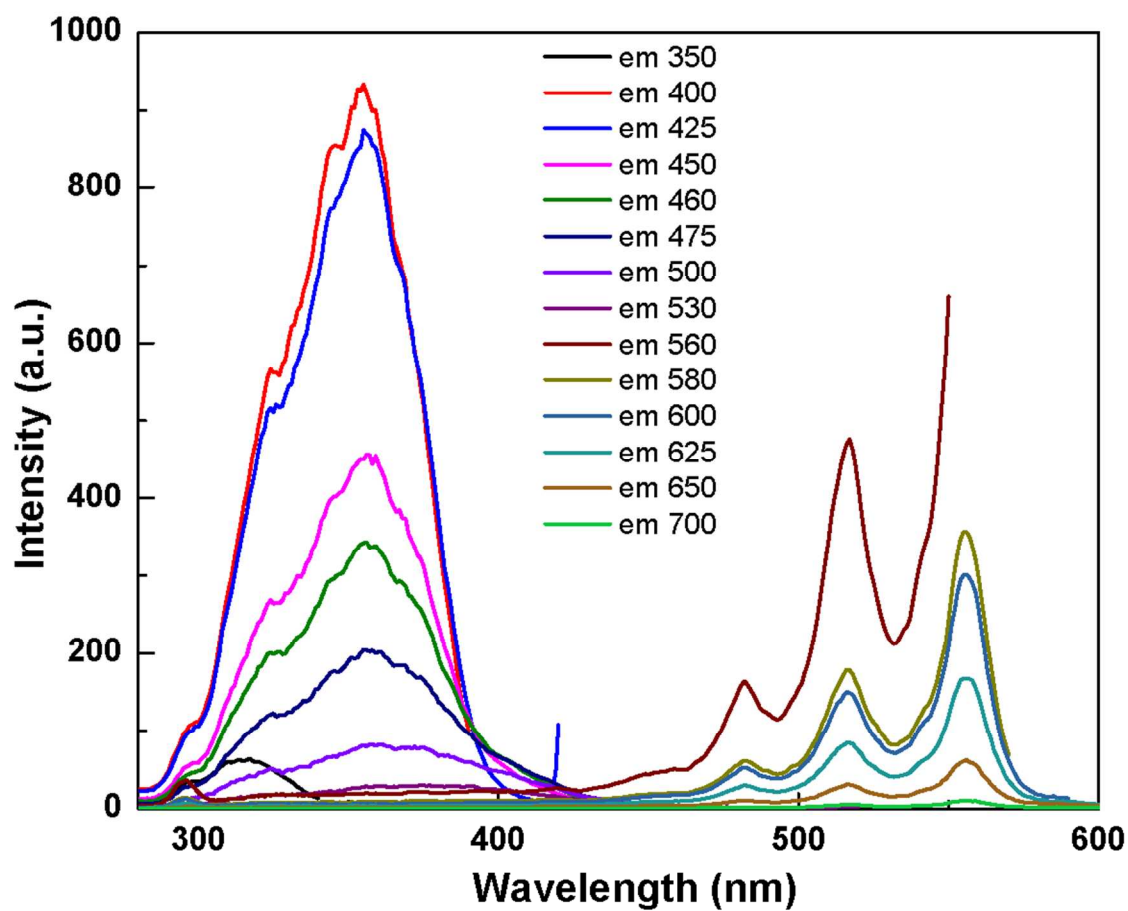


Figure 10. Excitation fluorescence spectra of G-Fol in THF at different emission wavelengths.

