Carbon 124 (2017) 133–141

Contents lists available at ScienceDirect

Carbon

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

Preparation of water-soluble graphene nanoplatelets and highly conductive films

Xuezhu Xu [a, **], Jian Zhou [a], Jacques Jestin [b], Veronica Colombo [a, c], Gilles Lubineau [a, *]

[a] King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division, COHMAS Laboratory, Thuwal, 23955-6900, Saudi Arabia
[b] Laboratoire Léon Brillouin (LLB), CEA Saclay, 91191, Gif-Sur-Yvette, France
[c] University of Padua, Chemical and Materials Engineering, Padova, 35122, Italy

ARTICLE INFO

Article history:
Received 23 February 2017
Received in revised form
26 July 2017
Accepted 3 August 2017
Available online 11 August 2017

Keywords:
Graphene nanoplatelets
Water-soluble
Sodium hypochlorite
Sodium bromide
Colloids
Surface and interaction
Electrical double layer
DLVO theory
Film
Conductivity

ABSTRACT

This paper tackles the challenge of preparation stable, highly concentrated aqueous graphene dispersions. Despite tremendous recent interest, there has been limited success in developing a method that ensures the total dispersion of non-oxidized, defect-free graphene nanosheets in water. This study successfully demonstrates that few-layer graphene nanoplatelets (GNPs) can form highly concentrated aqueous colloidal solutions after they have been pretreated in a low-concentration inorganic sodium-hypochlorite and sodium-bromide salted aqueous solvent. This method retains the graphitic structure as evidenced by nuclear magnetic resonance spectroscopy, X-ray photoelectron spectroscopy, and Raman spectroscopy. Vacuum-filtrated freestanding films demonstrate an electrical conductivity as high as 3000 S m^{-1}. This dispersion technique is believed to be applicable not only for GNPs, but also for dispersing other types of graphitic materials, including fullerenes, single/double/multi-walled carbon nanotubes, graphene nanoribbons and etc.

1. Introduction

The properties of graphene make it an attractive candidate for use in various electrical applications [1,2]. Graphene has a carrier mobility as high as 200,000 $cm^2\ V^{-1}\cdot s^{-1}$ [3] and a theoretical tensile modulus as high as 1 TPa [4]. It also has a high theoretical specific surface area (2630 $m^2\ g^{-1}$) [5], a high thermal conductivity (~5000 W m^{-1} K^{-1}), and an ultrahigh optical transmittance (~97.7%) [6]. Graphene can be obtained by "peeling off" single defect-free graphene sheets from layered graphite crystals [7] or by growing single graphene sheets directly on metals [8]. Single-sheet production, however, is not viable for mass production, and more scalable routes to graphene production are urgently required. Few–layer graphene nanoplatelets (GNPs), previously called few-layer graphene [9], graphene nanosheets [10], and graphene powder that are produced by micromechanical cleavage, are important nanoscale building blocks for various applications. It is surface functionalization-free, typically in the form of few layers (<3), with an average in-plane dimension of around 10 μm. Many applications require GNPs to be dispersed in a fluid medium. At this point, the dispersion becomes very critical [11].

Optimizing dispersion should be done in a non-aggressive and non-destructive way that does not compromise graphene's *sp*^{2} structure, which affords it its high carrier mobility and ultimately its high electrical conductivity [3]. A few examples of graphene dispersion in liquid media have been reported, and the efficiency of each dispersing fluid can be explained by different mechanisms, e.g., matching in surface free energy, acid protonation, π-π stacking, or Coulomb repulsion. For instance, direct mechanical exfoliation yielding soluble graphene is made possible by the similar surface free energies of graphene and the dispersing liquid medium N-methyl-2-pyrrolidone (NMP) [9,12], and acid protonation by chlorosulphonic acid (HSO_3Cl) has been used to generate repulsive

