Contribution (Poster)

Removal of oxidation debris from graphene oxide: influence on the formation of composites based on silver nanoparticles

Ana C. M. Moraes, Andréia F. de Faria, Diego Stéfani T. Martinez, Amauri J. Paula, Oswaldo L. Alves

Solid State Chemistry Laboratory (LQES), Chemistry Institute, State University of Campinas (UNICAMP), P.O. Box 6154, 13083-970, Campinas, São Paulo, Brazil

ana.moraes@iqm.unicamp.br

Graphene oxide (GO) is derived from the exfoliation of graphite oxide and its structure contains reactive oxygen functional groups e.g. hydroxyl, epoxide, carboxyl, carbonyls, yielding stable dispersions that consist mostly of monolayers or few-layered stacks. GO is highly hydrophilic, facilitating the intercalation with inorganic and organic compounds. Therefore, the chemically reactive oxygen functionality, renders GO a more attractive material for a wide range of applications [1]. GO silver nanoparticle decoration has opened applications of this hybrid material in sensors, polymeric composites and new antimicrobial agents [2].

The oxidation of carbon nanomaterials is a common method employed for water dispersion, functionalization and purification. This approach can introduce oxygen groups functionalities on carbon nanomaterial surface, but in parallel, carbonaceous byproducts can be generated after the oxidation process, named oxidation debris – polycyclic aromatic sheets with oxidized edges also termed fulvic acids [3,4]. Meanwhile, the presence of oxidation debris in GO has been recently reported by Rourke et al. [5]. It has been proposed that oxidation debris is acting as a surfactant to stabilizing aqueous GO suspensions. However, it is lacking the literature information about the influence of oxidation debris absorbed on GO surface and their scientific and technological implications.

In this endeavour, we have focused on the debris removal from GO and its effect on the colloidal stability of GO dispersions. We have also investigated the influence of debris removal on the formation of graphene oxide decorated with silver nanoparticles.

Oxidation debris removal was performed by heating of GO suspension in 1 M NaOH at reflux, resulting in GO without debris (GOwD) and a supernatant liquid, oxidative debris. Graphene oxide silver nanocomposites were synthesized in situ with two different GO samples, giving: GO-Ag (composite in the presence of debris) and GOwD-Ag (composite without debris). Colloidal stability assays were taken by measuring the light absorbance of graphene oxide suspensions in deionized water after centrifuging step. For this, aliquots of the supernatant were drawn from the suspension.

Figure 1 (a) shows colloidal stability assays. Both samples were submitted under centrifugation in various rotations per minute. It was found that the behavior of GO suspension is much more stable, moreover it suggests that debris acted as a stabilizer in the GO sheets suspensions, giving more stability in aqueous medium. Although, it is worth to say that GO dispersion is not totally dependent on the presence of debris. The removal of oxidative debris can affect the stability but not the ability of GO to form aqueous dispersions.

Homogeneous colloidal dispersions of graphene oxide were produced in aqueous medium (deionized water; 125 µg mL⁻¹). GO generated a light-brown suspension which was quite stable, no floating or precipitated particles were observed. The GOwD created a homogeneous black suspension which was quite stable also (Fig. 1b). The oxidation debris resulted in a yellow-brown solution dispersed in 1 M NaOH, as reported by Rourke et al.

According to TEM analysis, the Fig. 2 (a) and (b), in both cases, there was the formation of graphene based on silver nanoparticles. From the size distribution histograms of silver nanoparticles, the sizes of the nanoparticles on the GO without debris and GO in the presence of debris are widely distributed from 2 to over 40 nm and 4 to over 90 nm, respectively. The Gauss fits indicate that the maximum distributions of silver nanoparticles sizes are 5 and 18 nm, respectively. These results demonstrate that the silver nanoparticles distribution is dependent on the presence of debris on the GO surface. Finally, the oxidation debris removal led to an increase in the average size of silver nanoparticles formed during GO decoration.

References

Figure 1

(a) Colloidal stability assays of samples GO and GOwD in deionized water. (b) Picture of the GO and GOwD suspensions (125 µg mL⁻¹), respectively.

Figure 2

(a) TEM micrographs (bright field mode) of samples (a) GO-Ag (composite in the presence of debris) and (b) GOwD-Ag (composite without debris). Respective histograms are inserted in each image. The histograms of Ag nanoparticles size distributions were obtained by counting more than 1000 nanoparticles for each example.

References