

Supplementary Information for Manuscript

# Incorporation of Graphene into Silica-based Aerogels and Application for Water Remediation

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## Content Outline

S1. Role of Synthetic Parameters

S2. Details on Raman Analysis

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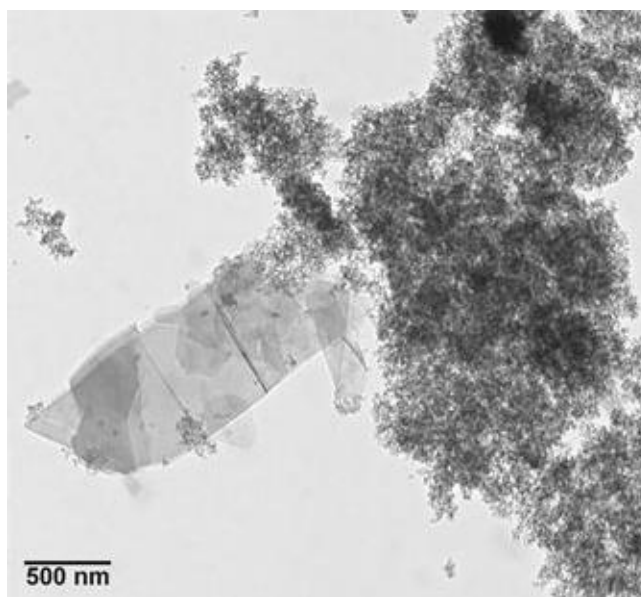
S4. Hydrophobic Stability and Reusability after Burning of the Graphene/Silica Aerogel Nanocomposites

## **S1. Role of Synthetic Parameters**

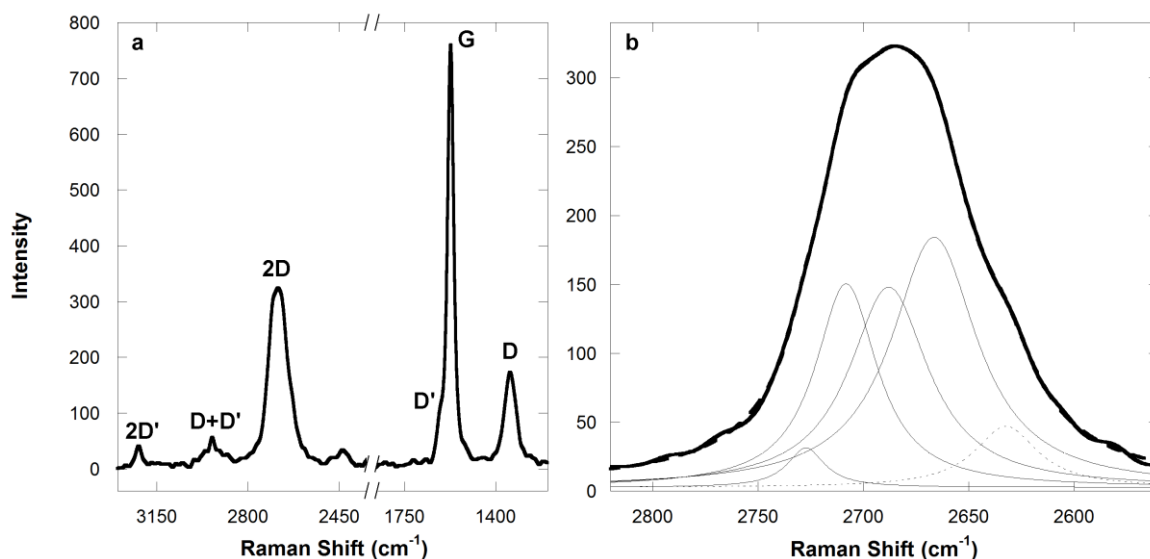
The preparation of a homogeneous nanocomposite aerogel relies on accurate control over several sol-gel parameters. In particular, we found that among all the available dispersions of graphene, the most suitable is the one based on DMF, which ensures at the same time effective dispersibility of graphene sheets, good miscibility with the ethanolic silica sol, and relative stability under the supercritical drying conditions.

