

Functionalized graphene-based thin films as tailored nanocatalysts and SERS substrate

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Abstract

Thin films of thiolated graphene oxide have been synthesized through interfacial method and applied in different applications.

Introduction

Graphene oxide (GO) surfaces are highly covered with oxygenated groups that may be targeting sites to carry out covalent functionalization, furnishing materials with synergistic effects and modulated properties. Besides, chemically modified GO could provide free groups to act as catalytic sites or metallic nanoparticles (NPs) passivation. In this sense, the aims of this work are to (i) functionalize carboxylate sites of GO with cysteamine (CA) by amide bonds, obtaining thin films through interfacial method,^[1] (ii) characterize with UV-Vis, infrared (FTIR) and Raman spectroscopy, X-ray diffraction (DRX) and scanning electron microscopy (SEM) and (iii) apply as nanocatalysts in the degradation of organophosphorus compounds and as SERS substrate.

Results and discussion

Figure 1 summarizes the experimental procedure: (i) GOSH1 was obtained with the formation of a GO film in the toluene/water interface followed by its reaction with CA^[2] and (ii) GOSH2 by hanging the deposited GO film in a sealed vessel containing CA. In the following, applications were carried out in the same vessel: GOSH1 and GOSH2 were evaluated as nanocatalysts through their immersion in the reaction medium and Ag⁺ cations were reduced in the presence of GOSH2, resulting in rGOSH2Ag nanocomposite applied as SERS substrate.

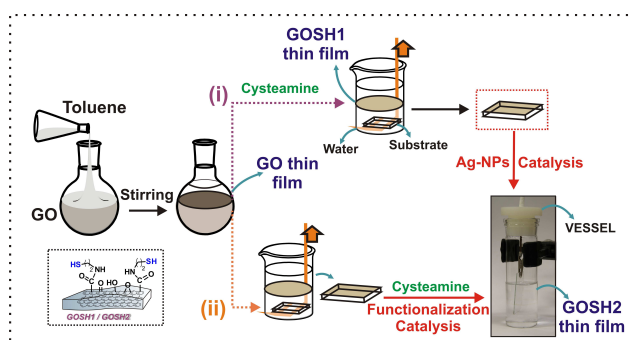


Figura 1. Scheme of the experimental procedure.

Functionalization of GO was confirmed by FTIR spectra, which evidenced bands at 3290 cm⁻¹ and 1542 cm⁻¹, assigned to N-H stretching; 1642 cm⁻¹ and 1737 cm⁻¹, related to C=O of amide and carboxylic acid, respectively.^[2] Besides, the band at 1737 cm⁻¹ was absent in GOSH1 spectrum, indicating an overall functionalized nature. Raman spectra showed the typical bands of carbonaceous materials and XRD diffractograms revealed a new 3D organization, as previously described.^[2] After characterization, the films were evaluated as nanocatalysts in heterogeneous dephosphorylation reactions, using diethyl 2,4-dinitrophenyl phosphate as a model, by following the appearance of the product by UV-Vis. Comparing with the spontaneous reaction, rate enhancements of 10⁶-fold ($k_{\text{nanocatalyst}}/k_{\text{H}_2\text{O}}$) were found. Moreover, nanocatalysts were consecutively recycled without losing activity and characterization by FTIR and Raman confirmed the preservation of overall properties. Also, we highlight the impressive rate enhancement of 10⁷-fold with the toxic pesticide Paraoxon when degraded by GOSH2, among the highest increments reported. Thus, these catalysts may be promising in the detoxification of organophosphorus chemical warfare and pesticides. Furthermore, the rGOSH2Ag nanocomposite was an effective SERS substrate for 4-ATP (10⁻³ M) detection.

Conclusions

GOSH thin films were obtained through the interfacial method, not reported for this synthesis before. The resulting materials presented high catalytic reactivity against dephosphorylation reactions, with the advantage of easy cleaning and handling. Besides, the derived nanocomposite was an efficient SERS substrate in the detection of 4-ATP.

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