HAL open science

Electrical conductive double-walled carbon nanotubes ï¿½ Silica glass nanocomposites prepared by the solï¿½gel process and spark plasma sintering

Mônica Jung de Andrade, Alicia Weibel, Christophe Laurent, Siegmar Roth, Carlos Pérez Bergmann, Claude Estournès, Alain Peigney

To cite this version:

Mônica Jung de Andrade, Alicia Weibel, Christophe Laurent, Siegmar Roth, Carlos Pérez Bergmann, et al.. Electrical conductive double-walled carbon nanotubes ï¿½ Silica glass nanocomposites prepared by the solï¿½gel process and spark plasma sintering. Scripta Materialia, 2009, 61 (10), pp.988-991. 10.1016/j.scriptamat.2009.08.015 . hal-03565088

HAL Id: hal-03565088

https://hal.science/hal-03565088v1

Submitted on 10 Feb 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Open Archive Toulouse Archive Ouverte (OATAO)
OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: http://oatao.univ-toulouse.fr/
Eprints ID: 3957

To link to this article: doi:10.1016/j.scriptamat.2009.08.015
URL: http://dx.doi.org/10.1016/j.scriptamat.2009.08.015

To cite this version: ung de Andrade, Moˆnica and Weibel, Alicia and Laurent, Christophe and Roth, Siegmar and Pe´rez Bergmann, Carlos and Estourne`s, Claude and Peigney, Alain (2009) *Electrical conductive double-walled carbon nanotubes – Silica glass nanocomposites prepared by the sol–gel process and spark plasma sintering.* Scripta Materialia, vol. 61 (n° 10). pp. 988-991. ISSN 1359-6462

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@inp-toulouse.fr

Electrical conductive double-walled carbon nanotubes – Silica glass nanocomposites prepared by the sol–gel process and spark plasma sintering

Mônica Jung de Andrade,[a,b] Alicia Weibel,[b] Christophe Laurent,[b] Siegmar Roth,[c] Carlos Pérez Bergmann,[a] Claude Estournès[b] and Alain Peigney[b,*]

[a]*Universidade Federal do Rio Grande do Sul, Porto Alegre-RS, Brazil*
[b]*Université de Toulouse, CIRIMAT, UMR CNRS-UPS-INP, Bât. 2R1, Université Paul-Sabatier, 31062 Toulouse cedex 9, France*
[c]*Max Planck Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

The electrical conductivity of suspensions in liquid of several kinds of carbon nanotubes (CNTs) is measured. Raw and soft-functionalized double-walled carbon nanotubes (DWCNTs) appear to be the most promising for achieving a low electrical percolation threshold. A 0.35 vol.% DWCNTs–SiO_2 nanocomposite is prepared by the sol–gel process and densified by spark plasma sintering. The obtained material presents a fairly good dispersion of DWCNTs and its electrical conductivity (10^{-4} S cm^{-1}) is six orders of magnitude higher than that previously reported for 1 vol.% multi-walled CNTs–SiO_2.

Keywords: Carbon nanotubes; Nanocomposites; Silica; Spark plasma sintering; Electrical conductivity

The outstanding electrical, thermal and mechanical properties of carbon nanotubes (CNTs) have broadened the research into nanocomposites [1]. In ceramic matrices, the addition of CNTs can not only improve mechanical properties, but also give rise to electrical percolation in an insulating matrix at a much lower content (<1 vol.%) than any other additives due to their huge aspect ratio (1000–10,000) [2]. However, the main challenges remain the dispersion of CNTs into the matrix and the densification of the material [1,2]. To overcome the first difficulty, CNTs can either be synthesized in situ in the ceramic powder or the ceramic precursor can be synthesized around CNTs dispersed in a solvent (with the aid of chemical functionalization or the use of surfactants, followed by sonication) [1,2]. To sinter the materials, spark plasma sintering (SPS) is preferred to hot-pressing (HP) because it allows densification at lower temperature and shorter times, thus limiting the damage to the CNTs [2].

