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Ceramics International 38 (2012) 3991–3998

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Microstructural features of nanocomposite of alumina@carbon nanotubes/alumina nanoparticles synthesized by a solvothermal method

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Received 19 December 2011; received in revised form 19 January 2012; accepted 20 January 2012
Available online 28 January 2012

Abstract

The present study focuses on the synthesis of nanocomposite gamma alumina (γ-Al_2O_3), boehmite and multi- walled carbon nanotubes (MWCNTs) via a solvothermal procedure. The method is based on the ex situ filling of opened CNTs by liquid reactants. The microstructure and morphology of the synthesized nanocomposite Al_2O_3@CNTs/Al_2O_3 was characterized by high resolution transmission electron microscopy (HRTEM), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) and N_2 adsorption–desorption analysis.

Based on the experimental results, it was determined that the volume ratio of γ-Al_2O_3/MWCNTs and the surface tension of the solvent both greatly influence the morphology of the nanocomposite. The resultant MWCNTs were coated and filled by homogeneous and uniform boehmite and γ-Al_2O_3 layers and nanoparticles with thicknesses of 1–3 nm and diameters of 20–40 nm, when the volume ratio of γ-Al_2O_3/$MWCNT_S$ is 1 and the surface tension of the solvent is approximately 26 mN m^{-1} at 20 °C, far below the maximum value (100–200 mN m^{-1}) for MWCNT filling.

Keywords: B. Nanocomposite; Solvothermal; Multi-walled carbon nanotubes; Gamma alumina; Boehmite; Microstructure

1. Introduction

The ability of MWCNTs to encapsulate foreign materials such as liquids, gases and solids is one of their most exciting properties. Many new applications above and beyond the application possibilities for pure MWCNTs have been suggested for filled MWCNT materials. These new materials and applications include Fe_2O_3-filled MWCNTs as the negative electrode for a Fe-air battery, Ni (OH) $_2$/CNTs as the electrode in asymmetric supercapacitors, SnO_2/MWCNTs, for higher reversible discharge capacity compared to pure nano-SnO_2, MnO_2/CNTs hybrid coaxial nanotubes with enhanced reversible capacity compared to pure MnO_2 nanotubes and, MgO/CNT hybrids as electrodes [1].

Methods for filling carbon nanotubes can be classifieds into two groups:

(I) In situ filling
(II) Ex situ filling

MWCNTs can be filled in situ during the synthesis process by either arc-discharge or CVD techniques. The advantage of in situ methods is that they allow MWCNTs to be filled with compounds that have very high surface tensions [2].

Ex situ filling is a most versatile route. The filling can be performed through a gas route (sublimation or capillary condensation) or through a liquid route (capillary wetting from suspension, solution or melt). The procedure can consist of one, two or three steps. The first step for all routes is opening the ends of the CNTs. This can be achieved by two different methods: using thermal treatments for oxidizing in the gas phase (air or O_2) or using a wet chemical approach.

In the liquid phase method, the liquid reactant must exhibit a surface tension below 100–200 mN m^{-1} and a viscosity low enough to allow reasonable filling kinetics [1,2]. The main advantages of the liquid phase method are flexibility and the

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doi:10.1016/j.ceramint.2012.01.054

level of experimental control, which allows for a wider variety of materials to be introduced into CNTs [2].

It is well-known that alumina (Al_2O_3) is an important technical and industrial ceramic with broad applications. Alumina may be formed by thermal decomposition of crystalline hydrated aluminum salts such as aluminum sulfate, nitrate and chloride. One important polymorph of alumina is γ-Al_2O_3, whose high thermal conductivity and surface area make it suitable for nanofluids [3]. Many strategies to synthesize nanohybrid CNT_S have been reported, such as the sol–gel, hydrothermal and Atomic Layer Deposition (ALD) methods [4].

In this work, nanocomposite Al_2O_3@CNTs/Al_2O_3, which have potential applications in nanofluids, have been successfully synthesized by a facile solvothermal method.

2. Experimental procedure: materials and methods

2.1. Material

The carbon nanotubes used in this study were synthesized using a Co–MgO based catalyst (Research Institute of Petroleum Industry (RIPI) of Iran). After synthesis, the carbon nanotubes were treated with a multi-step purification. A complete description of the production and purification processes can be found elsewhere [5]. The inner diameter, outer diameter and mean length of the MWCNTs were measured by transmission electron microscopy (TEM, Philips); they were 6–20 nm, 10–50 nm and 1–100 nm, respectively. Aluminum acetate (Al (OH)($C_2H_3O_2$)$_2$, (Sigma–Aldrich), ammonia (Merck, 25%), Triton X_{100} ($C_{14}H_{22}O$ (C_2H_4O)$_n$)