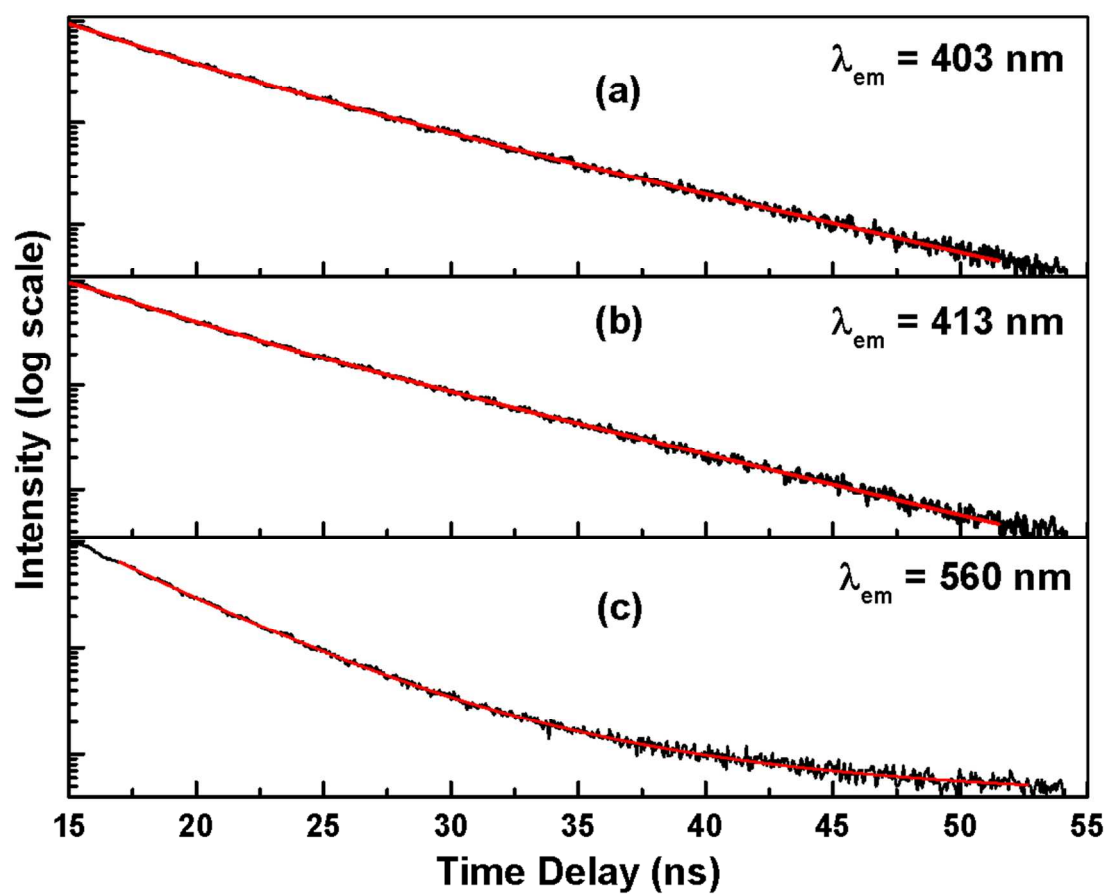


Figure 11. (a-c) TCSPC measurements of G-Fol in THF at λ_{exc} 280nm.

