Journal of Colloid and Interface Science 466 (2016) 425–431

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Photodegradation of dispersants in colloidal suspensions of pristine graphene

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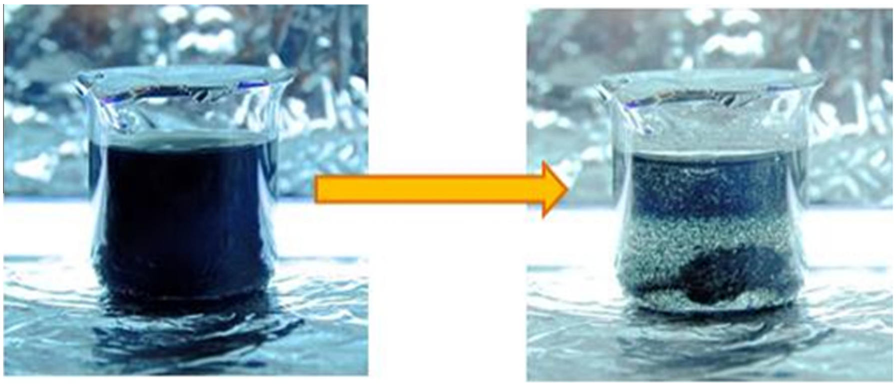
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 July 2015
Revised 9 October 2015
Accepted 12 October 2015
Available online 22 October 2015

Keywords:
Nanomaterials
Photodegradation
Graphene
Films

ABSTRACT

We demonstrate that UV degradation can remove polymeric dispersants from the surface of colloidal pristine graphene. In particular, we investigated the irradiation of polyvinylpyrrolidone (PVP)-dispersed graphene in water; this polymer has been established as a versatile nanosheet dispersant for a range of solvents, and it undergoes photo-oxidative degradation when exposed to UV light. We find that the molecular weight of PVP decreases with irradiation time and subsequently desorbs from the graphene surface. This causes gradual destabilization of graphene and agglomeration in water. The amount of adsorbed PVP decreases by approximately 45% after 4 h of irradiation in comparison with the non-irradiated dispersion. At this point, the majority of the stable graphene nanosheets flocculate, likely because of insufficient surface coverage as indicated by thermogravimetric analysis. Graphene aggregates were characterized as a function of irradiation time by optical microscopy, UV–vis spectroscopy, Raman spectroscopy, and conductivity measurements; the data suggest that the agglomerates maintain a graphene-like (rather than graphite-like) structure. The effect is also observed for another graphene dispersant (sapogenin), which suggests that our findings can be generalized to the broader class of photodegradable dispersants.

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http://dx.doi.org/10.1016/j.jcis.2015.10.027

1. Introduction

Graphene, a 2-D nanomaterial composed of sp^2-hybridized carbon atoms [1], is often produced by solution-processing methods from parent graphite. These methods hold the most promise for industrial use, as large amounts of graphene can be produced in a scalable fashion [2–4]. Solution processing entails exfoliation, by bath sonication or tip sonication of graphite powder within a solvent in the presence of a dispersant, followed by separation of exfoliated nanosheets from unexfoliated material. Without the dispersant, the sonication based technique becomes ineffective in most solvents due to re-aggregation of graphene nanosheets [5]. Applications of such non-covalently functionalized graphene dispersions include electrodes [6–8], conductive ink printing [9], transparent thin films [10], and polymer composite fillers [3,8,10–12].

A variety of dispersants have been reported by different groups to facilitate the liquid-phase production of pristine graphene from graphite [6,13–16]. For instance, our group has demonstrated the successful use of a range of compounds, such as functionalized pyrenes and polymers, as dispersants for maintaining stable graphene dispersions [17,18]. In such dispersions, a distinction must be drawn between bound (adsorbed) dispersant on the graphene surface and unbound (excess) dispersants that are freely floating in the solvent.

Unfortunately, the presence of these dispersants may be counterproductive in graphene-based composites and films [19]. Our prior work investigated various means of removing excess dispersants by dialysis, vacuum filtration or spray drying [19]. However, the possibility of removing bound dispersants from the graphene surface in solution is also intriguing. One possibility is the photodegradation of dispersants. Kaczmarek et al. demonstrated that polyvinylpyrrolidone (PVP) undergoes chain scission under ultraviolet (UV) light [20], with extensive data indicating that the average molecular weight of PVP in solution is reduced when the solution is exposed to UV-C light. This is promising, given that PVP functions as an effective dispersant for graphene and 2D inorganic nanomaterials in water and a range of organic solvents [18,21]. Interestingly, UV light exposure has been used to both reduce graphene oxide in solution as well as degradation of organic dyes [22].