When the nanocomposite synthesis is performed by using a DMF dispersion of graphene and a TEOS

ethanolic sol under acid-base catalysis, as described in the experimental section, an homogeneous graphene/silica composite aerogel is obtained where both the properties of graphene and porous silica are retained (see Figures S1, S2). The aerogel obtained by this procedure, however, is hydrophilic.



**Figure S1.** TEM image of hydrophilic graphene/silica aerogel nanocomposite.



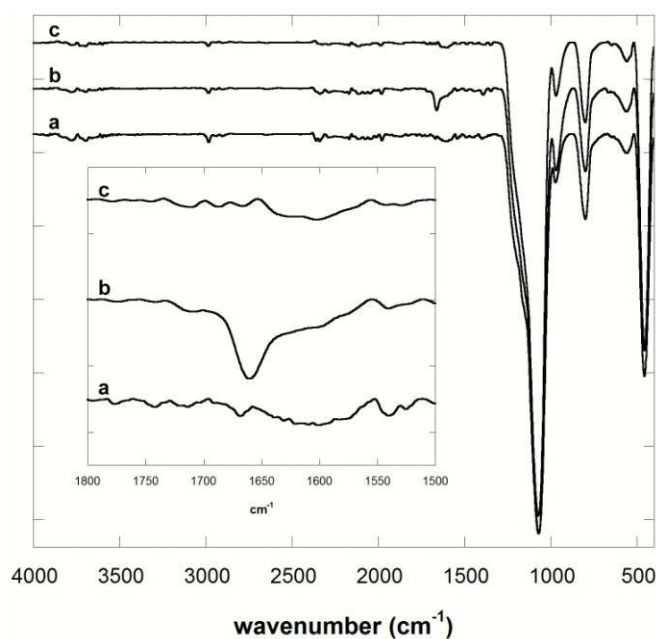
**Figure S2.** Raman spectrum of the hydrophilic graphene/SiO<sub>2</sub> aerogel nanocomposite (a) and detail of the 2820-2560 cm<sup>-1</sup> range (b): bold curve is the acquired Raman spectrum, bold dotted line describes the fitting obtained by combining the Lorentzian curves (thin line), and thin dotted lines are the fitted band of the silicon signal.

In order to render the aerogel hydrophobic, the addition of LiBH<sub>4</sub> as a reducing agent to the sol is required, and therefore this procedure was adopted to prepare the hydrophobic aerogels used for oil adsorption experiments.

We ascribe the hydrophilic behaviour of the aerogel obtained in the presence of DMF as due to surface modification of the silanols through hydrophylic carbonyl-based groups. Such groups can be reduced through the use of LiBH<sub>4</sub>, rendering the aerogel hydrophobic, as desired.