---

* Corresponding author.
** Corresponding author.
E-mail addresses: xuezhu.xu@kaust.edu.sa (X. Xu), gilles.lubineau@kaust.edu.sa (G. Lubineau).

http://dx.doi.org/10.1016/j.carbon.2017.08.007
0008-6223/

forces between layers, successfully dispersing high concentrations of graphene (up to 2 mg ml^{-1}) [13]. Moieties and polymers, such as pyrene derivative 1-pyrenebutyrate [14], dyes [15], 7,7,8,8-tetracyanoquinodimethane [16], porphyrin [17], flavin mononucleotide (FMN) [18–21], and poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) [22,23], have been used to facilitate the dispersion of graphene via π-π stacking. Water alone has proven not to be suitable as a solvent for GNPs because its high surface energy limits the dispersion of graphitic materials, but success has been made by adding a detergent or surfactant, such as bolaamphiphile or sodium dodecyl-benzene sulfonate [24,25].

However, techniques that use highly acidic/organic solvents can have explosive characteristics, be difficult to remove, or introduce components with low conductivity (e.g., PSS in the PEDOT/PSS) into the product. In addition, many of the techniques described above have low scalability, resulting in products with a low concentration of graphene. We report here a very simple and efficient procedure to disperse graphene by means of regular ultrasonic treatment of GNP powder in water aided by commercially available inorganic salts: sodium hypochlorite and sodium bromide.

2. Experimental section

Few-layered graphene powder (N002-PDR, Angstronmaterials Inc) was used throughout this work. NaClO and NaBr powders were used as the bleaching components (RICCA Chemical Company). NaClO (5 wt% in water) was used as received. Water used for experimentation was purified by distillation in a Milli-Q (Advantage A10 model) system.

To prepare WSGNPs in aqueous NaClO/NaBr salted colloidal solutions, graphene powder and bleach/water were mixed by a regular bath ultrasonic cleaner (Model: 8510E-MTH, Branson Company). The sonication process worked at the specification of 250 W and 44 kHz at room temperature. Samples were placed randomly in any location within the sonication bath. Sonication time ranged between 10 and 160 min. An Eppendorf 5810 centrifuge was then used to centrifuge the WSGNP/salts/water at 5000 rpm for 5 min to remove the NaClO/NaBr/water mixture. Corning polypropylene (PP) centrifuge tubes (50 mL, outer diameter: 29.1 mm) were used for the centrifugation. Afterward, the resultant WSGNP slurry and ~100 mL of pure water were loaded into a Spectra/Por1 dialysis membrane (64-mm tubing diameter and 6-8-kD pore width) to remove residual chemicals. These dialysis bags were immersed in 5000 mL of deionized water, which was changed every 12 h for 10 d. The concentration of the purified WSGNP/water colloidal solution was adjusted to its original concentration (1 mg ml^{-1}). Vacuum filtration to obtain free-standing WSGNP films was performed using a 47-mm diameter vacuum filter holder assembly (Wheaton Company), which was coupled with a 47-mm diameter, polycarbonate (PC) filter with 0.05-μm pores (Whatman Company). The filtration took ~3 h, leaving a wet membrane supported by the PC filter. This “wet-cake” was covered by another piece of PC membrane and was laminated between several layers of tissue papers and then placed between two metal cells (2.4 kg for each, pressure on the film: 0.36 kPa) to ensure that the resultant WSGNP film was compact. The drying process was conducted in a vacuum oven at 100 °C for 12 h.

