



Stability Study of Aqueous Graphene Oxide Suspensions Produced at CTNano/UFMG

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RESUMO

Este estudo avaliou a estabilidade a longo prazo de suspensões de óxido de grafeno (GO) produzidas no CTNano/UFMG. Amostras em diferentes pHs foram armazenadas por 24 meses e analisadas por diversas técnicas, incluindo espectroscopia Raman, análise termogravimétrica (TG), microscopia eletrônica de transmissão (MET) e potencial Zeta. As análises revelaram que as dispersões de GO em água permaneceram estáveis após 24 meses desde a sua preparação, independentemente do pH. Este estudo, em andamento, demonstra a alta estabilidade do óxido de grafeno em suspensão aquosa produzido pelo grupo do CTNano/UFMG, indicando que o material pode ser armazenado por pelo menos dois anos, mantendo sua adequação para diversas aplicações.

Palavras-chave: Óxido de grafeno, Suspensão coloidal, Estabilidade, Envelhecimento, Caracterização.

Introduction

Graphene oxide (GO) is a two-dimensional material composed of graphene nanosheets with sp²- and sp³-hybridized carbon atoms functionalized with oxygen-containing groups such as epoxy, hydroxyl, ketone, and carboxyl (1). It exhibits remarkable thermal, electrical, and mechanical properties, making it a promising candidate for applications across various fields of science and technology. The production of high-quality nanosheets through an economically viable synthesis route is a critical point in graphene production (2). CTNano/UFMG has developed a pilot synthesis route, aiming to optimize the production of GO nanosheets with large lateral dimensions and low thickness, features directly related to the material's quality and performance (3).

The colloidal stability of GO in aqueous dispersions is mainly associated with the electrostatic repulsion generated by the ionization of carboxylic and hydroxyl groups, which prevents nanosheet aggregation. Factors such as pH, ionic strength, oxidation degree, and atomic structure directly influence this stability, potentially leading to destabilization when altered (4). This aspect is crucial for both product quality and determining its shelf life. Therefore, this study aimed to understand and investigate the properties and stability of GO nanosheets at different pH levels over a two-year storage period.

Experimental

Aqueous GO suspensions were obtained using a modified Hummers method, based on a well-established pilot-scale synthesis protocol (3). After synthesis, three samples were prepared: one was kept unaltered, maintaining its original acidic pH (reference sample), while the other two were pH-adjusted to neutral and basic conditions using diluted ammonium hydroxide. All samples were stored in sealed containers, protected from light exposure. Over time, aliquots were periodically withdrawn and analyzed using various characterization techniques, including Raman spectroscopy, thermogravimetric analysis (TGA), transmission electron

microscopy (TEM) and zeta potential measurements via electrophoretic light scattering (ELS).

Results and Discussion

After 30 days of storage (Figure 1 – a, b, c), the samples exhibited the characteristic reddish-brown coloration of GO, with slight variations in hue depending on pH. After two years (Figure 1 – d, e, f), all samples showed a significant color shift to darker shades, ranging from dark brown to black. No signs of aggregation or precipitation were observed, and the color change suggests a partial reduction of functional groups (5), although this process was not substantial according to thermogravimetric analysis (Table 1) and other characterization techniques.

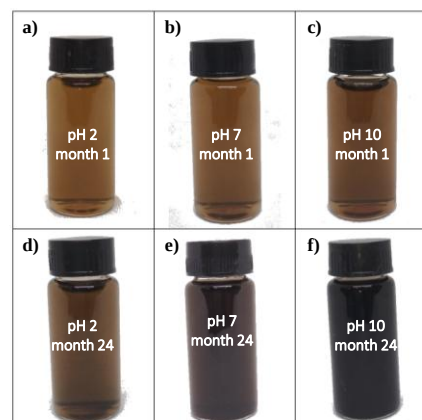


Figure 1. Photographic records over time of GO suspensions at different pH values. a) pH 2 month 1 ; b) pH 7 month 1; c) pH 10 month 1 ; d) pH 2 month 24; e) pH 7 month 24; f) pH 10 month 1

Mass loss (%) – 120-400 °C			
Month	pH 2	pH 7	pH 10
1	54	57	60
24	38	55	62

Table 1. Mass loss of samples treated at different pH values under the same temperature range (120–400 °C) of TGA.

The temperature range between 120 and 400 °C corresponds to the loss of oxygen-containing functional groups. It can be observed that, across all pH conditions, the degree of oxidation remained above 30%, even after 24 months of storage. This indicates the preserved stability of GO nanosheets in aqueous suspension.

