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A rapid and eco-friendly route to synthesize graphene-doped silica nanohybrids

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ABSTRACT

In the present study, the possibility to synthesize graphene oxide (GO)-based nanohybrids with pure and O_2-doped silica nanoparticles by a rapid and easy hydrothermal process has been explored. The nanohybrids were prepared by varying the type of silica nanoparticles (average diameter 7 nm or 40 nm) and the silica/GO weight ratio. All the materials were fully characterized by spectroscopic and morphological techniques.

The experimental results revealed that it is possible to tune the characteristics of the obtained nanohybrids, such as morphology and amount of ester/ether linkages upon varying the preparation parameters, together with the nanosilica's typology and the silica to GO ratio. By Fischer esterification it was possible to achieve GO-silica nanohybrid lamellae to be then reduced into nanostructured films by a hydrothermal process. These latter materials show a "lasagna-like" structure in which it is possible to observe fully exfoliated (and partially reduced) GO lamellae intercalated by silica nanoparticles agglomerates. The extension of silica layers, film morphology and structure, degree of functionalization, and thermal stability are strongly affected by the type of silica. Furthermore, after the hydrothermal treatment, the nanohybrids were found to be insoluble in water.

1. Introduction

The increasing interest in carbon based nanostructured materials like graphene [1–3], graphene oxide [4–6] and carbon nanotubes is related to their potential applications in many fields of materials science, medicine and environment [7–11].

Among the above materials, graphene, a flat monolayer of sp^2-bonded carbon atoms, is very promising due to its unique characteristics such as high electronic conductivity, large specific surface area, and high mechanical strength [1–3]. However, the poor dispersion of graphene in the most common solvents limits the preparation of nanohybrid materials, another task of particular concern. A possible way to overcome this problem is the use of a precursor of graphene: the Graphene Oxide (GO). GO honeycomb lattice is composed of two equivalent sub-lattices of carbon atoms bonded together with σ bonds and containing oxygen related moieties [12]. The presence of both sp^2-conjugated atoms and oxygen-containing functional groups provides to GO a strong hydrophilicity and the possibility to further functionalize it with other molecules (i.e. π− π interactions, covalent attachment, etc.) and to reduce it during or after processing through chemical or thermal reduction [13], evidencing interesting functionalization and tunable physical and chemical properties [14]. Furthermore, since the GO is biocompatible and noncytotoxic, many studies have been recently focused on the development of GO-based nanodevices for bioimaging, DNA detection, drug delivery [17–21]. On the other

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side, due to their low cytotoxicity and large specific surface, silica nanoparticles have been taken into account as promising material for biolabeling and drug loading/delivery [15]. In this context, silica nanoparticles opportunely functionalized show interesting emission properties in the Near Infrared spectral range (about 1.3 μm) arising from the presence of interstitial molecular oxygen [16]. This aspect is relevant for labeling applications and also interesting in perspective, considering the paramagnetic character of O_2. Particular consideration has recently been demonstrated for GO-silica composites because of the potentialities for electrical applications, their chemical inertia and stability toward ions exposure [17–20]. The possibility to combine the extraordinary properties of GO and silica offers several advantages for the realization of nanoprobes for biological applications and for biosensor too [21]. Many studies tackled this task but principally by using full chemical procedures involving silica preparation through sol–gel technique and GO by synthesis methods. This route has the limitation to hinder the functionalization of the silica component because of the need to grow the raw material itself.

Aim of the present work is the rapid and easy preparation of GO-silica nanocomposites starting from commercial silica nanoparticles, also opportunely functionalized, and laboratory synthesized GO, a tactic that could find application in diverse fields and could enable to obtain composites with functionalized silica.

The strategy for the fabrication of GO-nanosilica sandwich films, illustrated in Fig. 1, can be schematized as follows:

(i) synthesis of GO by oxidizing graphite powder through a modified Hummer method.
(ii) preparation of O_2 loaded silica nanoparticles of average diameter 40 or 7 nm [22].
(iii) Covalent immobilization of O_2 loaded silica nanoparticles onto GO lamellae via rapid esterification without using silica precursors, such as TEOS, etc.
(iv) hydrothermal stratification at 120 °C to produce water-resistant composites with enhanced thermal stability.