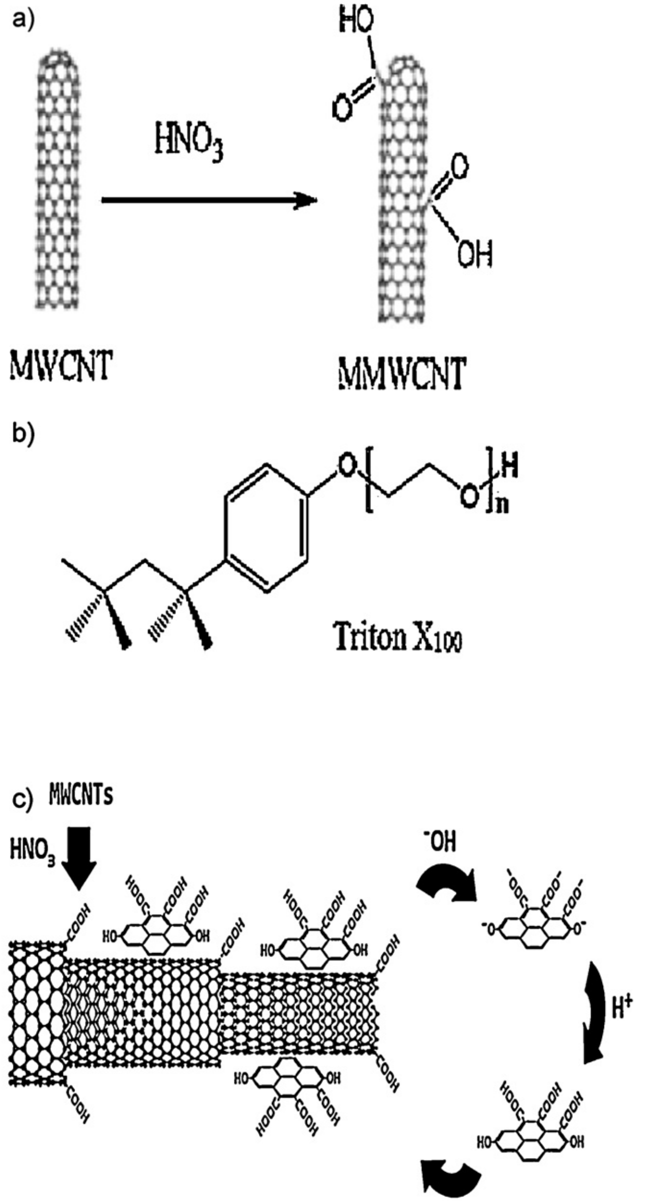


Fig. 1. (a) Chemical modification of MWCNTs through thermal oxidation [6]. (b) Molecular structure of Triton X_{100} [7]. (c) A simplified scheme of the generation of covalently bound surface acidic groups [8] and different functional groups through thermal oxidation and solvothermal synthesis.

(Merck), nitric acid (Merck, 65%) and absolute ethanol (Merck, 99.5%) were used as starting materials for the CNT filling.

2.2. *Preparation of materials*

The liquid reactants were used to open the tips of the MWCNTs. For each run, pure MWCNT, were added to nitric acid (65%) in a round bottom flask. The nitric-MWCNT solution was refluxed under magnetic stirring for 4 h. The suspension was ultrasonicated in an ultrasonic water bath at 60 °C for 4 h. Then, the resulting solid was washed to neutral pH, and the sample was dried at 90 °C for 24 h. Such conditions led to the removal of the catalyst from the carbon nanotubes and opened the tube caps. In addition, holes were formed in the sidewalls followed by an oxidative etching along the walls with the concomitant release of carbon dioxide. Less vigorous conditions minimized the shortening of the tubes, and the chemical modification was then limited mostly to the opening of the tube caps and the formation of functional groups at defect sites along the sidewalls. The final products were nanotube fragments whose ends and sidewalls were decorated with various oxygen-containing groups (mainly carboxyl groups) (Fig. 1) [6]. Moreover, the percentage of carboxylic functional groups on the oxidized MWCNT surface did not exceed 4% in the best cases, a number which corresponds to the percentage of MWCNT structural defects [5].

2.3. *Synthesis method*

Nanocomposite Al_2O_3@CNTs/Al_2O_3 was prepared by a solvothermal procedure using ethanol (C_2H_5OH) solution. In a typical experiment, aluminum acetate powder Al (OH) $(C_2H_3O_2)_2$, was dissolved into the absolute ethanol under vigorous magnetic stirring at room temperature and was continually stirred for 30 min until the aluminum acetate powders dispersed completely. The opened CNTs were mixed into the suspension and dispersed using the ultrasonic water bath at room temperature until no black agglomerates were observed in mixture. Then, the mixture was placed under vacuum (50 cm Hg) at room temperature. Under this condition, only capillary forces can cause the tubes to fill with solution. To obtain fine boehmite particles, ammonia solution (25%) was slowly added to the mixture after 24 h to adjust the pH to above 9. Then, the solution was transferred into a 350 ml Teflon-lined stainless steel autoclave chamber. Solvothermal synthesis was performed at 200 °C for 6, 12 and 24 h. The pressure of the autoclave for all synthesis runs was approximately 16 bar. The autoclave was subsequently allowed to cool to room temperature. The collected precipitate was washed with absolute ethanol several times up to neutral pH and then vacuum-dried at 60 °C for 6 h. The resulting powders were calcined at 500 °C for 1 h under argon atmosphere. Fig. 2 shows a schematic view of the process for coating and filling γ-Al_2O_3 nanoparticles in and on the surface of MWCNTs.