To evaluate the colloidal stability of GO suspensions in water, electrophoretic light scattering (ELS) was employed to determine the Zeta potential (ζ). Table 2 presents the average ζ values obtained for each of the three GO samples over time. These results indicate a high degree of oxidation in the GO, which promotes strong electrostatic repulsion between nanosheets, maintaining their dispersion in solution. This confirms the stability of the GO suspensions even after long-term storage.

Zeta Potential (mV)			
Month	pH 2	pH 7	pH 10
1	-50	-51	-48
24	-39	-46	-49

Table 2. Zeta potential values over time for GO suspensions at different pH levels.

The Raman spectra (Figure 2) show a high D/G band intensity ratio in all samples, indicating a significant level of structural defects caused by the presence of oxygenated functional groups. TEM images (Figure 3) reveal that both fresh and aged GO nanosheets, regardless of pH, exhibit typical wrinkles, low thickness, and micrometer-scale lateral dimensions. These results, consistent across all conditions of pH, confirm that the aqueous GO suspensions remained stable after 24 months of storage.

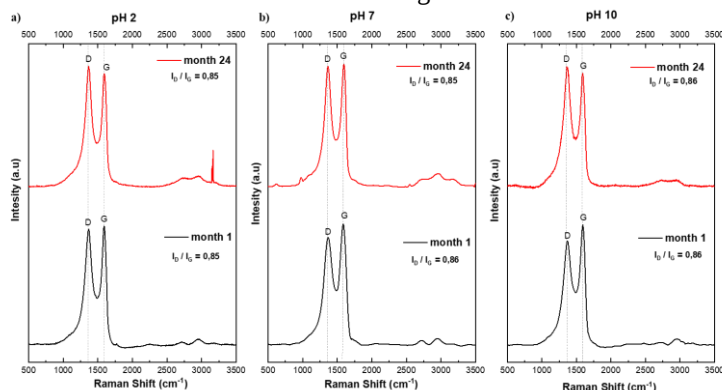


Figure 2. Raman scattering spectra of aqueous GO suspensions over time. a) pH 2 - month 1 and 24; b) pH 7 - month 1 and 24; c) pH 10 - month 1 and 24

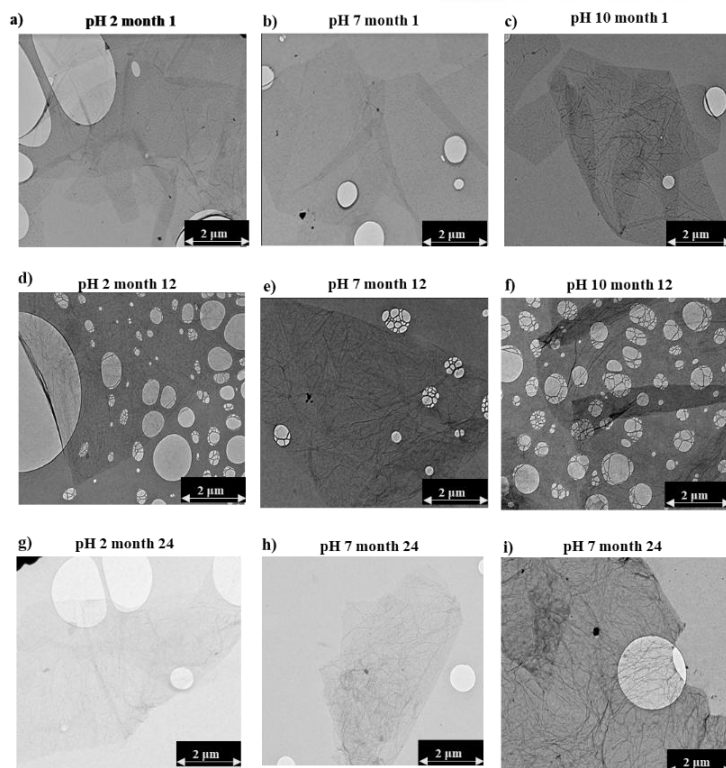


Figure 3. Transmission electron microscopy (TEM) micrographs of GO in aqueous suspension over time. a) pH 2 month 1; b) pH 7 month 1; c) pH 10 month 1; d) pH 2 month 12; e) pH 7 month 12; f) pH 10 month 12; g) pH 2 month 24; h) pH 7 month 24; i) pH 10 month 24

Conclusions

The material exhibits high stability and can be stored for at least two years while remaining suitable for various applications. This highlights the excellent quality of the aqueous graphene oxide produced by CTNano/UFGM.

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