Preparation of graphene and graphene-metal nanoparticle hybrids with enhanced catalytic activity by reduction of graphite oxide with efficient natural bioreductants

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Abstract
The implementation of green approaches towards the preparation of graphene-based materials with enhanced functionality from graphite oxide requires the use of appropriate reductants in place of the widely employed but highly toxic hydrazine. Vitamin C has been previously shown to efficiently deoxygenate graphene oxide in aqueous and organic dispersion [1]. In the present work, a large number of environmentally friendly, natural antioxidants (mostly vitamins, amino acids and organic acids) has been tested for their ability to reduce graphene oxide. Specifically, vitamin B6 (in two forms: pyridoxine and pyridoxamine dihydrochloride) and vitamin B2 [(−)-riboflavin and riboflavin 5′-monophosphate salt hydrate; the organic acids citric acid, fumaric acid, L-malic acid, and L-tartaric acid; a representative set of the 22 naturally occurring amino acids, as well as two peptides, namely: L-arginine, L-asparagine, L-carnosine (dipeptide), glycine, L-glutamic acid, L-glutathione (tripeptide), L-histidine, L-methionine, L-phenylalanine, L-tryptophan, and L-tyrosine have been investigated.

By establishing a protocol to systematically compare and optimize their performance, several new efficient bioreductants of graphene oxide have been identified, namely, pyridoxine and pyridoxamine (vitamin B6), riboflavin (vitamin B2), as well as the amino acids arginine, histidine and tryptophan. Indeed, as clearly seen in Fig. 1a, treatment of graphene oxide with any of these bioreductants prompted a significant decrease in the relative contribution of oxygen-bonded carbon to the XPS C1s signal, especially of carbon single-bonded to oxygen, which possesses a binding energy (BE) of 286.6 eV. The reduced sheets did not agglomerate and were kept as individual single-layer objects in their corresponding dispersions, even several months after the reduction treatment was carried out. Fig. 1b illustrates this point with some representative AFM images obtained from dispersions reduced with glutathione (b) and pyridoxamine (c). The reduced sheets are constituted by irregular (polygonal) objects a few to several hundred nm in lateral size and ~1 nm of apparent thickness, which indicates that they indeed correspond to single-layer sheets [2].

The aforementioned biomolecules were also successfully used to prepare reduced graphene oxide-silver nanoparticle hybrids (RGO-Ag NPs) by the simultaneous reduction of graphene oxide and Ag(I) (in the form of AgNO3). The grayish tinge of diluted RGO dispersions (inset to Fig. 2a, right cuvette) was replaced by a yellowish tone when graphene oxide and AgNO3 were co-reduced (inset to Fig. 2a, left cuvette). UV-vis absorption spectra revealed the appearance of a feature at ~420 nm for the latter (Fig. 2a), due to the surface plasmon resonance band characteristic of metallic Ag nanostructures [3]. The RGO sheets were decorated with either white (AFM, Fig. 2b) or black (bright-field STEM, Fig. 2c) dots, which were never observed for RGO sheets obtained in the absence of AgNO3 (AFM, Fig. 1b and c), and were therefore attributed to the Ag NPs. These were exclusively associated to the sheets, without stand-alone nanoparticles being generated (Fig. 2b and c). From the AFM images, the density of Ag NPs on the RGO sheets was estimated to be typically between a few and several μm².

The hybrids prepared with pyridoxamine exhibited a combination of long-term colloidal stability and exceptionally high catalytic activity among silver nanoparticle-based catalysts in the reduction of p-nitrophenol with NaBH₄ (see Fig. 3 for results on the reaction kinetics). Thus, in addition to expanding substantially the number of green reductants available for the deoxygenation of graphene oxide, the present results underline the idea that a proper selection of bioreductant can be relevant to achieve graphene-based materials with improved performance.

References
Figures

**Figure 1.** (a) Normalized, high resolution XPS C1s core level spectra for unreduced graphene oxide (orange) and graphene oxide reduced with pyridoxamine (red), B₃ (fluorescent green), B₂ salt (yellow), arginine (blue), glutathione (pink), histidine (black), tryptophan (olive green) and glucose (wine). (b) AFM images of graphene oxide sheets reduced with (b) glutathione, and (c) pyridoxamine.

**Figure 2.** (a) UV-vis absorption spectra and digital picture (inset) of a graphene oxide dispersion reduced with histidine in the absence (black curve and inset right) and presence (green curve and inset left) of AgNO₃. (b) AFM image of RGO-Ag NP hybrid prepared with pyridoxamine (1 mM). (c) STEM image of RGO-Ag NP hybrid prepared with arginine (1 mM).

**Figure 3.** (a) UV-vis absorption spectra of p-nitrophenoxide ion (dark yellow), and p-aminophenoxide ion (violet). The absorption peak at 400 nm of p-nitrophenoxide is used to monitor its conversion to p-aminophenoxide by reduction with NaBH₄. (b) Plot of absorbance at 400 nm for the reduction of p-nitrophenoxide with NaBH₄ catalysed with RGO-Ag NP hybrid prepared with pyridoxamine (black squares) and with stand-alone, citrate-capped Ag NPs prepared by NaBH₄ reduction of AgNO₃ following standard procedures (green squares). The experimental kinetic profiles could be well fitted to exponential decay functions, which are shown as overlaid red and orange lines, respectively. Experimental conditions: [p-nitrophenol] = 0.06 mM; [NaBH₄] = 0.018 M; [Ag NP] ~0.2 mg mL⁻¹.