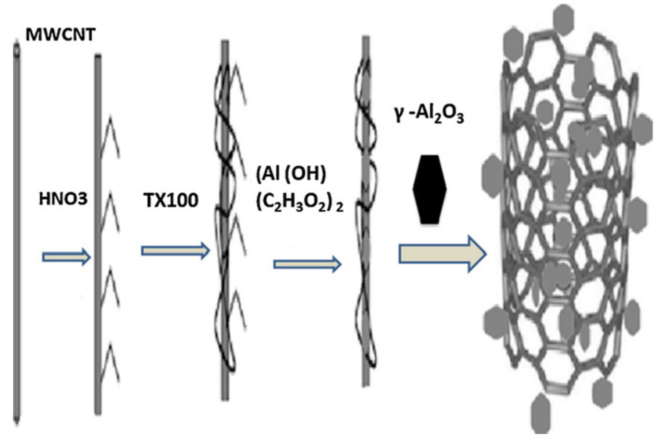


Fig. 2. Schematic view of the process for coating and filling γ-Al_2O_3 nanoparticles on the MWCNTs.

The processing conditions and microstructure of the nanocomposite Al_2O_3@CNTs/Al_2O_3 were characterized by XRD (PHILIP, with Co Kα, λ = 1.789010 Å, X'pert Pro, Netherlands), EDX (INCA, Oxford Instruments), FESEM (Hitachi, S-4160, V_{acc} 15Kv), TEM and HRTEM (FEG, Philips, CM200). The surface tension was also measured(KRÜSS, GERMANY). Following the synthesis, the physical surface area (BET), pore structure (volume and size), adsorption/desorption isotherm and BJH-plot of the adsorption of the resulting powders were determined by testing with N_2 (BEL Japan, Inc.).

3. Results and discussion

It is generally accepted that many experimental factors can affect the morphology of nanomaterials. The reaction times of the synthesis reaction, surface tension of the solvent and volume ratios of γ-Al_2O_3/$MWCNT_S$ play important roles in the formation and structure of the nanocomposite Al_2O_3@CNTs/Al_2O_3 and the γ-Al_2O_3 nanoparticles.

3.1. *XRD pattern*

Fig. 3 shows the comparative XRD patterns of the γ-Al_2O_3 without the MWCNTs prepared by the solvothermal method at

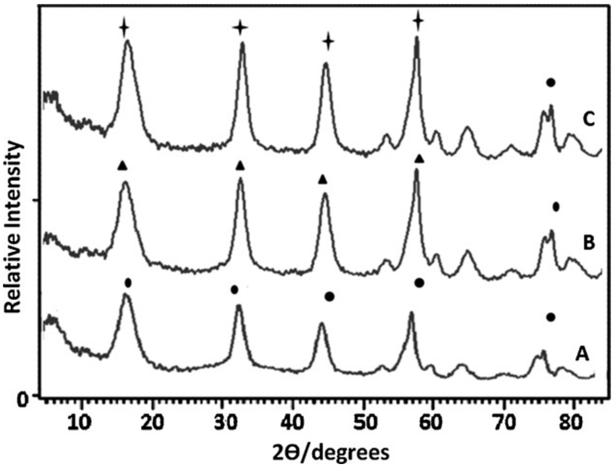


Fig. 3. Comparative XRD patterns of γ-Al_2O_3 without the MWCNTs prepared by a solvothermal method at 200 °C, for 6 h (pattern A), 12 h (pattern B) and 24 h (pattern C), ◆ Aluminum Oxide Hydrate), ● Aluminum Oxide Hydroxide), (▲ boehmite).

200 °C, for 6 h (pattern A), 12 h (pattern B) and 24 h (pattern C). The sample prepared at 200 °C for 6 h (pattern A) consisted mainly of crystalline aluminum hydroxide (boehmite-$Al_2O_3 \cdot H_2O$), with an orthorhombic structure (Ref: JCPDS21-1307).

When the reaction time was increased to 12 h (pattern B), the crystallinity of aluminum hydroxide, boehmite, was enhanced. When reaction time was increased further to 24 h (pattern C), a single phase of well-crystallized boehmite was obtained.

As the temperature was ramped up, transitional alumina phases formed from the boehmite. As mentioned in the literature [9,10], the sequence of the formed phases during the thermal treatment is anticipated to be:

Fig. 4 shows the XRD patterns of the calcined boehmite at 500 °C for 1 h, which is gamma alumina, the opened CNTs, the synthesized nanocomposite Al_2O_3@CNTs/Al_2O_3 prepared by solvothermal method at 200 °C for 24 h and calcined at 500 °C for 1 h under an Ar atmosphere. In pattern (a), the diffraction peaks at 16.845°, 32.882°, 44.855°, 57.491° and 58.002° were attributed to the (0 2 0), (1 2 0), (0 3 1), (0 5 1) and (2 0 0) planes of Al_2O_3 obtained from boehmite (JCPDS card no. 01-076-1871). In pattern (b), the peaks at 5.750°, 30.785° and 50.167° were identified as the (0 0 3), (0 0 2) and (1 0 0) reflections of graphite (marked with "C"), respectively. As shown in Fig. 4c, the two peaks from the $MWCNT_S$ are much lower than that of the opened CNTs, and a small shift was observed in comparison with that of the opened CNTs. Based