Due to the predicted good chemical interaction of CNTs with silica matrix without altering their original properties [3,4], CNTs–SiO_2 composites have many potential applications including optical materials [5,6] or opto-electronic devices, as well as electromagnetic interference shielding devices [7,8]. Since the precursor work of Gavalas et al. [9] on CNTs–silica xerogel composites, there have been several reports on CNTs–SiO_2 densified composites [5–7,10–12]. Different types of CNTs, dispersion methods and densification techniques have been used to prepare these composites. In most cases [7,8,10–12], multi-walled CNTs (MWCNTs) were preferably used probably due to their higher disponibility and lower costs in comparison to single-walled (SWCNTs) or double-walled CNTs (DWCNTs). Despite SWCNTs allowing percolation to be achieved with a lower load than MWCNTs, few studies have been dedicated to SWCNTs–SiO_2 composites [5,6]. Their functionalization would induce damage to their only wall, compromising their electronic properties. In this context, DWCNTs have recently gained special attention since functionalization can occur on the outer wall without damaging the electronic properties from its inner tube [13].

The large surface area and high aspect ratio of CNTs associated with their high hydrophobicity makes it difficult to properly disperse them in any medium at the

* Corresponding author. Tel.: +33 5 61 55 61 75; fax: +33 5 61 55 61 63; e-mail: peigney@chimie.ups-tlse.fr

concentrations required for their application in composites. Therefore, various approaches to improving the dispersion of CNTs into SiO_2 have already been tested in terms of modification of the interface (by use of surfactants [5,7,8,10,11] and chemical functionalization [6]), as well as methods of composite preparation (attrition mill with colloidal SiO_2 [12] or in situ production of silica by organic [6–8,10,11] or inorganic [5] sol–gel routes). In addition, the incorporation of CNTs into silica glass is detrimental to densification because it slows the sintering kinetics, as any fiber does in a glass matrix [14]. Consequently, several techniques have also been tested to densify these composites, including heat treatment in an inert atmosphere [5], HP [7,8,10,11], high-pressure cold quasi-isostatic pressing [6] and SPS [12].

In terms of electrical conductivity, the lowest loading exhibiting percolation that has been reported was 1 vol.% for MWCNTs–SiO_2 composites [9], which achieved an electrical conductivity of about 10^{-10} S cm^{-1}. A higher CNTs content results in a higher conductivity. For example, 0.08 and 0.65 S cm^{-1} were measured for 5 and 10 vol.% MWCNTs–SiO_2, respectively [12], while 0.15 S cm^{-1} was achieved with 4 wt.% of functionalized SWCNTs [5].

The aim of this work was to prepare an electrically conductive CNTs–SiO_2 composite with a much lower CNT content by properly selecting the appropriate CNTs, optimizing a method to achieve a good dispersion and using SPS to obtain a high densification without damaging the CNTs. DWCNTs (89.2 wt.% C) produced by catalytic chemical vapour deposition [15] were acid-functionalized (using nitric, sulphuric and chloridric acids at room temperature) [16]. Briefly, the DWCNTs were submitted to a soft functionalization that consists of adding them to a mixture of nitric and sulphuric acids and submitting the mixture to bath sonication for about 1 h, followed by 24 h of stirring. After that, chloridric acid was added and the mixture was stirred for 10 min. Finally, the acids were neutralized by the addition of ammonia solution followed by filtration and rinsing with deionized water. Functionalized DWCNTs (f-DWCNTs) were characterized by comparing the Raman spectra (1.96 eV, Jobin–Yvon LabRam) of the DWCNTs and f-DWCNTs. The spectra (Fig. 1a and b) were normalized to the G-band (ca. 1586 cm^{-1}). Raman breathing mode (RBM) peaks (ca. 156, 214 and 255 cm^{-1}) were observed for both samples. The ratio between the intensities of the D-band (ca. 1327 cm^{-1}) and the G-band, $I_{D/G}$, is higher for f-DWCNTs than for DWCNTs (0.2 and 0.1, respectively) due to the opening of the C—C bonds by functionalization [17]. A downshift (~2 cm^{-1}) of the G-band, the graphene dominant tangential mode and an upshift (~2 cm^{-1}) of the D* band (originally ca. 2616 cm^{-1}) were observed after DWCNTs were functionalized, probably reflecting a charge transfer caused by the chemical oxidation [13].