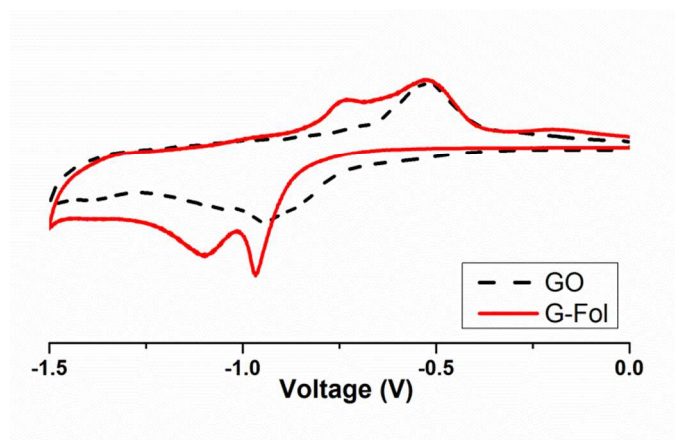
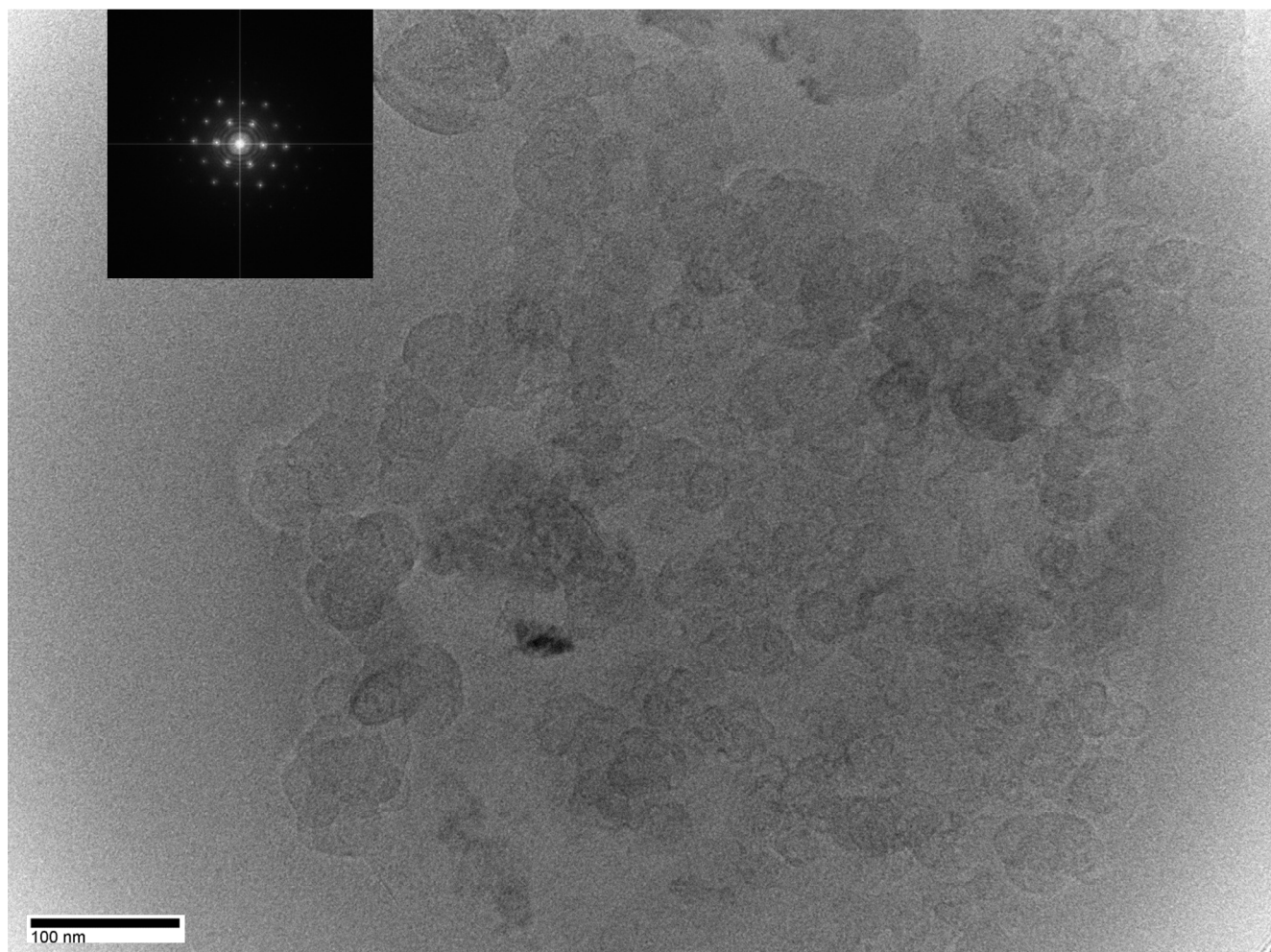


Figure 12. CV of GO and G-Fol samples recorded as films in acetonitrile using TBAPF₆ as supporting electrolyte.



(A)