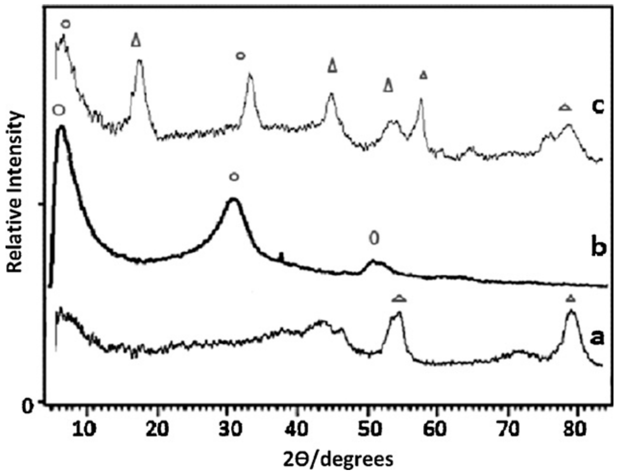
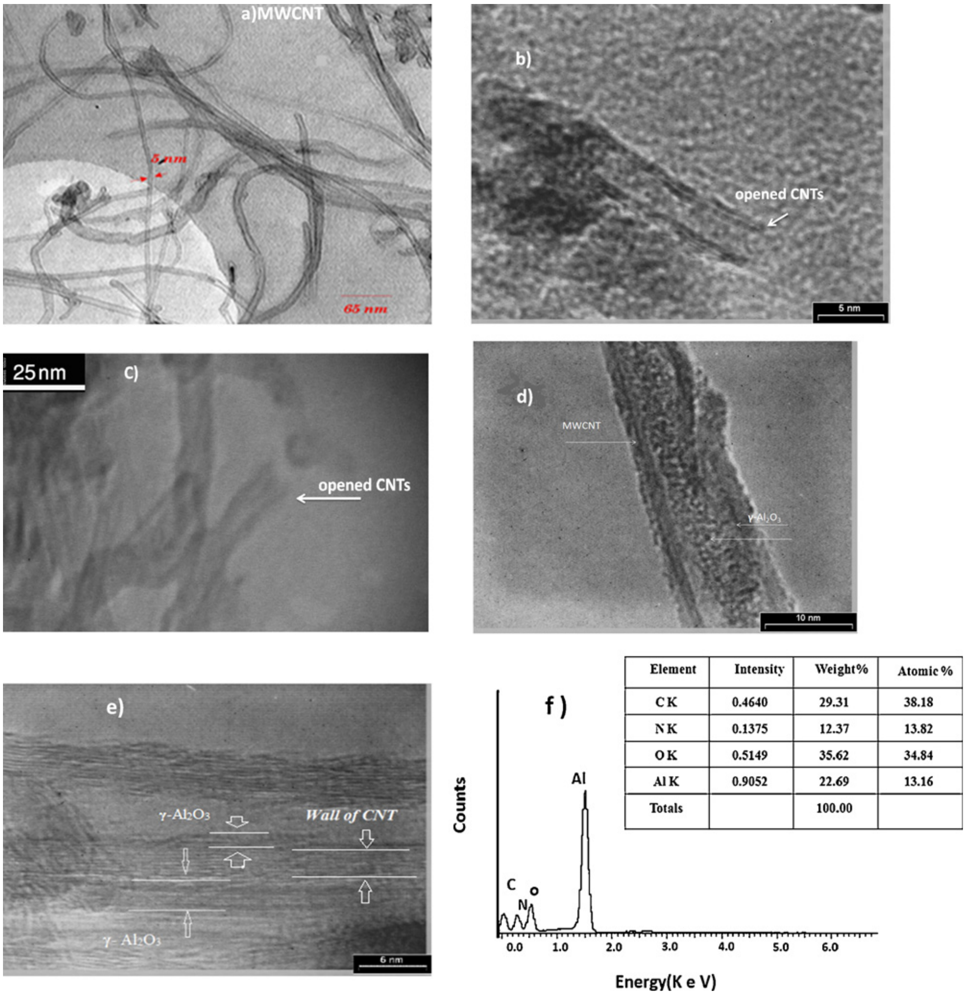


Fig. 4. The XRD patterns of (a) the calcined boehmite at 500 °C for 1 h, (b) the opened CNTs and (c) synthesized nanocomposite Al_2O_3@CNTs/Al_2O_3 calcined at 500 °C for 1 h under an Ar atmosphere (γ-Al_2O_3, MWCNT).



Element	Intensity	Weight%	Atomic %
C K	0.4640	29.31	38.18
N K	0.1375	12.37	13.82
O K	0.5149	35.62	34.84
Al K	0.9052	22.69	13.16
Totals		100.00	

Fig. 5. HRTEM and TEM images of (a) pristine $MWCNT_S$, (b, c) Opened tip of $MWCNT_S$ (d, e) γ-Al_2O_3/$MWCNT_S$ nanocomposite and (f) EDX spectrum of the nanocomposite.

on these data and the observed microstructure, the synthesized nanohybrid can be considered nanosized MWCNTs coated and filled with γ-Al_2O_3.

3.2. Surface tension

The surface tension of the solvent plays an important role in liquid phase methods for ex situ filling. Capillary action is the result of the interplay between surface tension and adhesive forces. The surface tension of water is 72 dynes/cm at 25 °C, which is very high for MWCNT filling. The surface tension of the ethanol solvent is approximately $26\ \mathrm{m\,N\,m^{-1}}$ at 20 °C, which is far below the threshold range (100–200 $\mathrm{mN\,m^{-1}}$) for MWCNT filling [2]. Ethanol combines a methyl group and a hydroxyl group in one molecule. The methyl group bonds very weakly with other methyl groups. The hydroxyl group is what makes ethanol soluble in water and creates the relatively high of surface tension. The opportunities for parts of an ethanol molecule to bond to another are far more limited than with water molecules. Triton X_{100}, a nonionic surfactant, has a hydrophilic polyethylene oxide group (on average, it has 9.5 ethylene oxide units) and a hydrophobic group. Thus, Triton X_{100} can cause maximal reduction of water surface tension in comparison with other surfactants [11,12].