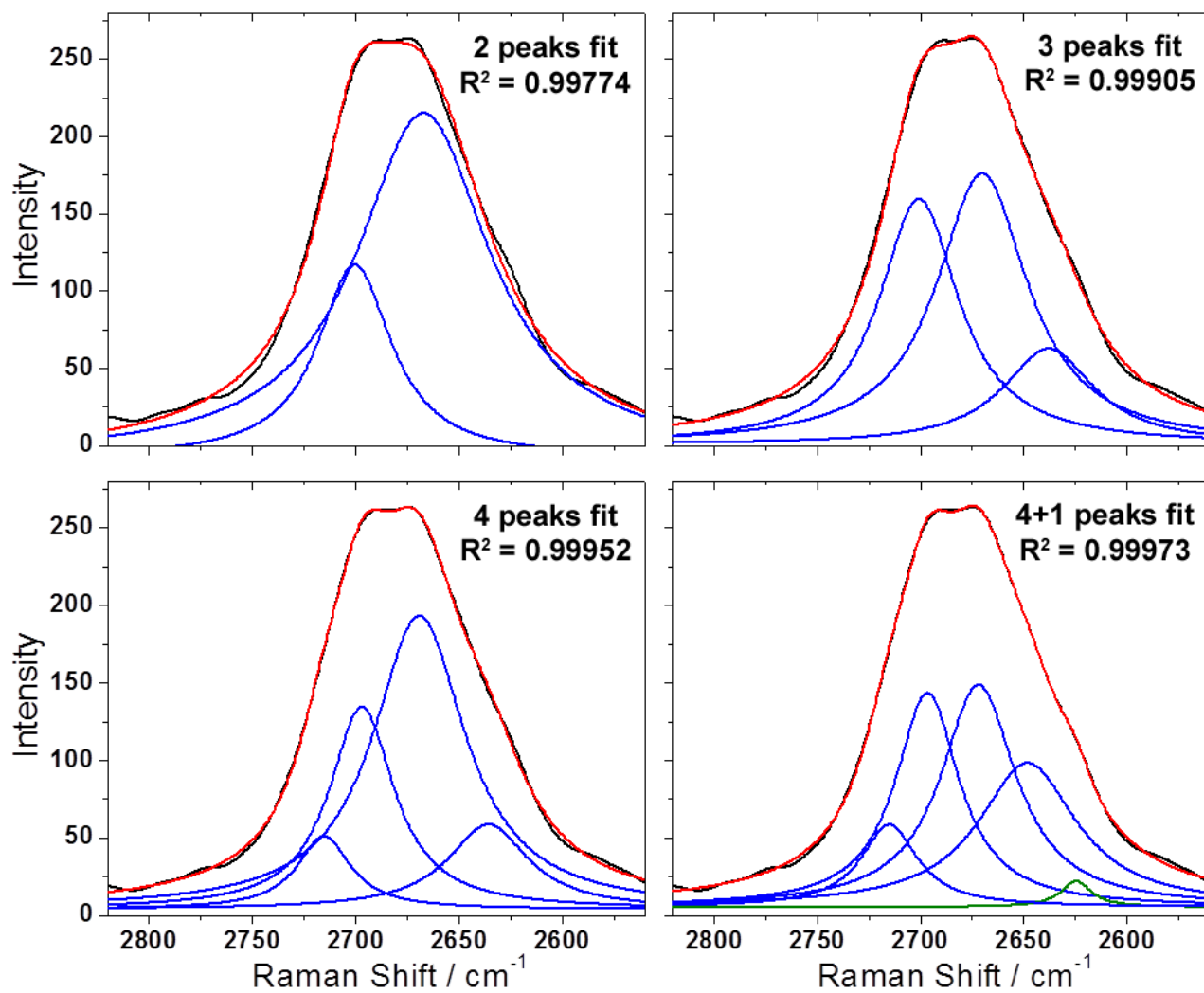
To support this view we have collected Mid-IR spectra (400-4000 cm<sup>-1</sup>) on the composite aerogels with the same composition (0.1 wt% graphene) but obtained with and without the use of LiBH<sub>4</sub> (see Figure S3, curves a and b respectively). All the spectra show the typical vibrations of sol-gel silica, such as O-Si-O bending (~ 450 cm<sup>-1</sup>), Si-O-Si bending (~ 560 cm<sup>-1</sup>), Si-O-Si stretching (~ 790 cm<sup>-1</sup>), Si-OH stretching (~ 960 cm<sup>-1</sup>) and Si-O-Si stretching (~ 1070 cm<sup>-1</sup>). The hydrophobic composite aerogel also shows the

occurrence of weak bands around  $2980\text{ cm}^{-1}$  due to the aliphatic C-H stretching of Si-OEt groups formed during the supercritical drying in the reaction between the Si-OH groups and ethanol in the autoclave while the amount of free silanols is negligible.<sup>S1</sup> On the other hand, in the hydrophilic composite aerogel (which was prepared without adding  $\text{LiBH}_4$ ) no evidence of aliphatic vibrations is observed, while the presence of the typical C=O band at  $\sim 1650\text{ cm}^{-1}$ , which does not occur in the hydrophobic aerogel, is observed.<sup>S2</sup> These data indicate that the use of DMF induces surface modification of silica through carbonyl groups which result in a hydrophilic behaviour, whereas reduction of the carbonyls through a borohydride enables to obtain hydrophobic aerogels. When the aerogel is prepared by conventional sol-gel routes in alcoholic solution (without the addition of DMF), as shown in curve *c*, the band at  $\sim 1650\text{ cm}^{-1}$  which we ascribe to C=O band is not detected, supporting previous discussion.



**Figure S3.** IR spectra for the hydrophobic (a), unmodified hydrophilic graphene/ $\text{SiO}_2$  nanocomposite (b) and pure hydrophobic silica aerogel (c).

