

EMPLOYMENT OF A FLOW SYSTEM COUPLED TO AN IONIC DIFFUSION CELL TO PURIFICATION OF GRAPHENE OXIDE DISPERSION

Marcos A. dos Santos, Lucas Marquês, Jairo J. Pedrotti, Cecília C. C. e Silva

alonemas13@gmail.com; marqueslucas504@gmail.com; jpeditotti@mackenzie.br; cecilia.silva@mackenzie.br

Abstract: *The synthesis of bidimensional materials (2D materials) has been expressive increasing in the last few years and the most obtained material is graphene and their derivatives graphene oxide (GO) and reduced graphene oxide (RGO). In the literature, there are several methods to obtain these materials; however, the most explored is the chemical exfoliation process, by the oxidation of the graphite for the obtention of the graphene oxide. In the end of the process, the GO dispersion should be purified, to remove the residues of the oxidation process and increase the pH value of the dispersion. Usually this process is performed through several steps of centrifugation of the GO dispersion and exchange of the supernatant by deionized (DI) water, which represents a lot time consuming and volume of DI water. Aiming to overcome these issues, we address a new method to purify GO dispersion employing a flow system coupled to an ionic diffusion cell, which promotes the removal of the ions, by diffusion, minimizing the process time, the volume of DI water consumed and turn possible to concentrate the GO dispersion and to select the size of the GO sheets.*

Key-Words: *Exfoliation of 2D materials; graphene oxide dispersion, purification; flow system; ionic diffusion cell*

Introduction: The materials in two-dimensional scale present a range of new properties in relation of existing materials (in the bulk scale), enabling new application; in this case it is possible to highlight hexagonal boron nitride, the transition metal dichalcogenides (TMDs), black phosphorus and mainly graphene. Graphene was the first 2D atomic crystal isolated and characterized [1]. Graphene shows several outstanding properties, such as high surface area (theoretically $2630 \text{ m}^2 \text{ g}^{-1}$, per sheet), excellent electronic properties and high charge-carrier mobility ($2.5 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), flexibility, impermeability to any liquid or gas, high mechanical resistance, good electrical and thermal conductivity (above $3,000 \text{ W mK}^{-1}$) and optical transparency (97.7%) [1]. However, for several application a derivative of graphene has been exhaustively used, the graphene oxide (GO). The GO is obtained by the chemical exfoliation process, through the oxidation of the graphite flakes. The most widespread oxidation method and used until today is the Hummer's method [2], that consists in the employment of graphite, sulfuric acid (H_2SO_4), sodium nitrate (NaNO_3) and potassium permanganate (KMnO_4). After the oxidation and exfoliation process it is necessary to perform the purification of the GO dispersion, to remove the residues from the oxidation process, mainly ionic species from the reagents, and to increase the pH value of the GO dispersion around 6 [3-5]. Usually this process is performed through several steps of centrifugation of the GO dispersion and exchange of the supernatant by hydrochloric acid solution (10% v/v) (3 times) followed by deionized (DI) water. To complete the full process, usually it is necessary few days and the dedication of a trained person to manipulate the GO dispersion. Besides that, a high volume of DI water is consumed and the efficiency in the removal of residues ions is poor. Aiming to overcome the issues set out above, we address a new method to purify GO dispersion employing a semi-automated flow system coupled to an ionic diffusion cell, which promotes the removal of the ions, by diffusion, minimizing the process time, the volume of DI water consumed and turn possible to concentrate the GO dispersion.

Experimental: The GO dispersion was prepared based on the Hummer's method [2]. To carry out the purification step after the GO synthesis, it was employed a flow system coupled to an ionic diffusion cell. The flow system was setted out with two fluidic channels, one to pass the GO dispersion, called of donor channel, and other to pass the DI water, to collect the residual ions from the synthesis and the protons, called of acceptor channel. To inject the fluids, a peristaltic pump from Ismatec, Reglo model, was used. Teflon fluidic tubes, with 0.5 mm of internal diameter, were connect to the peristaltic pump through the Tygon tubes. The ionic diffusion cell was made with two pieces of acrylic the dimension of $90 \times 18 \times 40 \text{ mm}$ that were pressed by six screws localized in the edges. In each one of the top of the acrylic pieces were engraved fluidic channels in a triangle shape, with 1.0 mm of width, 10 mm of length and 0.20 of depth [6]. The ionic diffusion occurred through a cellulose acetate membrane with a porosity of $0.22 \text{ } \mu\text{m}$ that was setted between the fluidic channels in the acrylic pieces. In the donor channel it was used a flow of 0.54 mL min^{-1} and in the acceptor channel 0.23 mL min^{-1} . The