Therefore, it were expected to be fully impregnated by the (Al (OH) $(C_2H_3O_2)_2$ by capillary suction via the solvothermal method.

3.3. Electron microscopy

Field emission scanning and transmission electron microscopy were used to detect possible morphological changes in the MWCNTs. Fig. 5(a) shows TEM images of pristine carbon nanotubes. Their length is 5–10 micrometers with closed cap. After oxidation with a strong oxidant such as nitric acid (Fig. 5b and c), it is clear that the cap of nanotube is opened and their length is shorter than compared to pristine carbon nanotubes. As could be seen from Fig. 5(d), that after solvothermal synthesis MWCNTs showed rough surface, indicating the intense deposition of nanoparticles. The homogeneous contrast of the γ-Al_2O_3 particles in Fig. 5(d) is an indication of encapsulated nanoparticles of γ-Al_2O_3 with a uniform distribution. The filled carbon nanotubes have darker contrast after filling, as shown in Fig. 5(c and d). Fig. 5(e) shows a HRTEM image of the Al_2O_3@CNTs/Al_2O_3 nanocomposite, illustrating the periodic walls of the MWCNTs and γ-Al_2O_3 coating layers. In addition, Fig. 5(b–e) shows the homogeneous and uniform γ-Al_2O_3 coating layers on the surface of MWCNTs, which is evidence of the attraction between the MWCNTs and γ-Al_2O_3 nanoparticles as a result of good functionalization of the surface of the MWCNTs.

In Fig. 5(f), the EDX spectrum of the nanocomposite with ratios of γ-Al_2O_3/MWCNTs:1, is shown in which C, O, N and Al are detected. The absence of the metal-catalyst-related peaks in the EDX spectrum indicates that the filled part is not metal catalyst. EDX analysis reveals that the weight ratio of O to Al is approximately equal to 1.5, suggesting that the layer coating the MWCNTs is Al_2O_3. The N-related peaks in the spectrum shows that the functional groups are present in the inner and on the outer wall of MWCNTs after treatment with nitric acid.

Under solvothermal conditions, aluminum acetate undergoes a decomposition to form acetic acid (CH_3COOH) and boehmite (γ-Al_2O_3). The aluminum acetate and ethanol decompose according to the following reaction under solvothermal conditions [13]:

$$Al(OH)(C_2H_3O_2)_2 + H_2O \rightarrow (\gamma\text{-}Al_2O_3) + 2CH_3COOH \tag{A.1}$$

The ethanol decomposition reactions generate radicals via C–C or C–O bond dissociation, including CH_3. These radicals can further react with abstracting H atoms, producing intermediates leading to C_2H_4, CH_4 and so on, according to Eqs. (B.2) and (B.3) [14]:

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \tag{B.2}$$

$$C_2H_5OH \rightarrow CH_3 + CH_2OH \tag{B.3}$$

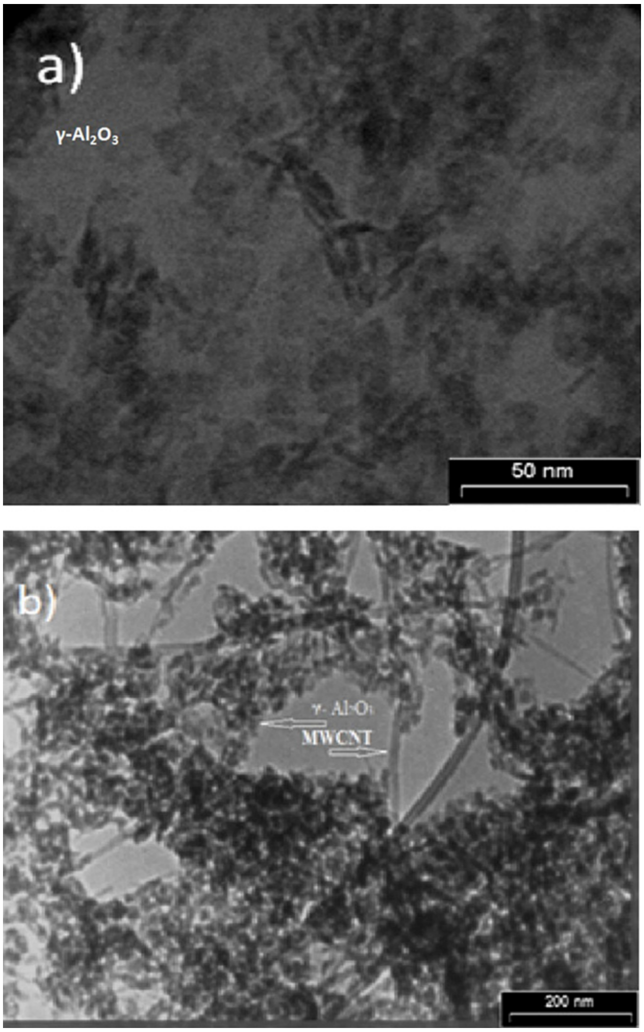


Fig. 6. TEM images of synthesized (a) gamma alumina, (b) Al_2O_3@CNTs/Al_2O_3 nanocomposite particles after thermal treatment at 500 °C for 1 h.