## S2. Details on Raman Analysis

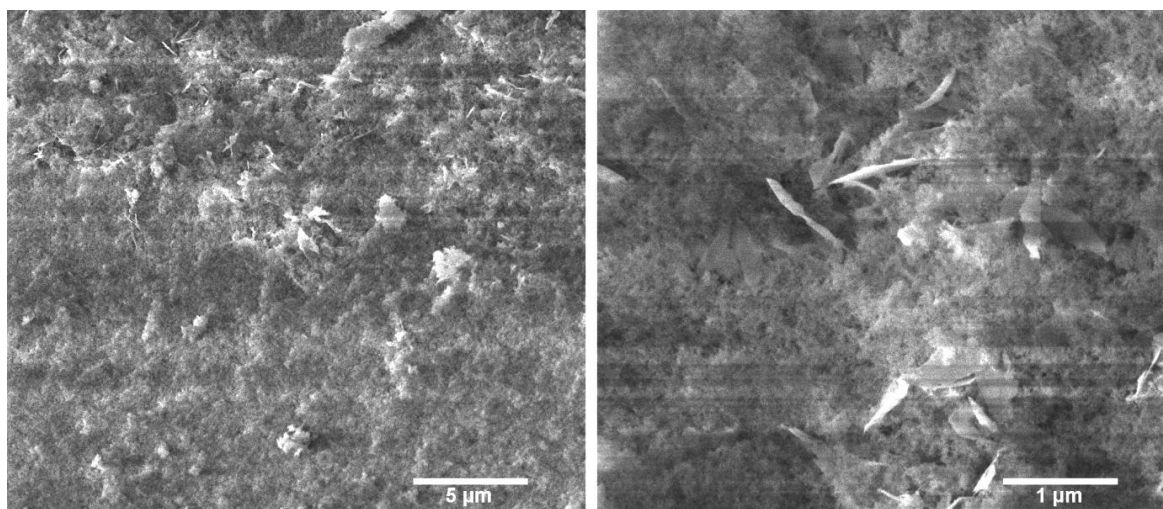


**Figure S4.** Raman spectrum of the hydrophilic graphene/SiO<sub>2</sub> aerogel nanocomposite in the 2820-2560 cm<sup>-1</sup> range with different number of Lorentzian curves: black curve is the acquired Raman spectrum, red line describes the fitting obtained by combining the Lorentzian curves (blue lines), and green line is the fitted band of the silicon signal.

The fitting with “low n” compared with the fitting reported in the paper are shown in Figure S4 in order to verify the need of using 4+1 peaks to achieve the best fit of the 2D band of graphene. As reported by Malard et al.,<sup>S3</sup> the number of Lorentzian curves fitting the 2D band can be related with the aggregation state of the graphene layers. As shown in Figure S4, it is not possible to achieve a good fit of the band with only two (R-square = 0.99774) or three (R-square = 0.99905) curves. The best fit can be obtained only with four peaks and it can further optimized with a 4+1 fitting by taking into account also the silicon signal, used as substrate for sample analysis. Taking into account also the silicon contribution slightly improves the overall goodness of the fit, as evidenced by the R-square value of 0.99973 as compared to the value of 0.9952 obtained by using 4 components. Moreover, it is expected that there is no physical meaning for fitting with a number of components higher than 1 and lower than 4, especially when the shape of the 2D band does not show a substantial splitting in two peaks. Based on these considerations, the observed peak features as obtained by the fitting can be ascribed to the occurrence of both single- and 2-layer graphene, although no definitive information can be inferred.

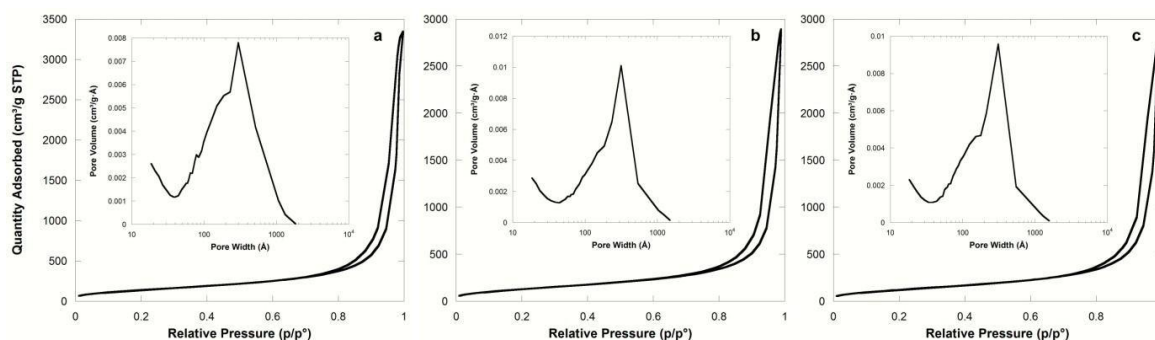
### **S3. Texture and Morphology of the Graphene/Silica Aerogel Nanocomposites**

