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Graphene oxide reinforced high surface area silica aerogels

Saoirse Dervin [a,b], Yvonne Lang [a,c], Tatiana Perova [d,e], Steven H. Hinder [f], Suresh C. Pillai [a,b,]*

[a] Nanotechnology & Bio-Engineering Research Group, Department of Environmental Science, School of Science, Institute of Technology Sligo, Ash Lane, Sligo, Ireland
[b] Centre for Precision Engineering, Materials and Manufacturing Research (PEM), Institute of Technology Sligo, Ash Lane, Sligo, Ireland
[c] CERIS, School of Science, Institute of Technology Sligo, Sligo, Ireland
[d] Department of Electronic and Electrical Engineering, Trinity College Dublin, Dublin 2, Ireland
[e] ITMO University, 49 Kronverkskiy pr., Saint Petersburg, Russia
[f] The Surface Analysis Laboratory, Faculty of Engineering & Physical Sciences, University of Surrey, Guildford, Surrey GU2 7XH, UK

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ABSTRACT

Silica aerogel structures were intercalated with graphene oxide (GO) *via* the addition of GO to the colloidal silica sol and subsequent sol–gel polymerization. The potential of GO to act as a nanofiller, for ambient pressure dried, hydrophobic silica aerogels, was systematically investigated. The influences of 0 to 2 wt% GO loadings, on the physical properties of silica aerogels, were analysed by examining the bulk density, volume shrinkage (%), pore volume and surface area of the composite aerogels. Additionally, the chemical composition of the composite gels was determined using FTIR, Raman, XRD and XPS. The study revealed that a GO addition of as little as 0.5 wt% is capable of supporting the porous framework of silica aerogels and also enhancing the properties of the gels simultaneously. The additions of 0.5 wt% GO increased the surface area and pore volume of the aerogel from 390 to 700 m^2/g and 0.59 to 0.99 cm^3, respectively, and decreased aerogel density from 0.19 to 0.14 g/cm^3. The investigation therefore revealed that intercalation of the silica aerogel matrix with small quantities of GO can inhibit volume shrinkage during drying without hindering the physical properties of silica aerogels.

1. Introduction

The remarkable features of silica aerogels including ultralow density (~0.003 g/cm^3), high specific surface area (500 m^2/g to 1200 m^2/g), high porosity (80–99.8%), high thermal insulation values (0.005 W/mK) and versatility have resulted in their application in a number of industrial fields including aerospace, ultrasonic sensing, gas sensing, waste removal, optics, energy storage, catalysis and insulation [1–3].

Traditionally silica aerogels were prepared *via* supercritical drying [4–6]. This route uses supercritical fluids, elevated temperature and pressure to remove the liquid component of a gel, in the absence of capillary stress and surface tension. Though once a favoured method, this technique is expensive, time consuming and often hazardous, rendering the process impractical for industrial use. In order to exploit aerogels commercially, cost effective drying routes are required. Consequently, many upsurges in aerogel research have focused on the determination of alternative preparation routes [7–23].

In recent times, ambient pressure drying (APD) of sodium silicate gels has been identified as a feasible approach for the production of silica aerogels [24,25]. This method, however, often yields fragile gels [26]. Solvent extraction under atmospheric pressure evokes lateral compressive stress amongst the gel network in order to redress the loss of pore liquid during drying [27]. Polar Si–OH functionalities, located on the surface of the gels, interact with adjacent chains and give rise to relentless condensation reactions, which continue after complete formation of the silica network [27,28]. The interaction between the subsequent surface silanol groups has an elastic effect on the inner surfaces of the porous walls comprising the gel network [29]. The adjoining walls of the pores are drawn towards one another and eventually cause the porous network to collapse [29]. This results in irreversible shrinkage of the aerogel network [28,29]. The consequential innate brittleness of the silica network often limits extensive application of these materials. Accordingly, the mechanical properties of the interconnected silica network must be improved for commercial applications.

Several measures to enhance the mechanical properties and circumvent shrinkage of the aerogel network have been explored [30]. Surface modification or silylation, is one technique which has proved effective in preparing mechanically amended silica aerogels [14]. The process uses organosilanes such as hexamethyldisiloxane (HMDSO), hexamethyldisilazane (HMDZ), methyltriethoxy-silane (MTES) and trimethylchlorosilane (TMCS), converting Si–OH functionalities into

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* Corresponding author at: Nanotechnology & Bio-Engineering Research Group, Department of Environmental Science, School of Science, Institute of Technology Sligo, Ash Lane, Sligo, Ireland.
E-mail address: pillai.suresh@itsligo.ie (S.C. Pillai).

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alkyl or aryl radicals, creating hydrophobic aerogels and preventing further interaction of adjacent Si–OH functionalities [31–35].

Alternatively several studies have integrated the gel network with composite materials, such as crosslinking polymers, nanoparticles and/or ceramic fibres [36–46]. Conversely, it is often difficult to improve the mechanical properties of silica gels with the use of nanofillers or cross-linking reagents without altering or hampering additional properties such as the bulk density and surface area [36,47]. However, with effective control of each stage of aerogel synthesis and composite integration, the incorporation of additional materials between the weaker neck regions of the silica nanoparticles enhances the strength of the gel network and can also yield aerogels with improved or additional properties [30].