Carboxylic acid (COOH) and hydroxyl (OH) groups can attach to the surface or open ends of the MWCNTs during the solvothermal synthesis, effectively resulting in the functionalization of the MWCNTs. Subsequently, the aluminum ions in the solution are adsorbed at the inner wall and on the surface of the MWCNTs due to electrostatic attraction. Finally, γ-Al_2O_3 nanoparticles are formed in situ at the inner wall and on the surface of MWCNTs in a procedure similar to that proposed for the formation of carbon nanotube/boehmite- derived alumina ceramics obtained by hydrothermal synthesis [13].

Fig. 6(a) shows TEM images of the γ-Al_2O_3 crystals with a length of 30–40 nm and shows nanorods with diameters ranging from (10 to 30) nm, with lengths ranging from 50 to 100 nm. Fig. 6(b) shows γ-Al_2O_3/MWCNT nanohybrids particles indicating that MWCNT is covered with γ-Al_2O_3 particles.

The TEM, HRTEM and FESEM images show that the γ-Al_2O_3/MWCNT ratio greatly influences the morphology of the nanocomposite. Fig. 7(a, b), (c, d) and (e, f) show TEM and FESEM images of the nanocomposites obtained with 30, 50 and 70 vol% γ-Al_2O_3, respectively. When the volume ratio was higher or lower than 1, the γ-Al_2O_3 nanoparticles could not form a uniform cover on the surface of the MWCNTs and could not fill the MWCNTs. When the volume ratio reached 1, a uniform and homogeneous cover of γ-Al_2O_3 formed on the surface of the MWCNTs. In addition, encapsulated γ-Al_2O_3 clusters formed with a uniform density distribution.

3.4. BET analysis

Brunauer–Emmett–Teller (BET) gas-sorption measurements were performed to investigate the specific surface area of the γ-Al_2O_3, opened CNTs and γ-Al_2O_3/MWCNT (50/50) nanocomposites powders. The capillary adsorption data for the above samples was recalculated using the Barrett–Joyner–Halenda