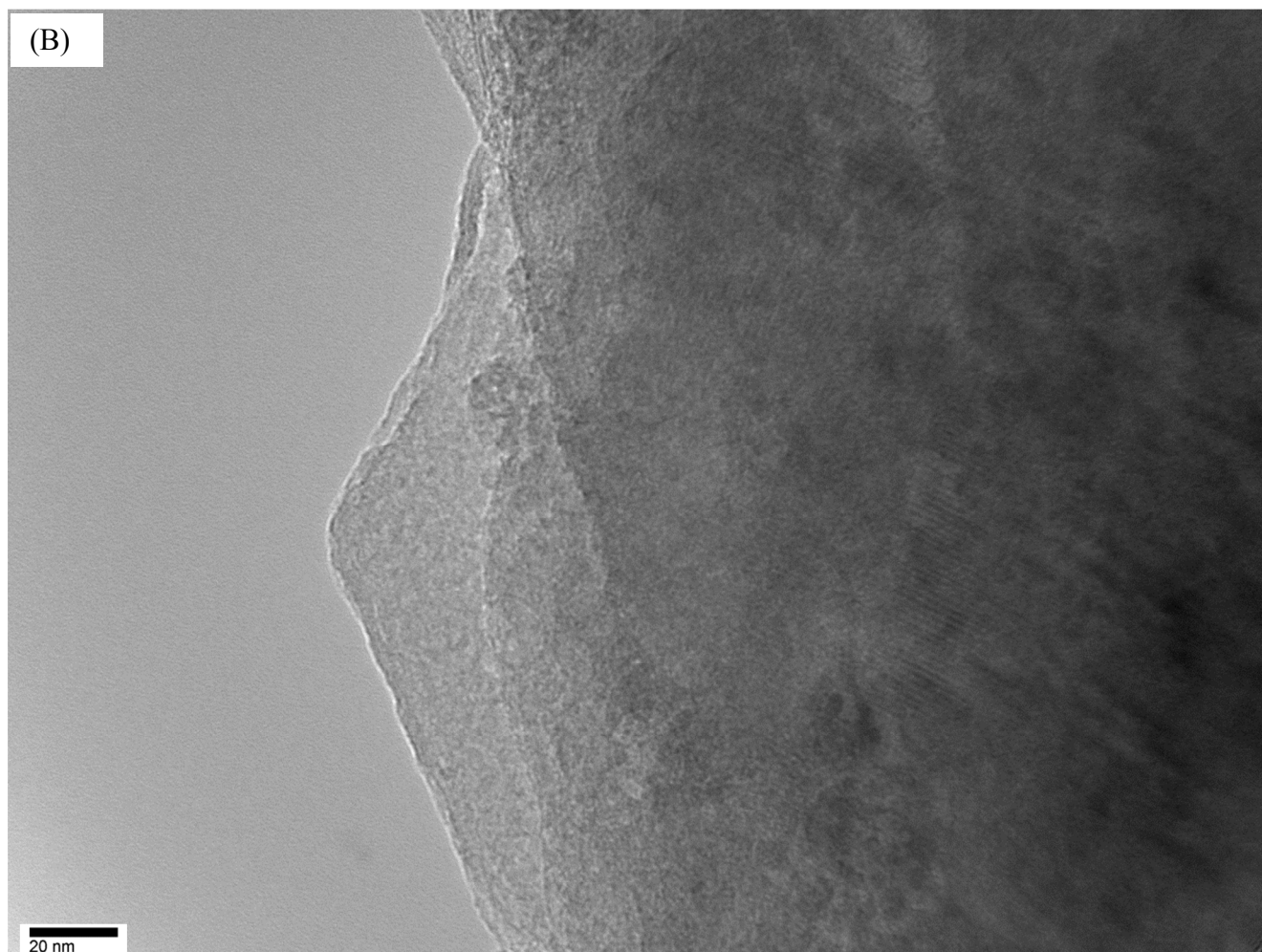


Figure 12. HRTEM images of G-Fol (a) exfoliated graphite sheets showing graphene flakes, (inset: graphene lattice with FFT), and (b) few layered graphene sheet.

Table 1. Time constants with their relative amplitudes to fit the TRF decay curves for G-Fol.

λ_{ex} nm	λ_{em} Nm	τ_1 (relative amplitude) ns	τ_2 (relative amplitude) ns	τ_3 (relative amplitude) ns
280	403	3.2 (23.72)	0.25 (3.8)	7.2 (72.48)
280	413	3.9 (57.35)	0.8 (12.6)	9.1 (30.05)
280	562	0.62 (0.38)	3.68 (79.9)	9.4 (19.72)

TOC

A promising and mild methodology for the preparation of stable exfoliated graphite has been demonstrated by insertion of water soluble fulleranol molecules, providing less chemically defected few layered graphene.

