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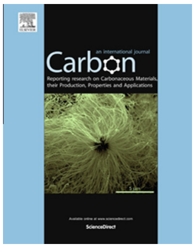

Facile and scalable one-step production of organically modified graphene oxide by a two-phase extraction

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ABSTRACT

The time-consuming purification of graphene oxide (GO) including reduction of the excessive ionic strength represents a serious bottleneck for its mass production. Moreover, for the application as a filler in polymer nanocomposites, the hydrophilic GO has to be organophilized by cation exchange, e.g. with alkylammonium. Here, we propose a facile one-step process that produces highly delaminated organically modified GO suspended in various organic solvents and which spares any additional purification steps. The organically modified GO is instead directly extracted from the oxidation mixture into diethyl ether with the help of 1-dodecylamine. The organically modified GO can then be transferred into a broad variety of organic solvents. Elemental analysis shows the extracted GO to be highly pure and atomic force microscopy images suggest that surprisingly, the material was even delaminated.

1. Introduction

While graphite oxide has been known for 150 years [1], only more recently has its delaminated form, graphene oxide (GO), attracted considerable interest as a reinforcing filler in nanocomposites due to its remarkable mechanical [2–6] and thermal properties [7–10] as well as an intermediate for the production of graphene [11–15]. Unfortunately, all well-established synthesis protocols established by Brodie [16], Staudenmaier [17], and Hummers/Offeman [18] require an extremely time-consuming purification step in which the large excess of ionic side products and excess reactants originating from the previous intercalation and oxidation steps are removed. In particular the reduction of ionic strength is indispensible to achieve delamination of GO via osmotic swelling [19]. Therefore GO is usually washed excessively either with diluted hydrochloric acid and water or is dialyzed for several weeks with repeated exchange of the dialysis medium. Both purification methods are exceedingly waste-water-intensive and vastly time-consuming methods, rendering this purification step a bottleneck and hamper large scale industrial fabrication.

Optimization of the performance of nanocomposites additionally requires the adjustment of the surface tension of the filler and the hydrophobic matrix. Hydrophobization of GO can be achieved by covalent bonding of alkyl chains to the hydroxyl- and/or carboxyl-groups on the basal planes or edges, respectively. The reagents for ester- or etherification are, however, extremely water-sensitive. Therefore, prior to covalent modification, GO has to be dried [20] which inevitably will induce aggregation into band-like structures where the huge basal surfaces partially overlap and external

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surfaces are converted into interlamellar space. Disaggregation of such restacked GO platelets requires, if possible at all, intense ultrasonication, which breaks the platelets and decreases the aspect ratio [21]. Alternatively, the hydrophobization of GO can be done by a cation exchange of internal and external cations with long chain alkylammonium or alkylamines [22–25]. While most work in this direction focused on the characterization of the intercalation compounds, to our knowledge Liang et al. [25] were the only ones who have applied cation exchange to facilitate suspension of GO in chloroform. In this work, however, lyophilized GO was purified prior to hydrophobization by washing and subsequent dialysis.

To explore the full potential of GO-polymer-nanocomposites, stable suspensions in a variety of organic solvents (polar to non-polar) would be highly desirable for solution blending with various polymer matrices. These suspensions, moreover, should be readily available in larger quantities while the GO should be delaminated to the greatest possible extent to maximize the aspect ratio and the specific interface area [26]. Certainly most ambitious, purification steps should be avoided to minimize waste and make the process as technically benign as possible.

Here, we propose a one-step process that produces highly delaminated organically modified GO suspended in various organic solvents and which spares any additional purification steps. The organically modified GO is instead directly extracted from the reaction mixture with the help of alkylammonium.

2. Experimental

Graphite flakes (Reinstflocke (RFL) 99.5) were provided by Kropfmühl AG. All chemicals were of analytical grade and used without further purification.