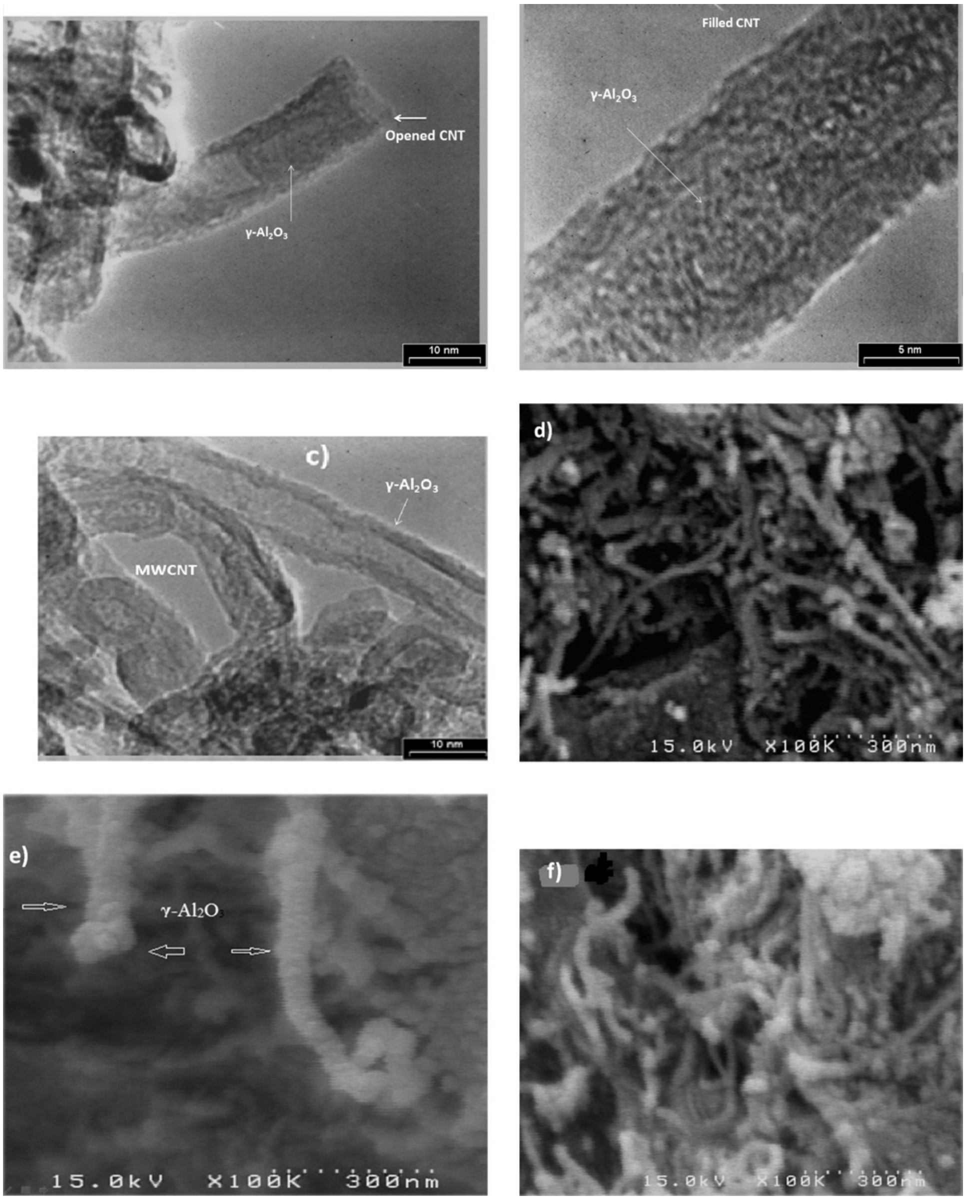


Fig. 7. TEM and FESEM images of synthesized nanocomposites at 500 °C for 1 h with different ratios of γ-Al_2O_3/MWCNTs: (a, d) 30/70, (b, e) 50/50, (c, f) 70/30.

Table 1
Nitrogen adsorption–desorption analysis data of pristine MWCNTs, opened CNTs, γ-Al_2O_3 and nanocomposite Al_2O_3@CNTs/Al_2O_3.

Sample name	S_{BET} ($m^2\ g^{-1}$)	MR_p (nm)	V_p ($cm^3\ g^{-1}$)
Pristine MWCNTs	330	14.35	1.18
Opened CNTs	244	18.31	1.1
Nanocomposite Al_2O_3@CNTs/Al_2O_3	236	8.03	0. 49
γ-Al_2O_3	181	10.94	0.49

(BJH) approach and did not reveal any meaningful increase in the specific surface area of the opened CNTs. This is related to the fact that the hydroxyl (OH) groups can attach to the surface and the inner wall of the MWCNTs during oxidation, which results in the functionalization of the MWCNTs [15,16]. The nanocomposite Al_2O_3@CNTs/Al_2O_3 show a slight increase in the specific surface area, with approximately unchanged pore size distribution, which may be due to the filling of the inner cavities of MWCNTs. BET surface area (S_{BET}), pore volume (V_p) and mean pore diameter (MR_p) of the γ-Al_2O_3, opened CNTs and nanocomposite Al_2O_3@CNTs/Al_2O_3 are shown in Table 1.

The nitrogen adsorption/desorption isotherms of the nanocomposite Al_2O_3@CNTs/Al_2O_3 (50/50) are presented in Fig. 8. Based on the available data [17], the nanocomposite Al_2O_3@CNTs/Al_2O_3 isotherm is type IV (BDDT classification). At relatively low pressure, $0.4 < p/p_o < 0.7$, the hysteresis loop is type H2, which can be observed in the pores with narrow necks and wider bodies [18]. We believe the hysteresis may be due to the behavior of γ-Al_2O_3, which blocks the pores of opened CNTs after the γ-Al_2O_3 nanoparticles fill the cavity of the opened CNTs. At relative high pressure, $0.7 < p/p_o < 1$, the isotherm loops is type IV, which is characteristic of mesoporous materials [19].

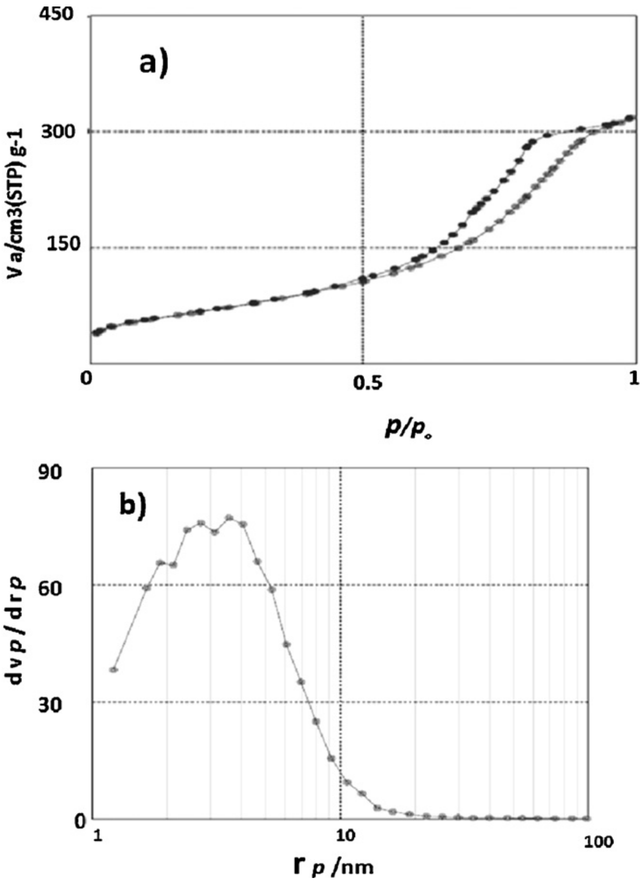


Fig. 8. (a) Adsorption/desorption isotherm and (b) Barrett–Joyner–Halenda (BJH) plots of the nanocomposite Al_2O_3@CNTs/Al_2O_3.