Scanning Electron Microscopy experiments were performed on a dual beam FEI Nova Nanolab 600 high resolution SEM at the Polaris Facility (Pula, CA) on a block of graphene/silica aerogel placed on conductive tape for observations. As shown in representative images at low and high magnification reported in Figure S5, the nanocomposite shows the typical aerogel porous texture and the occurrence of dispersed layered structures which can be ascribed to graphene sheets. No evidence of segregation between the inorganic and organic phases was observed. SEM images support that the sol-gel procedure used to produce the composite is effective in preserving the porous texture of aerogels while enabling to effectively disperse graphene sheets.



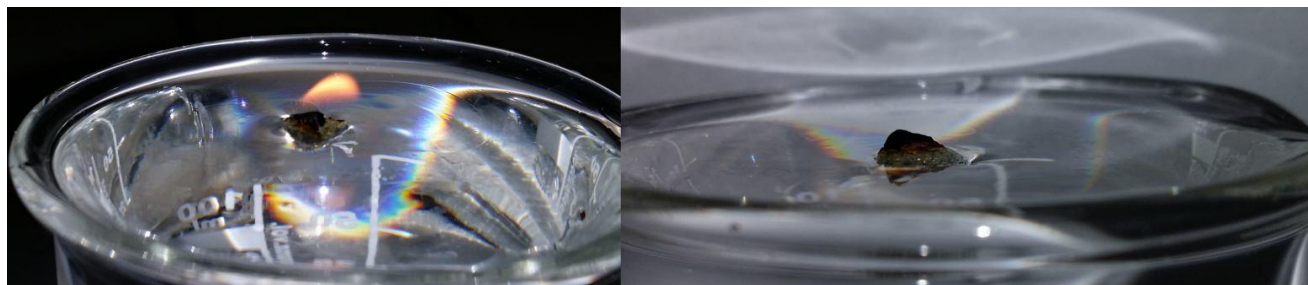
**Figure S5.** SEM images of hydrophobic graphene/silica aerogel nanocomposite having a content of dispersed phase 0.1 wt%.

$N_2$  physisorption measurements at 77 K on the undoped  $SiO_2$  aerogel and on the composites with a graphene loading of 0.003 and 0.1 wt% (reported in Figure S6), indicate the occurrence of a highly porous structure which is very similar for all the aerogels. The presence of an hysteresis loop at high relative pressures is associated to the occurrence of large mesopores with a relatively broad diameter size, centered at 30 nm for all samples.



**Figure S6.** N<sub>2</sub> physisorption isotherms at 77 K and corresponding BJH pore size distribution as derived from the desorption branch (inset) for the 0 wt% (a), 0.003 wt% (b) and 0.1 wt% (c) graphene/SiO<sub>2</sub> aerogel nanocomposites.

#### **S4. Hydrophobic Stability and Reusability after Burning of the Graphene/Silica Aerogel Nanocomposites**



**Figure S7.** Photographic sequence showing that the hydrophobic character of the graphene/silica aerogel nanocomposite is retained after oil burning.

The aerogel nanocomposite retains its hydrophobicity even after burning oil (Figure S7) and is still an active sorbent, although its adsorption capacity drops significantly (50%) after the first oil burning. The adsorption capacity after additional 5 cycles of oil uptake and burning leads to a more limited decrease of 5-7%.



## References

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S2 M. Tanhaei and V. Mohammady, *Int. J. Nano Dimens.*, 2014, **5**, 351-363.

S3 L. M. Malard, M. A. Pimenta, G. Dresselhaus and M. S. Dresselhaus, *Physics Reports*, 2009, **473**, 51-87.