Graphene oxide (GO) [48], has recently been regarded as an attractive nanofiller for 3D architectures due to its unique two-dimensional structure [49], and other attractive properties (fracture stress $B = 63$ GPa). However, little information regarding the effect of GO on the silica matrix is provided within current literature. Previous studies have demonstrated the successful incorporation of reduced graphene oxide (rGO) within the matrices of silica aerogels, however, to date, no systematic studies have explored the reinforcement of silica aerogels with GO [50]. Composite formation of GO intercalated silica aerogels concedes the possibility of preparing high surface area, porous materials with improved properties. Alternatively, incorporating GO amongst the silica network may increase the mechanical properties of the aerogel but may also hinder the material's properties.

The current study therefore aims to introduce GO into the matrix of silica aerogels to determine the potential of the carbonaceous material as a nanofiller for silica aerogels. The effect of GO loading on the density, pore volume/diameter and surface area of the composite gels was investigated.

2. Experimental

2.1. Synthesis of graphite oxide (GtO)

Graphite oxide (GtO) was prepared from natural graphite following an improved synthesis [51]. In a typical procedure, a solution containing 360 ml concentrated H_2SO_4 and 40 ml concentrated H_3PO_4 was added to 3 g of graphite flakes and 18 g $KMnO_4$. Once an emerald green homogenous mixture had been obtained the solution was heated to 50 °C and stirred for 12 h. After observation of a green–brown colour change the solution was cooled to room temperature poured over 400 ml deionised (DI) ice and H_2O_2 was subsequently added until a bright yellow colour was achieved. The obtained yellow mixture was allowed to cool before washing with water, 30% HCl and ethanol, respectively *via* centrifugation at 10,000 rpm for 20 min. Finally, the obtained pellet was coagulated with diethyl ether and the resulting suspension was filtered over a PTFE membrane with a 0.45 μm pore size. The solid substance obtained on the filter was dried overnight at ambient conditions.

2.2. Preparation of silicic acid (S.A.) solution

The source of silica used for the preparation of hydrogels was waterglass *i.e.* sodium silicate (≥27 wt%) from Sigma Aldrich, Ireland. For the preparation of a 20 ml composite sol 5.93 ml sodium silicate solution was diluted with 7.035 ml DI water. The dilute sodium silicate solution was passed through an ion-exchange resin (Amberlite® IR120 hydrogen form; Sigma Aldrich, Ireland) (Scheme 1) in order to remove the Na^+ ions and obtain a silicic acid solution with a pH of 2.5–3.0.

2.3. Preparation of graphene oxide (GO) solution

Various amounts of GtO were added to 7.04 ml DI water. Typically, 41.21 mg, 82.43 mg and 164.85 mg GtO were added to 7.04 ml DI water in order to prepare GO aqueous solutions which would account of a 0.5, 1 and 2 wt% loading in the silicic acid sol. The dispersed GtO sheets were then exfoliated *via* ultrasonication for 1 h in order to obtain an aqueous dispersion of GO.

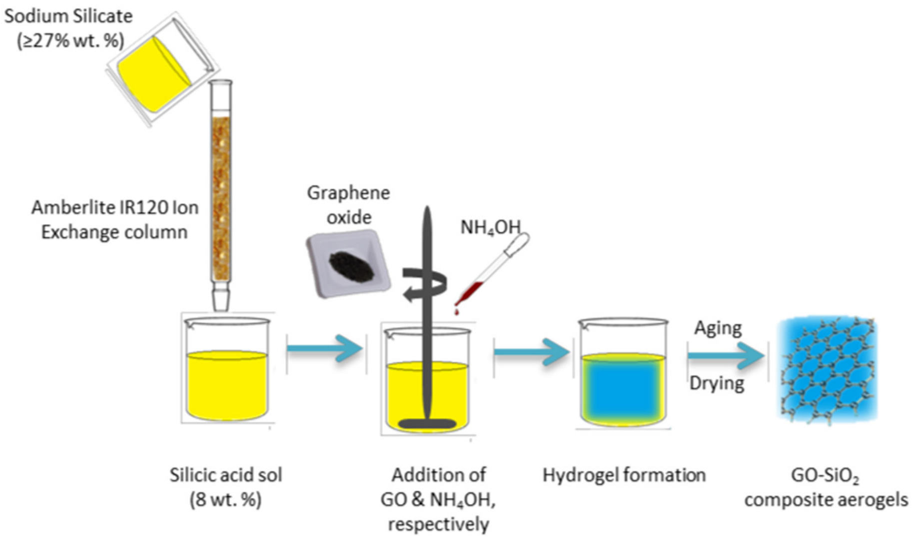
2.4. Preparation of GO–S.A. solution

GO–SiO_2 composite aerogels were prepared by sol–gel polymerization of silicic acid sols containing different loadings of GO in the range of 0–2 wt% (scheme 1).

The weight varying GO solutions were added to each of the 20 ml silicic acid solutions in order to obtain composite sols which contained various loadings of GO ranging from 0 to 2 wt% (weight percentage of the aerogel, assuming full conversion of silicic acid into SiO_2 aerogel).

2.5. GO–SiO_2 wet gel formation

Concentrated NH_4OH (typically one drop) was added to the pure SiO_2 sol and the GO–SiO_2 sols until the pH of the sols reached pH 6–7. The sols were then kept at 50 °C for gelation. The obtained hydrogels were aged for 3 h at 50 °C to strengthen the silica network of the composite materials. The strengthened monoliths then underwent a 24 h



Scheme 1. Preparation of GO–SiO_2 composite aerogels.

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