4. Conclusions

This investigation showed the successful synthesis of nanocomposite Al_2O_3@ CNTs/Al_2O_3 by a solvothermal method using aluminum acetate and opened CNTs. During this process, functional groups were modified on the MWCNTs. Our observations indicate that the solvothermal time, volume ratio of γ-Al_2O_3/MWCNT and the amount of Triton X_{100} had significant effects on the formation and morphology of the nanohybrids. It has shown that, after calcinations of the nanocomposite at 500 °C for 1 h, the resulting encapsulated nanoparticles and continuous MWCNT surface coating were γ-Al_2O_3 with a thickness of 1–3 nm. The results showed that the optimum volume of γ-Al_2O_3/MWCNT was 1:1.

References

[1] Dominik Eder, Carbon nanotube – inorganic hybrids, Chemical Reviews 110 (2010) 1348.

[2] M. Monthioux, E. Flahaut, J-P. Cleuziou, Hybrid carbon nanotubes: strategy, progress, and perspectives, Journal of Materials Research 21 (11) (2006) 2774.

[3] C.J. Ho, L.C. Wei, Z.W. Li, An experimental investigation of forced convective cooling performance of microchannel heat sink with Al_2O_3/water nanofluid, Applied Thermal Engineering 30 (2010) 96.

[4] J.S. Lee, B. Min, K. .Cho, S. Kim, J. Park, Y.T. Lee, N.S. Kim, M.S. Lee, S.O. Park, J.T .Moon, Al_2O_3 nanotubes an nanorods fabricated by coating and filling of carbon nanotubes with atomic-layer deposition, Journal of Crystal Growth 254 (2003) 443.

[5] Z. Talaei, A.R. Mahjoub, A.M. Rashidi, A. Amrollahi, M. Emami Meibodi, The effect of functionalized group concentration on the stability and thermal conductivity of carbon nanotube fluid as heat transfer media, International Communications in Heat and Mass Transfer 38 (2011) 513.

[6] F.A. Abuilaiwil, T. Laouil, M. Al-Harthil, M.A. Atieh, Modification and functionalization of multiwalled carbon nanotube (MWCNT) via Fischer esterification, The Arabian Journal for Science and Engineering 35 (No. 1C) (2010) 37–48.

[7] H. Chen, J. Shen, G. Longhua, Y. Chen, D. Kim, Cellular response of RAW 264.7 to spray- coated multiwalled carbon nanotube films with various surfactants, Journal of Biomedical Materials Research A 96 (2) (February 2011) 413–421.

[8] Z. Wang, M.D. Shirley, S.T. Meikle, R.L.D. Whitby, S.V. Mikhalovsky, The surface acidity of oxidized multi-walled carbon nanotubes and the influence of in situ generated fulvic acids on their stability in aqueous dispersions, Carbon 47 (2009) 73–79.

[9] A.C. Zaman, C.B. Üstündağ, N. Kuşkonmaz, F. Kaya, C. Kaya, 3-D micro- ceramic components from hydrothermally processed carbon nanotube- boehmite powders by electrophoretic deposition, Ceramics International 36 (2010) 1703.

[10] M. Ma, Y. Zhu, G. Cheng, Y. Uang, Solvothermal synthesis of boehmite and γ-Al_2O_3 nanorods, Journal of Materials Science Technology 24 (4) (2008) 637.

[11] V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis, C. Galiotis, Chemical oxidation of multi walled carbon nanotubes, Carbon 46 (2008) 833.

[12] K. Szymczyk, B. Jánczuk, The adsorption at solution–air interface and volumetric properties of mixtures of cationic and nonionic surfactants, Colloids and Surfaces A: Physicochemical and Engineering Aspects 293 (2007) 39–50.

[13] A.C. Zaman, C.B. Üstündağ, A. Çelik, A. Kara, F. Kaya, C. Kaya, Carbon nanotube/boehmite- derived alumina ceramics obtained by hydrothermal synthesis and spark plasma sintering (sps), Journal of the European Ceramic Society (2010).

[14] J. Li, A. Kazakov, F.L. Dryer, Experimental and Numerical Studies of Ethanol Decomposition Reactions, Journal of Physical chemistry A 38 (2004) 7671–7680.

[15] S. Bi, X. Su, G. Hou, G. Gu, Z. Xiao, Microstructural characterization of alumina-coated multi-walled carbon nanotubes synthesized by hydrothermal crystallization, Physica B 405 (2010) 3312–3315.

[16] H. Ogihara, S. Masahiro, Y. Nodasaka, W. Ueda, Synthesis, characterization and formation process of transition metal oxide nanotubes using carbon nanofibers as templates, Journal of Solid State Chemistry 182 (2009) 1587–1592.

[17] G. Li, Y. Liu, D. Liu, L. Liu, Ch Liu, Synthesis of flower- like Boehmite (AlOOH) via simple solvothermal process without surfactant, Materials Research Bulletin 45 (2010) 1487–1491.

[18] M.V. Chernysheva, A.A. Eliseev, A.V. Lukashin, Yu.D. Tretyakov, S.V. Savilov, N.A. Kiselev, O.M. Zhigalina, A.S. Kumskov, A.V. Krestinin, J.L. Hutchison, Filling of single -walled carbon nanotubes by CuI nanocrystals via capillary technique, Physica E 37 (2007) 62.

[19] L. Qu, Ch He, Y. Yang, Y. He, Z. Liu, Hydrothermal synthesis of nanotubes template by anionic surfactant, Materials Letters 59 (2005) 4034–4037.