The electrical conductivity in dynamic mode [18] for DWCNTs and f-DWCNTs suspensions in liquid chloroform was measured (Fig. 2) in order to check the effect of the chemical oxidation. A two-probe cell configuration was used (the immersed 15.5 × 5.2 mm electrodes were 5 mm apart) with continuous probe ultrasonication (probe diameter of 2.5 mm) using a GW Instek GPS-18300 DC power supply and a Philips PM2525 apparatus. The measures were made for progressively increasing CNTs contents. For the maximum f-DWCNTs content (0.28 vol.%) in liquid chloroform, the conductivity was ca. 6.10^{-3} S cm^{-1} (about three times lower than for DWCNTs). However, for lower f-DWCNTs contents, the difference decreases and even disappears, indicating that the oxidation has not severely damaged the f-DWCNTs. Commercial DWCNTs (Nanocyl, 90 wt.% C) were tested as well and always showed a lower conductivity. In comparison to previous results with commercial (HipCO, 81.3 wt.% C) SWCNTs [18], at higher CNTs contents, the conductivity was similar to or slightly higher than that for DWCNTs. However, for lower CNTs contents, the conductivity of SWCNTs decreased sharply (by far the lowest of all tested materials), reflecting their lower aspect ratio [18]. Considering that these CNT dynamic dispersions in chloroform are optimal [18], these results shows that the DWCNTs and the f-DWCNTS used in the present study are better suited to obtain the electrical percolation in the SiO_2 matrix than the other tested CNTs. Only f-DWCNTs will be considered for the rest of the study because

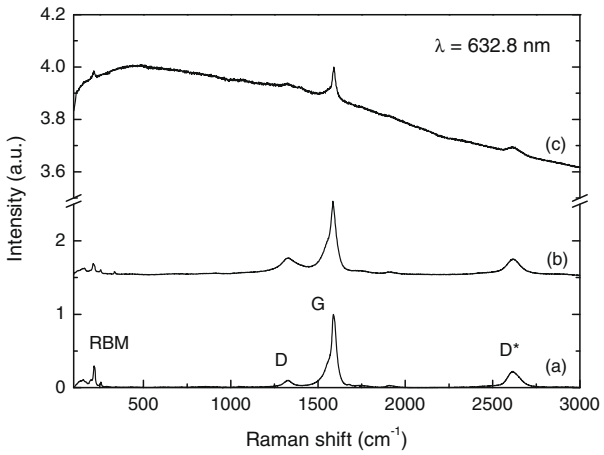

Figure 1. Raman spectra of the DWCNTs (a), f-DWCNTs (b) and f-DWCNTs–SiO_2 composite after SPS at 1000 °C (c).

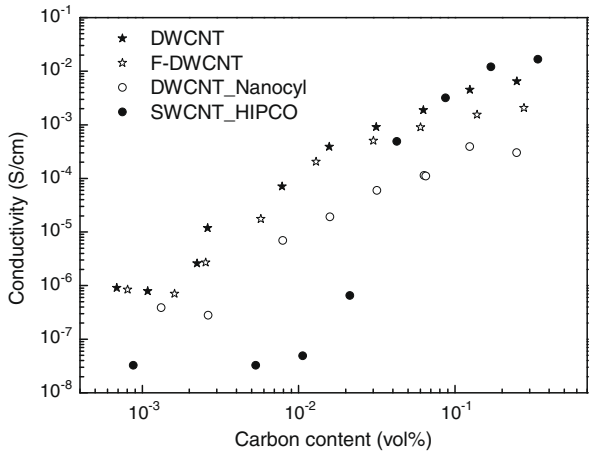

Figure 2. Conductivity in dynamic state for chloroform suspensions of DWCNTs, f-DWCNTs and commercial SWCNTs [18] and DWCNTs.

functionalization is essential for developing a good dispersion in the matrix.