Graphene oxide (GO) was prepared by a modified Hummers/Offeman method [18]. In a typical experiment flake graphite (10 g, 125–250 μm) and sodium nitrate (10 g) were mixed with concentrated sulfuric acid (300 mL, 98%). Subsequently, potassium permanganate (30 g) was interspersed over a period of 3 h and the reaction was kept at room temperature for 12 h. Thereafter, the mixture was slowly poured into ice-cooled deionized water (300 mL) and hydrogen peroxide (30%) was then added until the solution turned golden. The suspension was mixed with the same volume of ethyl alcohol and various amounts of 1-dodecylamine (12AM). Afterwards, GO modified with 12AM (GO12AM) could be extracted into diethyl ether. To further reduce impurities, traces of ions carried over into the organic phase may be extracted in an optional step with 100 mL of water (GO12AM W). In a final step the desired organic solvent was added and the diethyl ether was removed by distillation.

As a reference, a fraction of the GO was purified in the traditional way by repeated (3×) washing/centrifugation followed by a dialysis to an ionic conductivity of 2 μS cm^{-1}. Post purification, this GO was cation exchanged with an excess of 12AM, the precipitate was then washed with water and dried for elemental analysis (dGO12AM).

Elemental analysis was performed at the Bayreuth Center for Ecology and Environmental Research using ICP-OES.

Topographic AFM imaging was conducted using an Asylum Research MFP3D™ AFM operating in intermittent contact mode (silicon cantilever with a typical spring constant $k_c = 46$ Nm^{-1}). The samples were prepared by drop-casting of diluted (0.01 mg mL^{-1}) GO and GO12AM suspensions in water and 2-butanone, respectively, onto a silicon wafer.

Textured, restacked, samples were prepared by slowly drying more concentrated suspensions (1 mg mL^{-1}) on glass slides and Powder X-ray diffraction (PXRD) patterns were obtained using nickel filtered Cu-Kα radiation ($\lambda = 1.54187$ Å) on a Bragg–Brentano-type diffractometer (XPERT-PRO, PANalytical B.V.) equipped with an X'Celerator Scientific RTMS detector.

^{13}C and ^{15}N MAS solid-state NMR spectra were recorded at ambient temperature on an Avance II 300 (Bruker) spectrometer operating at resonance frequencies of 75.5 MHz (^{13}C) and 30.4 MHz (^{15}N). The samples were packed in 4-mm ZrO_2 rotors which were mounted in standard triple-resonance MAS probes (Bruker). The ^{13}C spectra were measured with a standard one-pulse sequence and Spinal-64 proton decoupling during acquisition. The observation of the ^{15}N signal was made using a cross polarization transfer via the proton bath. The ^{13}C signals were referenced with respect to tetramethylsilane. For ^{15}N signals nitromethane was used.

The cation exchange capacity (CEC) was determined for two different samples of GO, which had been purified by dialysis, by means of a photometric method applying a Varian Cary 3 UV–Vis spectrometer and $[Cu(trien)]^{2+}$ as a dye. $CuSO_4$ (99.99+%) and triethylenetetramine (>97%, trien) were purchased from Sigma Aldrich. The preparation of the complex and the CEC measurements were performed according to procedures described in detail in the literature [27,28]. The samples were centrifuged and 3 mL of the supernatant were transferred into plastic cuvettes. The adsorption was measured using monochromatic light at 577 nm. The CEC was measured to be 3.34 ± 0.02 mmol g^{-1}. Since the CEC of GO is known to depend on the pH and the ionic strength [29], these parameters were fixed prior to the CEC determination. First the ionic strength was fixed to 0.025 M by addition of a NaCl-solution. Then the pH of the suspension was adjusted to 3, the lowest value where GO is still colloidally stable and complete cation exchange is assured, by addition of 0.01 M HCl. At pH = 0, as given in the reaction mixture, the CEC is expected to be slightly lower. The CEC as determined by the copper complex method appears high at any given pH compared to both literature values [30] and the CEC of 1.32 mmol g^{-1} determined at pH = 0 by the ammonium content. At this stage only some potential explanations can be given: At such a low pH the copper complex might no longer be stable and copper might coordinate directly to GO in excess to cation exchange. Alternatively, lateral interactions of complex cations might trigger adsorption in excess of the actual CEC.

3. Results and discussion

Following oxidation of graphite in a modified Hummers/Offeman procedure, the organically modified GO (GO12AM) is directly extracted from this harsh, highly acidic (pH = 0) and concentrated reaction mixture of extremely high ionic