

NEW POROUS ORGANO-HETEROSTRUCTURES BASED ON ORGANO-MODIFIED GRAPHENE-OXIDE

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ABSTRACT

In this work, highly porous heterostructures with tailored properties were produced, through the silylation of organically modified graphene oxide (GO). Three different organo-silica precursors with various structural characteristics (rendering alkyl or phenyl groups) were employed to create high-yield silica networks as pillars between the organo-modified GO layers. Phenyl group bridged samples showed the maximum amount of silica content in the final heterostructure. Subsequent pyrolysis created porous structures, with surface areas of up to 550 m²/g, which are very attractive for potential CO₂ adsorption applications. The porous heterostructure that showed the maximum surface area was chosen for investigating its CO₂ adsorption properties.

INTRODUCTION

Graphene Oxide (GO), a layered structure produced by the oxidation of graphite, has been identified as an excellent host matrix for the accommodation of molecular structures for the fabrication of hybrid materials for energy ^[1] environmental ^[2] and sorption ^[3] applications. Many studies have been published regarding the pillaring of graphene-based materials originated from the incorporation of different silicon sources mainly by the sol-gel method. Matsuo's group has studied the synthesis of pillared GO with various silylating reagents such as 3-aminopropylethoxysilanes or alkyl trichlorosilane with various alkyl lengths ^[4,5]. A pyrolysis step is essential for these materials in order to obtain large surface areas and controlled pores. Matsuo et al. have shown that the BET surface area of porous graphene heterostructures can be increased up to 756 m²/g after intercalation of graphene with two different organosilanes in a two-step process ^[6]. In a similar work, the repeated silylation process of graphene oxide by trichlorosilane has been proven to affect the density of the siliceous pillars, varying the BET surface area between 77 and 723 m²/g ^[7].

AIM AND METHODOLOGY

In this work, highly porous heterostructures with tailored properties were produced, through the silylation of organically modified GO. They can be obtained with only one silylation step, i.e. through a much faster method than previous reported in the literature ^[6] Three silica precursors with various structural characteristics (rendering alkyl or phenyl groups) were employed to create high-yield silica networks as pillars between the organo-modified graphene oxide layers. The removal of organic molecules through thermal decomposition generates porous heterostructures with high surface areas in the order of > 500 m²/g, which are very attractive for potential use in applications such as catalysis, absorption and as fillers in mixed matrix polymer nanocomposite membranes. The final hybrid products were characterized by X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), ThermoGravimetric Analysis (TGA) and nitrogen porosimetry measurements. The porous heterostructure with the maximum surface area was chosen for investigating its CO₂ absorption properties.

EXPERIMENTAL

Materials

Graphite (powder ≤ 0.2 mm), Nitric acid (65% HNO₃) and Potassium chlorate (KClO₃, 98+%) were obtained from Fluka incorporation. Dodecylamine (DDA), 1,4-bis(triethoxysilyl)-benzene (BTB 99%), tetraethylorthosilicate (TEOS 98+%) and (3-aminopropyl)triethoxysilane (APTEOS $\geq 98\%$), sulfuric acid (H₂SO₄, 95–97%) and n-butanol were acquired from Aldrich and used as received.

Graphene Oxide

Graphene oxide, denoted as **GO** in the following, was synthesized using a modified Staudenmaier's method [8]. In a typical synthesis, 10 g of powdered graphite was added to a mixture of 400 mL of 95–97 % H₂SO₄ and 200 mL of 65 % HNO₃, while cooling in an ice–water bath. 200 g of powdered KClO₃ was added to the mixture in small portions under continuous stirring and cooling. The reaction was quenched after 18 h by pouring the mixture into distilled water and the oxidation product was washed until the pH reached 6.0, and finally air dried by being spread on a glass-plate.

Organo-modified graphene oxide

Dodecylamine in ethanol solution was added slowly to an aqueous **GO** suspension under vigorous stirring. The mixture was stirred for 24 h, centrifuged, washed three times with ethanol/ water: 1/1, and air-dried by being spread on a glass-plate. The organo-modified **GO** is denoted as **org-GO**.

Silica-GO heterostructures

Before silylation, **GO** was dried a second time under vacuum at room temperature overnight. **Org-GO** were dispersed in n-butanol, sonicated for 30 minutes and left under stirring overnight. The organo-silica precursor (APTEOS, BTB or TEOS) was slowly added into the **org-GO** dispersion under stirring for 2 hours before adding the water (containing a drop of hydrochloric acid) keeping constant the molar ratio Si source / H₂O / n-butanol: 1/4/54. The sol-gel reactions were performed at 50 °C while stirring, and the obtained gel was placed in the oven at 50 °C overnight (the silica-GO organo-heterostructures are denoted as **GO-BTB**, **GO-APTEOS** and **GO-TEOS** for the three organosilica precursors respectively). The final porous structures were collected after calcination in air at 370 °C for 120 min. The calcinated samples are denoted as **G-BTB**, **G-APTEOS**, and **G-TEOS**.