A nitric acid aqueous solution containing f-DWCNTs was prepared with the aid of probe sonication (Bioblock Scientific Vibracell 75042). This suspension was poured into an alcoholic solution containing tetraethylorthosilicate (TEOS) as silica precursor, sonicated for 1 min and then left to gelify at room temperature for several days with stirring. For comparative purposes, a product without CNTs was prepared by the same route. The molar ratio of water to TEOS was 20 for the composite and 4.5 for pure silica. The xerogels were ground and calcinated in air at 400 °C. The carbon content in the thus-obtained composite powder was 0.29 wt.% (i.e. ca. 0.35 vol.% f-DWCNTs, taking 1.80 g cm^{-3} for the f-DWCNTS). The powders were densified by SPS (Dr. Sinter 2080, SPS Syntex Inc. at the Plateforme Nationale CNRS de Frittage-Flash – PNF2, Toulouse) using a 20 mm diameter graphite die (1000 °C, 5 min dwell time, 50 MPa). The density measured by Archimedes' method was found to be 2.134 and 2.112 g cm^{-3} for SiO_2 and f-DWCNTs–SiO_2, respectively. These values correspond to relative densities of ca. 97% and 96%, respectively, using 2.20 g cm^{-3} for SiO_2 [19] and 1.80 g cm^{-3} for the DWCNTs. X-ray diffraction (XRD; Bruker D4 Endeavor) pattern analysis (Fig. 3) revealed that pure SiO_2 was still amorphous, whereas a peak was observed for the composite, showing the beginning of crystallization. These observations are in good agreement with other works [11] and suggest that CNTs might act as germs for the heterogeneous nucleation of crystalline SiO_2 [20]. Moreover, one should not forget the possible effect of residual water since the large surface area of the DWCNTs might make complete outgassing difficult during the calcination and densification steps.

The Raman spectrum for the densified f-DWCNTs–SiO_2 nanocomposite (Fig. 1c) is dominated by the fluorescence of silica, thus masking many features corresponding to the CNTs. Nevertheless, the most intense RBM peak observed for f-DWCNTs (Fig. 1b) is still detected and there is no obvious increase in the D band intensity, which could reflect that the DWCNTs were not grossly damaged by SPS. The frequency of the G-band (1591 cm^{-1}) is upshifted (~5 cm^{-1}) compared to f-DWCNTs. Puech et al. [21] showed through in situ Raman spectroscopy of DWCNTs in a diamond anvil cell that there is a linear dependence between the shift in the frequency of the G-band and the applied isostatic pressure up to 12 GPa. Thus, these results could suggest that the f-DWCNTs remain under residual pressure in the matrix, which could also reflect the good interaction between the SiO_2 and CNTs mentioned in other studies [3,4]. A G-band upshift was also reported for f-SWCNTs–SiO_2 composites [6]. Moreover, the D* band upshift of ~6 cm^{-1} (from 2616 to 2622 cm^{-1}) also suggests a good interaction.

Field emission gun-scanning electron microscopy (FESEM; JEOL JSM 6700F, at TEMSCAN, Université Paul-Sabatier) observations of the fracture surface of the composite (Fig. 4a) revealed the good dispersion of the f-DWCNTs in the matrix. However, the observation of a few agglomerates and some areas apparently without any f-DWCNTs indicated that it was still not optimal. Good wetting of the f-DWCNTs by the matrix was achieved, as shown in Figure 4b, with CNTs protruding out of an SiO_2 grain (confirming our Raman spectroscopy results and predictions [3,4]).