The process is ecofriendly and rapid, as the steps (iii) and (iv) require less than 1 h.

To the best of our knowledge, the easiest method to prepare GO-silica nanohybrids via direct esterification in water requires 24 h under high pressure [23], the method here proposed allows instead to obtain nanohybrids in less than 1 h.

2. Experimental details

2.1. Materials

Neat graphite (grade Ma 399, 45 μm) was purchased by NGS Naturgraphit (Germany). Two samples of fumed silica nanoparticles, namely AEOX50 and AE300 (Aerosil® OX50 and Aerosil300), which properties are summarized in Table 1 [24], were provided by Evonik Industries (Germany). Finally, H_3PO_4, H_2SO_4, $KMnO_4$, HCl, H_2O_2, C_2H_5OH and diethyl-ether were purchased by Sigma Aldrich. All the reactants were used as received without any further purification.

2.2. Synthesis of GO

The GO was synthesized via chemical oxidation and exfoliation of natural graphite, according to our previous work [7], by slightly modifying the method illustrated by Marcano et al. [25]. Several parameters, such as reaction time, solid reactant to liquid solvent ratio (S/L) and stirring speed (i.e. melt viscosity) and concentration of HCl during the purification step, were changed in order to maximize the content in –OH and –COOH. Finally, the sample prepared according to the operative set listed in Table 2 was selected for the silica-functionalization. More in details for GO preparation, a solid mixture of neat graphite flakes (5 g, 1 wt equiv) and $KMnO_4$ (30 g, 6 wt equiv) was added to a 9:1 mixture of concentrated H_2SO_4/H_3PO_4, which volume was 600 mL (540:60 mL) and stirred at 64 rpm. The reaction was heated to 50 °C and the temperature was kept constant in order to avoid the

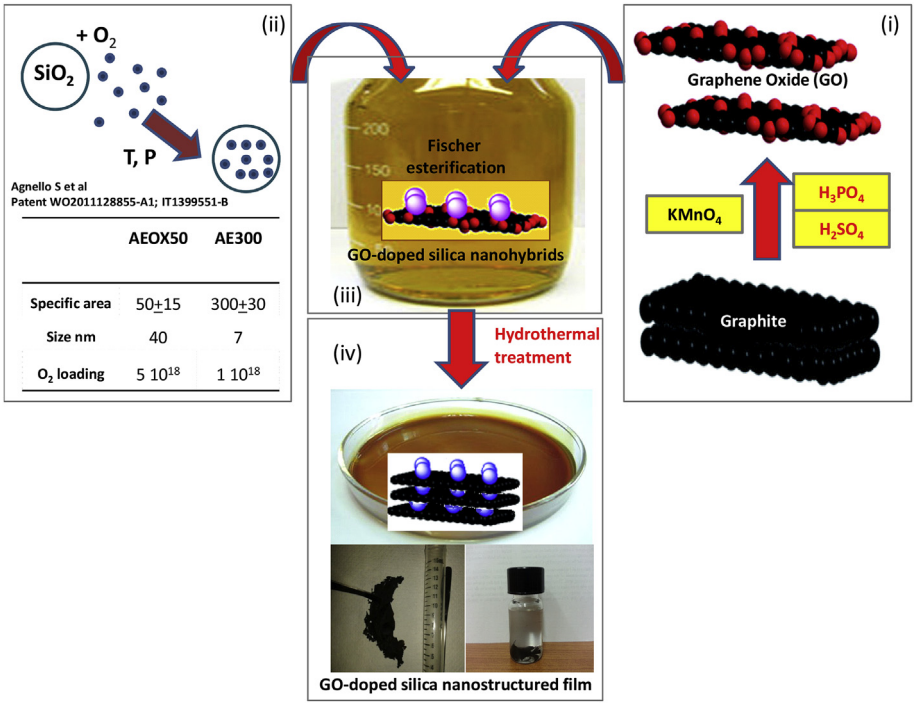

Fig. 1. Schematics of the route for the preparation of GO-silica bulky films.