RESULTS AND DISCUSSION

The XRD patterns of the initial materials and of the final hybrids after the sol-gel modification are shown in **Figure 1a**. The XRD pattern of pristine graphite shows the characteristic peak corresponding to the 002 reflection of graphite at 26.6°, with a basal spacing of 3.3 Å. This peak disappeared after the oxidation process, when the 001 reflection peak is found at 12.0°, corresponding to a basal spacing of 7.4 Å, characteristic of layered **GO** [9]. After the intercalation of **GO** with dodecylamine, the 001 reflection moved to even lower angles, resulting to an increase of the d_{001} spacing of **GO** and hence to the successful insertion of the guest molecules in the interlayer space. More specifically, the basal spacing d_{001} of the **org-GO** shifts to 18.4 Å corresponding to an interlayer separation of $\Delta = 18.4 - 6.1 = 12.3$ Å, where 6.1 Å is the thickness of the GO monolayer [10]. Through the organo-modification, the interlayer space of the **GO** becomes more accessible and ready to be modified with the silica precursors.

After the sol-gel reaction with silica alkoxides, the 001 reflection of the final hybrid materials is shifted to lower angles than for **org-GO**, confirming the successful expansion of the interlayer space and indicating the formation of a silica network for each precursor. When **org-GO** was treated with the silica precursor TEOS (**GO-TEOS**), the d spacing was calculated to be ~ 24.5 Å while even higher d values (26–27 Å) were achieved for APTEOS and BTB silica precursors. These higher values may be attributed to steric effects from the amino-terminated alkyl chains or phenylene ring anchored/bridged by silane centers of APTEOS and BTB, respectively.

Figure 1b displays the XRD patterns of the silica-GO heterostructures obtained after calcination of G-TEOS, G-APTEOS and G-BTB at 370 °C. For all hybrid heterostructures, there is a loss of the 001 reflection at low angles (2-10°), which confirms that the graphene layers have lost their ability to stack and shows that the silica-GO heterostructures are exfoliated due to the violent reduction of graphene oxide upon heating^[11].

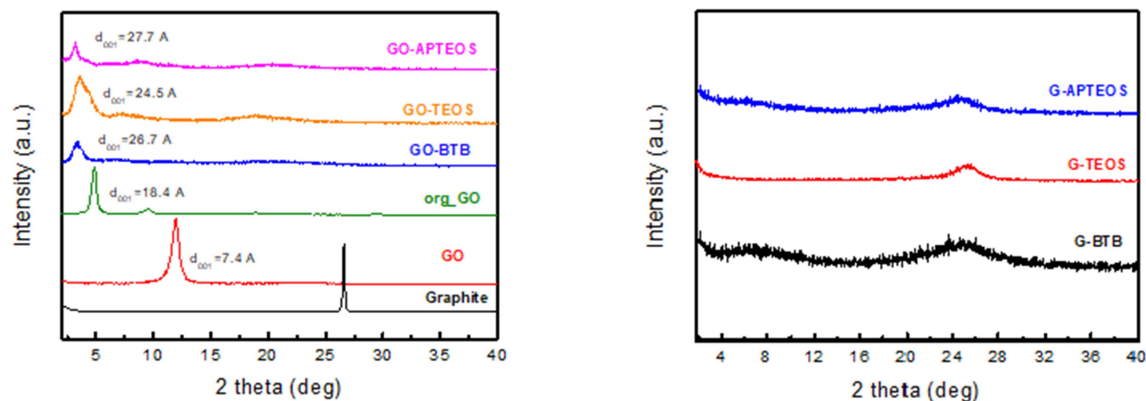


Figure 1. a. XRD patterns of pristine clay, organo-modified clay, and heterostructures prepared by silylation with the different organosilane precursors, TEOS, APTEOS and BTB. **b.** XRD patterns of GO heterostructures obtained after calcination of GO-APTEOS, GO-TEOS and GO-BTB at 370 °C to yield G-APTEOS, G-TEOS and G-BTB.

Figure 2 compares the FTIR spectra of GO-BTB before and after (G-BTB) the calcination treatment with those of graphite, pristine (GO) and organo-modified graphene oxide (org-GO). The spectrum of org-GO shows two additional bands at 2847 cm⁻¹ and 2919 cm⁻¹ associated with the asymmetric and symmetric stretching vibrations of CH₂ groups as well as a band at 1450 cm⁻¹ due to the vibrations of the N-H bond of the amino group molecule and a band at 1462 cm⁻¹ attributed to C-N vibrations. These signatures clearly indicate the presence of dodecylamine in org-GO and subsequently the success of the organo-modification.