Both pristine GNP and WSGNP were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA was scanned by a NETZSCH TG, 208 F1 instrument from 27 to 880 °C at 20 K/min under nitrogen atmosphere protection. DSC was performed on a NETZSCH DSC 204 F1 Phoenix instrument, which was operated from 25 to 400 °C at 25 K/min under nitrogen atmosphere. Fig. S1 shows the thermogravimetric (TG) plot of our GNP material together with that of WSGNP after post-treatment. The figure shows a mass loss (~10%) below 100 °C, which we attributed to the removal of adsorbed water and NaClO (boiling point at 101 °C). It also shows a slower, steady mass loss (~12%) over the whole temperature range to 377.7 °C, which is likely caused by the removal of oxygen functionalities [20]. The final weight of WSGNP is 8.3% of the initial weight, which is believed to be from the attached inorganic salts (NaClO, NaBr) on the WSGNP that were introduced during dispersion. The DSC scan of WSGNP is shown in Fig. S2. Compared with the pristine GNP, WSGNP has an additional peak at ~100 °C. This peak is very likely introduced by volatile substances, possibly NaClO, given that the DSC of graphite or graphene oxide does not have this peak in the literature [26]. The expected endothermic peak associated with water removal is hidden by another exothermic process that is not identified at this point. Conclusively, both TGA and DSC demonstrate how WSGNP differs from graphene oxide, which has a 65% weight loss at 230 °C, [27].

TEM images were taken using a Tecnai Twin microscope (FEI). TEM samples were prepared from GNP/water and WSGNP/water solutions at 1 mg ml^{-1} for 60 min. SAED pattern was obtained from TEM images. SANS for the dispersed samples were measured at rest at the Laboratoire Léon Brillouin (LLB Saclay) on the spectrometer PAXY, by varying the wavelength λ and the sample-to-detector distance D. The three configurations defined by $l = 6$ Å at a sample-to-detector distance of 1.2 m, $l = 6$ Å at a sample-to-detector distance of 6.7 m and $l = 15$ Å at a sample-to-detector distance of 6.7 m enable to cover a total q-range from 3.10^{-3} Å^{-1} to 0.4 Å^{-1}. Samples were measured in calibrated quartz cells of 1 mm pathway in H_2O as solvent. The 2D patterns were reduced to 1D spectra I(q) versus q after a radial averaging around the center of the scattered beam. Standard corrections by sample thickness, neutron beam transmission, and empty cell signal subtraction, detector efficiency, electronic background and subtraction of incoherent scattering were applied to get the scattered intensities on an absolute scale (cm^{-1}). Data reduction was done using a home-made software “Pasinet”. NMR spectroscopy on dried graphene powders were measured at 18 kHz with samples encapsulated in a 3.2-mm rotor with an Ultrashield 400 WB plus (Bruker Corporation). Raman measurements were conducted on a LabRAM ARAMIS using a 473-nm laser source. Zeta potentials of WSGNP dispersions were measured by a zeta-sizer (Malvern Company). The FT-IR spectroscopy measurements were performed on a Nicolet iS10 (Thermoscientific Inc). Dried powders from WSGNP dispersions were produced using a Christ Alpha 1–2 LD plus freeze dryer (Martin Christ Company). We conducted the XPS studies in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Ka X-ray source ($h\nu = 1486.6$ eV) operating at 150 W with a multichannel plate with a delay line detector under a vacuum of ~10-9 mbar. All spectra were recorded using an aperture slot of 300 μm × 700 μm. Survey spectra were collected using a pass energy of 160 eV and a step size of 1 eV. A pass energy of 20 eV and a step size of 0.1 eV were used for the high-resolution spectra. Samples were mounted in the floating mode to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to the sp2 hybridized (C=C) carbon with the C 1s peak from the carbon nanomaterials set at 284.5 eV. Ion chrotomography was measured with an ICS-3000 t purchased from Dionex Corporation, and measurements were performed with a 4 × 250-mm analytical tube (IonPac AS15, for anions) from the same company. Ultraviolet–visible (UV–vis) spectroscopy measurements on WSGNP powders in various solvents were recorded from 800 nm to 190 nm at 1-nm intervals by a Cary100 ConC UV–vis spectrophotometer (Agilent Technologies). Sheet resistances were measured using a CMT-SR2000N four-probe system (probe space 1 mm, Materials Development Corporation).