In this paper, we investigate the effects of photodegradation of PVP in PVP-enabled graphene suspensions in the context of graphene dispersant removal. In particular, we examine the stability of the graphene dispersions and the nature of graphene aggregates forming in solution after PVP degradation by UV irradiation. In addition, the electrical properties of graphene films made from irradiated dispersions are explored; these experiments can address the differing roles of bound vs. free dispersant in inter-sheet electrical connectivity in graphene films. We examine PVP not only for its own utility but also as a model photodegradable dispersant; parallel investigations of sapogenin indicate that our results are generalizable.

2. Materials and methods

2.1. Materials

Expanded graphite (EG) (CAS # 7782-42-5, grade-3772) was graciously provided by Asbury Carbons. Polyvinylpyrrolidone (PVP) (MW = 10,000 g mol^{-1} and MW = 360,000 g mol^{-1}) and hydrogen peroxide (H_2O_2) (30% w/w in H_2O) were purchased from Sigma–Aldrich. All of these were used as received without any further purification. Saponin (sapogenin content ~8–25%) was also procured from Sigma–Aldrich.

2.2. Graphene dispersion

10 mg mL^{-1} of polyvinylpyrrolidone (PVP) was added to water and then magnetically stirred until the PVP completely dissolved. 50 mg mL^{-1} graphite was added to the stirring solution. The mixture was subjected to 1.5 h tip sonication and 4 h centrifugation (Centrific Centrifuge 225, Fisher Scientific) at 3500 rpm. After centrifugation, the supernatant graphene dispersion was separated from the bottom layer of graphite sediment. The concentration of graphene in the final dispersion is calculated using the Lambert–Beer law in conjunction with the UV–vis absorbance data. The concentration of graphene was measured to be 1.3 mg mL^{-1}. Sapogenin-stabilized graphene dispersion was also prepared in the same manner as PVP-stabilized graphene dispersion. The concentration of sapogenin in the solution was 6 mg mL^{-1} and the concentration of graphene was 0.15 mg mL^{-1}.

2.3. UV–vis spectroscopy

UV–vis spectra were measured using a Shimadzu UV–vis spectrophotometer 2550 at wavelengths of 200–800 nm. The concentration of graphene in solution is determined from the absorbance at 660 nm [23,24] by using the Lambert–Beer law [25]:

$$A = \alpha L c$$

where A is the absorbance of solution at 660 nm, α is the experimentally determined extinction coefficient, L is the path distance, and c is the concentration of nanomaterial in solution. The extinction coefficient was determined as 1293 mL mg^{-1} m^{-1} for graphene/PVP dispersions [18] and 4592 mL mg^{-1} m^{-1} for graphene/sapogenin dispersions.

2.4. UV irradiation

40 mL of water was poured into a quartz beaker (Chemglass 50 mL quartz beaker, Fisher Scientific) and 10 mg mL^{-1} PVP (MW = 360,000 g mol^{-1}) was added. This solution was stirred for 10 min in order to ensure that the PVP was completely dissolved in the water. At this point, 2 wt.% H_2O_2 was added to the solution. The dispersion was then stirred for another 5 min. Before each irradiation, the UV bulb (50 W high output germicidal UV bulb, Emperor Aquatics) was allowed a ten minute warm-up time. The solution was placed in the photodegradation enclosure (constructed in house) and allowed to irradiate for a given time. The solution was magnetically stirred throughout the course of the irradiation.

Graphene dispersion was diluted with H_2O for a dilution ratio of 1:8. 2 wt.% of H_2O_2 with respect to the diluted solution was then added. The diluted graphene dispersions were then irradiated in the same conditions as the previous solutions.

2.5. Viscometry

Viscosity of the aqueous solution of 10 mg mL^{-1} PVP (MW = 360,000 g mol^{-1})/H_2O_2 was measured using an Ubbelohde viscometer. 6.7 mL of this solution was placed in the viscometer, and the elution time was measured. After this, the solution was irradiated for one hour. After the first hour of irradiation, the elution time was once again measured. This process was repeated until the solution had been irradiated for a total of four hours.

After all of the elution times were measured, the data was converted to viscosity using the following formula [26]:

$$\upsilon = kt$$

where v is the dynamic shear viscosity of the solution, t is the elution time, and k is a temperature-dependent constant associated