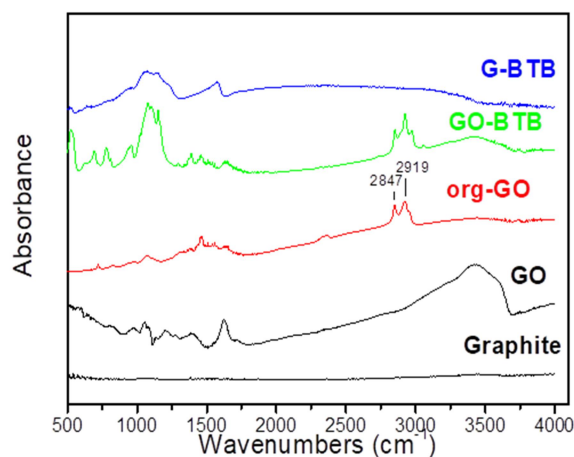


Figure 2. FTIR spectra of GO-BTB heterostructure before and after (G-BTB) calcination; the spectra of graphite, pristine graphene oxide (GO) and organo-modified graphene oxide (org-GO) are plotted for comparison.

The spectrum of the heterostructure obtained by reaction with the silica precursor BTB, exhibit a set of new peaks before (GO-BTB) and after calcination (G-BTB), which can be attributed to vibrations of the silicate matrix: the peaks at 520 cm⁻¹ and 1065 cm⁻¹, are due to Si-O-Si stretching

vibrations of Si-O-Si, while the one at 950 cm^{-1} are assigned to the stretching vibrations of Si-OH^[12]. Similar results were also found on the other spectra confirming the presence of silica networks in all three heterostructures before and after calcination. For the BTB precursor, two new peaks at 1396 and 3059 cm^{-1} corresponding to the vibrations of the double bond C=C and C-H of the phenyl rings appear in the GO-BTB spectrum. The characteristic bands of the intercalated dodecylamine identified in the spectrum of org-GO (2847 , 2919 and 1483 cm^{-1}) are absent from the spectrum of G-BTB, pointing to the successful removal of the surfactant molecules and therefore the development of porous silica-GO heterostructures after the calcination.

Figure 3 presents the TGA of all three heterostructures. Initially, the small weight loss up to about $250\text{ }^\circ\text{C}$ is due to the removal of the hydroxy, epoxy and carboxyl groups, plus the of adsorbed water. Increasing the temperature up to $450\text{ }^\circ\text{C}$, the combustion of dodecylamine molecules takes place^[13], while between 500 - $700\text{ }^\circ\text{C}$ the loss mass is attributed to the combustion of the graphene layers^[14,15] as well as the dehydroxylation of the developed silica network^[16]. In the case of GO-BTB, in the temperature range between 500 to $650\text{ }^\circ\text{C}$, the combustion of phenylene groups from the silica precursor occurs^[12], contributing to the mass loss. The residual mass, 8 % for GO-TEOS, 30 % for GO-APTEOS and 40 % for GO-BTB, corresponds to silicon oxide. These percentages can be explained by the chemical structure of each silica precursor. In the case of APTEOS and BTB alkoxides, the amino-terminated alkyl chain is covalently bonded to GO, while the phenylene group bridged to silane centers interact via π - π with the graphene oxide layers. Thus, a larger amount of silica precursor has been activated/reacted to give GO-APTEOS and GO-BTB than in the treatment with TEOS, which does not have any functional group favouring bonding.

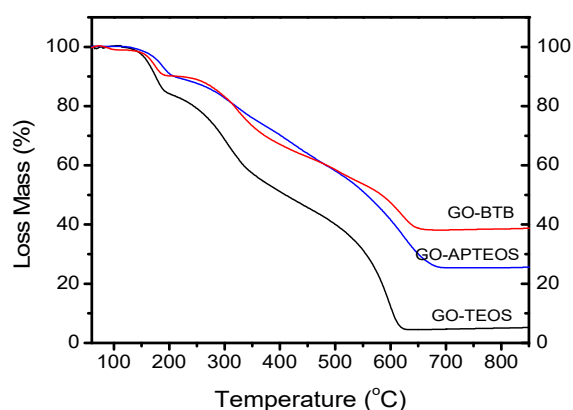


Figure 3. TGA curves of heterostructures prepared by silylation of organo-modified graphene oxide with 1,4-Bis(triethoxysilyl)-benzene (GO-BTB), with (3-aminopropyl)triethoxysilane (GO-APTEOS) and with tetraethylorthosilicate (GO-TEOS).

