Vitamin C as an innocuous and safe reductant for the preparation of graphene suspensions from graphite oxide

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Liquid-phase processing of graphite and its derivatives (particularly graphite oxide) is currently a very attractive option for the high-throughput production of colloidal suspensions of graphene [1, 2]. This preparation typically involves a reduction step using hydrazine [1], but the use of such a reagent in the large-scale implementation of this approach is not desirable due to the high toxicity and potentially explosive character of this compound [3].

In the present work, we compare the deoxygenation efficiency of graphene oxide suspensions by different reductants (sodium borohydride, pyrogallol, and vitamin C, in addition to hidrazine), as well as by heating the suspensions under alkaline conditions [4]. The progress of reaction as a function of time was monitored through UV-vis absorption spectroscopy. It is well-known that the position of the absorption peak of graphene oxide dispersion gradually shifts to red from a value of 231 nm as reduction proceeds [1].

The reduced dispersions were processed into paper-like films, and characterized by TGA, ATR-FTIR and XPS spectroscopy, and also by electrical conductivity measurements.

The spectroscopic techniques showed a decrease in the intensity of the bands associated with oxygen functional groups that depends on the reducing agent used (Figure 1, Figure 2). Thus, Figure 1 shows that the IR bands at 3000-3500 cm^{-1} (O-H stretching vibrations) and 1720 cm^{-1} (C = O stretching vibrations from carbonyl and carboxyl groups) decreased significantly with increasing reducing power. Figure 2 shows that the XPS band at 286.6 eV (attributed to carbons in hydroxyl and epoxy groups and also possibly to C-C bonds in defected structures [5]) virtually disappears when using the most effective reducing agents (ascorbic acid and hydrazine). These data were corroborated by means of TGA and electrical conductivity measurements.

In almost all cases, the degree of deoxygenation attainable and the subsequent restoration of relevant properties (e.g., electrical conductivity) lag significantly behind those achieved with hydrazine. Only vitamin C was found to yield highly reduced suspensions in a way comparable to those provided by hydrazine. Stable suspensions of vitamin C-reduced graphene oxide can be prepared not only in water, but also in common organic solvents, such as N,N-dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP). These results open the perspective of replacing hydrazine in the reduction of graphene oxide suspensions by an innocuous and safe reductant of similar efficacy, thus contributing to facilitate the use of graphene-based materials for large-scale applications.

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Figures

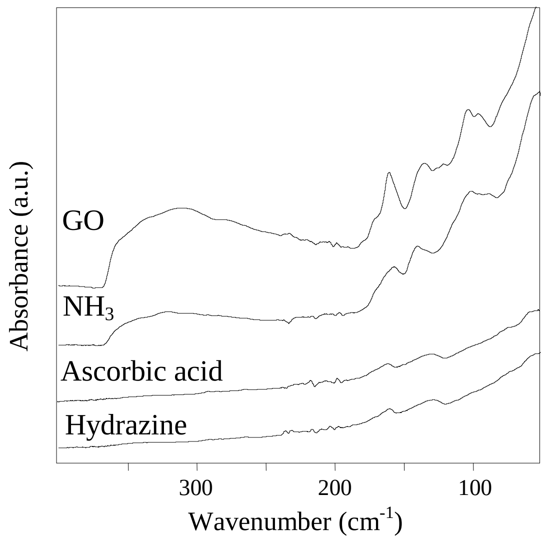

Figure 1. *ATR-FTIR spectra of unreduced graphene oxide and deoxygenated samples.*

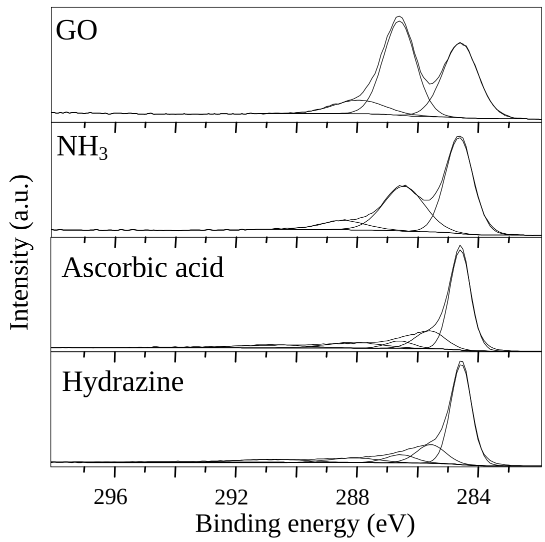

Figure 2. *High resolution C1s X-ray photoelectron spectra for unreduced graphene oxide and deoxygenated samples.*