The densified samples were cut and polished into bars ~10 mm long (~2 mm × 2 mm in section) and metallized on the two square faces by a silver paste. The electrical conductivity of the f-DWCNTs–SiO_2 nanocomposite was measured on six bars (Philips PM2525 apparatus). The average electrical conductivity was $(1.0 \pm 0.1) \times 10^{-4}$ S cm^{-1}. This value is lower than that obtained in liquid (6×10^{-3} S cm^{-1} for 0.28 vol.% f-DWCNTs, Fig. 2), probably due to the better dispersion of f-DWCNTs in the chloroform suspension with constant sonication than in the composite (even more so as the CNTs were dispersed in acidic medium [22]). However, the obtained value is six orders of magnitude higher than that reported by Xiang et al. [10] for 1 vol.% MWCNTs–SiO_2 and might possibly still be increased, for the same CNTs content, with a better dispersion, thus creating more possibilities of conduction paths.

In conclusion, we prepared an electrical conductive CNTs–SiO_2 composite with a very low CNT content. Measurements of the electrical conductivity of CNT

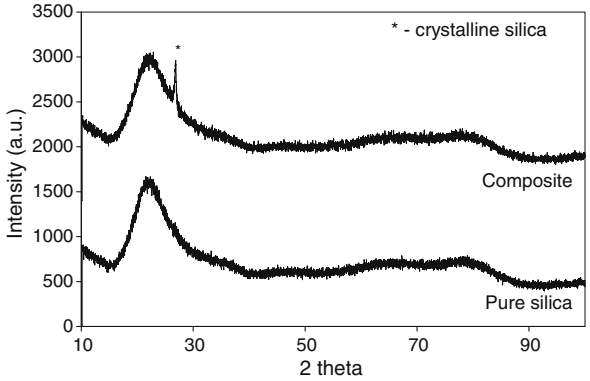

Figure 3. XRD patterns of the SiO_2 and f-DWCNTs–SiO_2 materials consolidated by SPS.

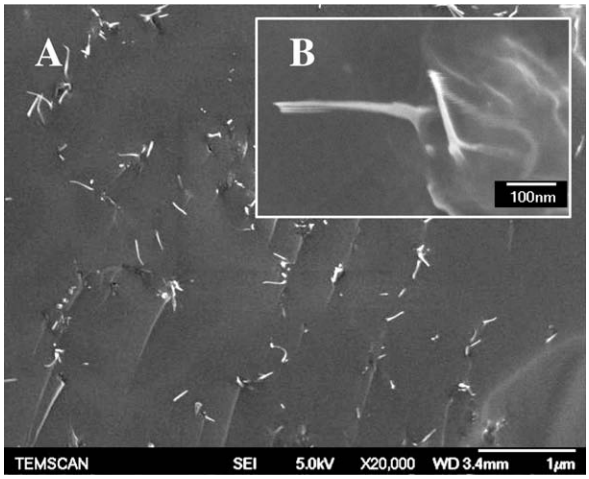

Figure 4. FESEM images of the fracture surface of the 0.35 vol.% f-DWCNTs–SiO_2 nanocomposite.

suspensions in liquid showed that the present DWCNTs, pristine or functionalized, are better suited to obtaining the electrical percolation at a low content compared to commercial SWCNTs or DWCNTs. The soft functionalization by chemical oxidation at room temperature did not cause any gross damage. A 0.35 vol.% f-DWCNTs–SiO_2 nanocomposite was prepared by the sol–gel process and sintered by SPS. The f-DWCNTs were fairly well dispersed, although it could still be improved, and a good interaction with SiO_2 was evidenced. The electrical conductivity (ca. 10^{-4} S cm^{-1}) is six orders of magnitude higher than that reported [10] for 1 vol.% MWCNTs–SiO_2. Furthermore, if further works are needed to obtain transparent materials by avoiding the presence of remaining pores, the achieved electrical conductivity for this composite is high enough to anti-electrostatic [23] or heating elements [24].