Figure 4 shows the isotherms of the heterostructures after calcination (G-BTB, G-APTEOS and G-TEOS), recorded during N_2 adsorption and desorption at 77 K . The isotherms are characterized by an H4 hysteresis loop (based on IUPAC classification), while their shape is pointing out slit-shaped pores. At low relative pressures ($P/P_0 < 0.01$), the G-BTB heterostructure shows the highest N_2 adsorption, which indicates that a significant amount of micropores is accessible after the creation of the silica network. For this system the maximum BET surface area was calculated to be $576\text{ m}^2/\text{g}$, which is more than twice that of G-APTEOS ($227\text{ m}^2/\text{g}$) and more than 20 times that of G-TEOS ($27\text{ m}^2/\text{g}$). Note that for all three heterostructures the final increase of the N_2 uptake at relative pressures above 0.95 is attributed to adsorption on the external surface and/or the surface of macropores. Further thermal treatment at $900\text{ }^\circ\text{C}$ induces the collapse of heterostructures showing a non-porous behavior and pointing out the vital role of graphene layers to the final hybrid material.

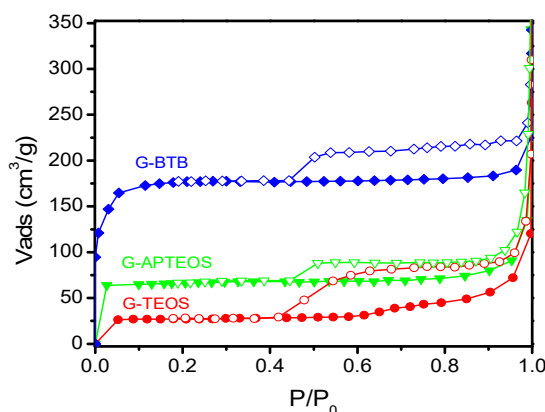


Figure 4. *N₂* adsorption (full symbols)-desorption (empty symbols) isotherms at 77 K of heterostructures prepared by silylation of organo-modified graphene oxide with either 1,4-Bis(triethoxysilyl)-benzene, or with (3-aminopropyl)triethoxysilane, or with tetraethylorthosilicate, followed by calcination, to give G-BTB, G-APTEOS and G-TEOS.

CO₂ adsorption

Emission of CO₂ from industrial and power plants remains nowadays a major threat for global warming. To this end, graphene-based materials hold an important position as they combine a series of significant advantages such as excellent physicochemical properties, high specific surface areas, low energy adsorption, high selectivity and light weight ^[17]. We therefore chose CO₂ adsorption on G-BTB as proof-of-principle example to testify to the potential applications of our porous graphene-based heterostructures. The CO₂ adsorption behavior of G-BTB was studied at 0°C and for pressure up to 20 bars (**Figure 5**). An adsorption capacity of 2.8 mmol/g at 5 bar and 0°C and of 3.5 mmol/gr at 17 bar and 0°C was recorded. Such high values agree with the high BET surface area and the presence of microporosity. Therefore, G-BTB appears to be a very interesting candidate as CO₂ storage material, which combines the properties of graphene with the very high porosity of silica resulting from the sol-gel procedure.

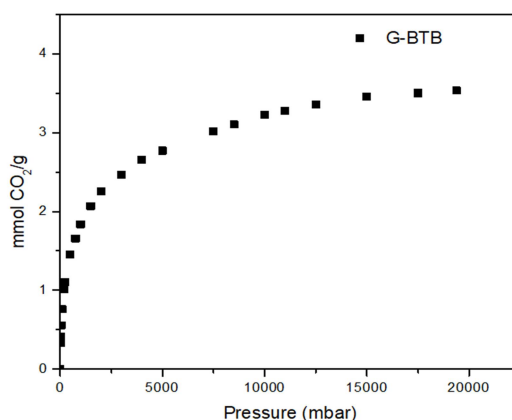


Figure 5. CO₂ adsorption at 0°C on the heterostructure prepared by silylation of organo-modified graphene oxide with either 1,4-Bis(triethoxysilyl)-benzene, after calcination to give G-BTB

CONCLUSIONS

Porous heterostructures based on graphene were produced combining organo-modified graphene oxide and three different organo-silica precursors through sol-gel reactions. After one-step silylation, the interlayer space increased for all the heterostructures compared to organo-modified GO and was maximum for BTB due to steric effects. FTIR spectroscopy gave evidence for the reduction of graphene oxide to graphene after calcination of the heterostructures. The thermogravimetric analysis showed that BTB (with the bridged phenyle group) as silica precursor,

gave the highest degree of silylation. Thermal treatment was essential in order to obtain highly porous materials with sponge-like structures, characterized by BET surface area of 550 m²/g in the case of G-BTB. The latter heterostructure was found to have a high CO₂ adsorption capacity of 2.8 mmol/g at 5 bar and 0°C, which is promising for further consideration as CO₂ storage material.

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