Mechanistic insight on the rational modulation of size/shape of nanocomposites of Ag nanoparticles and functionalized graphene nanoribbons

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Introduction

Functionalized carbon-based nanomaterials are a promising tool when modulating size/shape of nanoparticles (NPs), which is essential to control their properties and project applications. In this sense, we highlight graphene nanoribbons (GNR), a material that stands out due to its high reactivity and dangling bonds at the edges, being suitable for anchoring chemical compounds. Targeting this, the aim of this work is the synthesis of nanocomposites of Ag-NPs and functionalized GNR derivatives, and their characterization with X-ray photoelectron (XPS) and Raman spectroscopy, thermogravimetric analysis (TGA), X-ray diffraction (XRD) and scanning (SEM) and transmission electron microscopy (TEM).

Results and discussion

The experimental procedure is summarized as: GNR obtained through the aerosol assisted chemical vapor deposition method;¹ then oxidized, obtaining GONR; and functionalized on its carboxylate sites with cysteamine² (obtaining GONRSH); lastly the precursors (GNR, GONR and GONRSH) and AgNO³ were simultaneously reduced with NaBH⁴ obtaining the respectively nanocomposites: rGNRAg, rGONRAg and rGONRSHAg. Functionalization of GNR was confirmed by XPS and TGA analysis, indicating respectively: (i) the increase in O/C atom ratio for GONR and the presence of amodic bonds and free thiol groups on GONRSH surface;² and (ii) characteristic mass losses of the functional groups present in the precursors.² Besides, XRD diffractograms revealed a new 3D organization for GONRSH and confirmed the presence of Ag-NPs in the nanocomposites. TEM and SEM supported the latest results, exhibiting smaller distributed spherical NPs on rGONRAg than on rGNRAg, possibly due to the potential stabilizing oxygenated groups, evidencing a size control feature. Surprisingly, multiple GONRSH ribbons are overlaid and organized in a cube/retangular matter with thiol moieties preferentially concentrated on the borders, where NPs may favorably be passivated, self-organizing in order to fully cover the cubic-shaped precursor (Figure 1). Thus, by varying the experimental conditions we proposed a mechanistic scenario explaining for the first time the formation of these fascinating cubes. In fact, we have followed various stages of the cube growth by SEM analysis. Moreover, TEM in dark-field mode evidenced that the growth of Ag-NPs happens through an oriented mechanism induced by the thiol groups on the edges, in which the adjacent NPs keep the crystallographic orientation.

Conclusions

Results confirmed the synthesis of nanocomposites with size and shape-controlled features. Besides, the growth mechanism of the cubic-like structures was presented along with a concise model. This elucidation is a powerful tool for projecting optimized nanocomposites with specific applications.

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² Orth, E.S. et al. Carbon. 2013, 61, 543.