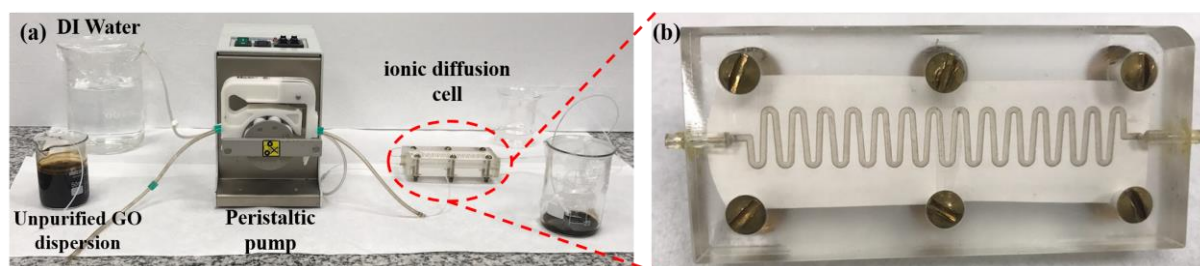


Figure 1. Picture of flow system (a) and the ionic diffusion cell (b) employed for the purification process of the GO dispersions.

To evaluate the initial efficiency of the proposed system, it was used 70 mL of the GO dispersion. After each time that this volume has passed through the ionic diffusion cell (process called number of cycles), the pH value of final acceptor solution (DI water) was monitored and when the process ended, the concentration of the final GO dispersion was determine.

Results and discussion: The Figure 2 shows the variation of the pH value of the collected acceptor solution in function of the number of cycles. It is possible to see, that after 14 cycles the pH value of the acceptor solution reached approximately 6, that represented 21 hours of process. During the passage of the GO dispersion in the flow system, the addition of DI water were made necessary in the third, fifth and last cycle, due the increased of the viscosity of GO dispersion, in this way, in the ended of the purify process 285 mL of DI water were consumed to purified 70 mL of GO dispersion.

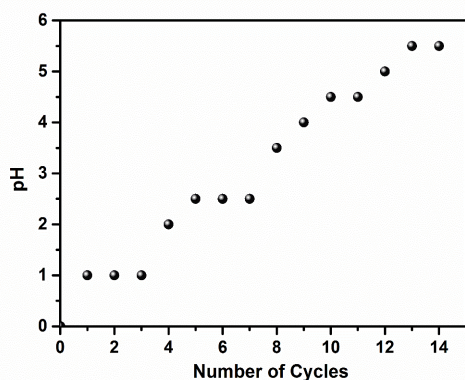


Figure 2. Variation of the pH value of the final acceptor solution in function of the number of cycles.

The mechanism of operation of the proposed system is based on the diffusion process of ions from GO dispersion, in the donor fluidic channel, through the pores of the membrane, to the DI water in the acceptor channel, that is governed by the concentration gradient. The hydronium ions (H_3O^+) diffuses through the membrane, promoting dehydration of the GO dispersion, indicating the pre-concentrating of the dispersion and increasing the viscosity of the fluid. The diameter of the pores of the membrane ($0.22 \mu m$) avoid that the GO sheets diffused to the acceptor solution and could be used as an alternative to select the size of the GO sheets. After to complete the purification process, the GO dispersion presented a concentration of $4mg mL^{-1}$.

Conclusion: The purification of the GO dispersion post-synthesis represents a very important step, because this remove the residues from the oxidation process, mainly ionic species from the reagents, and to increase the pH value of the dispersion around 6,

its use. The most used process is based on several steps of centrifugation of the GO dispersion and exchange of the supernatant by deionized (DI) water, which represents a lot time consuming (few days), high volume of DI water and the dedication of a trained person to manipulate the GO dispersion. With the system developed in this work (semi-automated), it was possible to perform the same process with expressive decrease of time and volume of DI water, besides that it was achieved a faster way to concentrate the GO dispersion and select the size of the GO sheets, by change the pore size of the cellulose acetate membranes. The next steps of this work are related with the employment of the ion-chromatography to deeper evaluate the presence or not the residues, in the trace levels, of ions in the GO dispersion.

References and acknowledgements:

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