The support of CAPES-COFECUB research Grant 562/07 is gratefully acknowledged. The SPS was performed at the Plateforme Nationale CNRS de Frittage-Flash (PNF^2, Toulouse, France).

[1] Ch. Laurent, A. Peigney, in: H.S. Nalwa (Ed.), Encyclopedia of Nanoscience and Nanotechnology, American Scientific Publishers, Stevenson Ranch, CA, 2004, p. 635.
[2] A. Peigney, Ch. Laurent, in: J. Low (Ed.), Ceramic Matrix Composites: Microstructure-Property Relationship, Woodhead Publishing Limited, Cambridge, 2006, p. 309.
[3] L. Tsetseris, S.T. Pantelides, Phys. Rev. Lett. 97 (2006) 266805.1.
[4] J.C. Wojdel, S.T. Bromley, J. Phys. Chem. B 109 (2005) 1387.
[5] M.J. de Andrade, M.D. Lima, L. Stein, C.P. Bergmann, S. Roth, Phys. Status Solidi B 244 (2007) 4218.
[6] M.J. de Andrade, M.D. Lima, C.P. Bergmann, G.O. Ramminger, N.M. Balzaretti, T.M.H. Costa, M.R. Gallas, Nanotechnology 19 (2008) 265607.1.
[7] C. Xiang, Y. Pan, J. Guo, Ceram. Int. 33 (2007) 1293.
[8] C. Xiang, Y. Pan, X. Liu, X. Sun, X. Shi, J. Guo, Appl. Phys. Lett. 87 (2005) 123103.
[9] V.G. Gavalas, R. Andrews, D. Bhattacharyya, L.G. Bachas, Nanoletters 1 (2001) 719.
[10] C. Xiang, X. Shi, Y. Pan, J. Guo, Key Eng. Mater. 280–283 (2005) 123.
[11] J. Ning, J. Zhang, Y. Pan, J. Guo, Ceram. Int. 20 (2004) 63.
[12] S. Guo, R. Sivakumar, H. Kitazawa, Y. Kagawa, J. Am. Ceram. Soc. 90 (2007) 1667.
[13] E.B. Barros, H. Son, Ge.G. Samsonidze, A.G. Souza Filho, R. Saito, Y.A. Kim, H. Muramatsu, T. Hayashi, Phys. Rev. B 76 (2007) 1–045425.1.
[14] M.J. Pascual, A. Durán, M.O. Prado, E.D. Zanotto, J. Am. Ceram. Soc. 88 (2005) 1427.
[15] E. Flahaut, R. Bacsa, A. Peigney, Ch. Laurent, Chem. Commun. (2003) 1442.
[16] Q. Chen, C. Saltiel, S. Manickavasagam, L.S. Schadler, R.W. Siegel, H. Yang, J. Colloid Interf. Sci. 280 (2004) 91.
[17] U.J. Kim, C.A. Furtado, X. Liu, G. Chen, P.C. Eklund, J. Am. Chem. Soc. 127 (2005) 15437.
[18] M.D. Lima, M.J. de Andrade, V. Skákalová, C.P. Bergmann, S. Roth, J. Mater. Chem. 17 (2007) 4846.
[19] W.D. Callister, D.G. Rethwisch, Fundamentals of Materials Science and Engineering – An Integrated Approach, Wiley, Danvers, MA, 2008.
[20] V.M. Fokin, E.D. Zanotto, N.S. Yuritsyn, J.W.P. Schmelzer, J. Non-Cryst. Solids 352 (2006) 2681.
[21] P. Puech, E. Flahaut, A. Sapelkin, H. Hubel, D.J. Dunstan, G. Landa, W.S. Bacsa, Phys. Rev. B 73 (2006) 23408–23411.
[22] W. Zhao, C. Song, P.E. Pehrsson, J. Am. Chem. Soc. 124 (2002) 12418.
[23] US Patent 7108758, 2006.
[24] US Patent 4371778, 1983.