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Growth of Carbon Nanotube Forests on Carbon Fibers with a SiO_2 Interlayer

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ABSTRACT

Ceramic barriers avoid catalyst diffusion to produce better multiwall carbon nanotubes (CNT) on carbon fiber fabrics (CF). We developed a simple method to produce efficiently a silica layer from TEOS pyrolysis at similar conditions of CNT growth from camphor and ferrocene mixtures. This protective layer prevents iron diffusion and allows the vertical alignment of CNTs.

INTRODUCTION

Nowadays the literature has given special attention in producing laminates with vertically-aligned carbon nanotube (CNT) films among the plies. This is known as "nano-stitching". Composites of ceramic fiber fabrics (SiC, Al_2O_3) coated with aligned CNTs have shown gains up to 348% at interlaminar fracture toughness (G_{IC}) [1-4]. Carbon fibers (CF) are more commonly commercialized than the ceramic fibers, but metal diffusion is a critical problem on growing CNTs on CF.

In 2010, our research group published a paper on deposition of amorphous silicon coatings on CF, before depositing vertically-aligned CNTs [5]. Although an efficient way to avoid iron diffusion, the plasma enhanced process used is not easily scalable. Other groups [6,7] have invested efforts in production of ceramic nanocoatings, mainly Al_2O_3 and SiO_2. Feng and co-workers [6] coated CF with Al_2O_3 from a 0,1 M solution of aluminum nitrate, followed by a heating to 250^{o}C at rating of 2oC/min. Fv and co-workers[7] got a solid SiO_2 coating from a hydrolysis, followed by a pyrolysis a solution of toluene with 5 vol.% tetraethoxy silane and 5 vol.% silicon tetrachloride.

At current work, we have developed a CF coatind made of amorphous-SiO_2 for deposition of vertically-aligned CNT from camphor/ferrocene pyrolysis. We established a simple way to coat the CF fabrics from TEOS pyrolysis, at similar conditions of CNT production. A study of the deposition time of SiO_2 layer evaluated the minimal thickness for this layer works as barrier against iron diffusion.

EXPERIMENTAL DETAILS

The SiO_2 layer was deposited on CF surface before CNT growth. Three pieces of the polyacrylonitrile-based CF cloths (Texiglass, CCS200) were simultaneously placed into the

oven. The reaction happened inside a quartz tube with 4 cm of internal diameter. Each piece sized 170 x 35 mm, but the reaction zone measured only 150 mm. The SiO_2 deposition was achieved by the decomposition of tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$) at 700 ºC, at selected times (1, 3, 5 and 10 min). Before pyrolysis step, the TEOS bottle was evacuated at 10^{-2} Torr, filled with N_2, heated at 140°C, and the vapor was carried to the reaction zone by a N_2 flow of 1.5 LPM.

The CNTs grew in the same oven. The CVD process was carried out at atmospheric pressure and at 850 °C. Carbon (camphor, $C_{10}H_{16}O$, 84% of the total mass) and the Fe catalyst (ferrocene, Fe $(C_5H_5)_2$, 16%) sources were evaporated at 200°C and carried into the quartz tube by a N_2 flow of 1.5 LPM. After 5 min of reaction, the vapors were cut down and the furnace cool down to room temperature under N_2 flow.

A JEOL JSM 5610 VPI scanning electron microscope (SEM), and a CM120 transmission electron microscope (TEM) from Philips enabled examining the SiO_2 and CNT morphologies. A Fourier transformed infrared spectroscopy (FTIR) equipment from Perkin Elmer, operated at the attenuated total reflectance (ATR) mode, confirmed the presence of amorphous SiO_2 coatings. Raman spectra, recorded from 1000 to 3500cm^{-1}, by using of a Renishaw 2000 system equipped with Ar laser (514.5 nm) allowed evaluating the crystalline quality of CNT produced on CF.

RESULTS and DISCUSSION

Figure 1 shows SiO_2 layer deposited on CF at (a) 1min, (b) 3 min, (c) 5 min, and (d) 10 min. The macroscopic aspect of SiO_2 layers are showed in Fig.1(a1-d1). Notice that all the three CF pieces with the SiO_2 layer acquire a homogeneous grey color for all extension of the reaction zone (15cm) after 3 min of deposition. Exhaustive tests were performed until the deposition area to be optimized, mainly about temperature parameter. Temperatures around 850°C promotes an excessively reactivity for TEOS decomposition, forming a great quantity of SiO_2 nanoparticles in homogeneous phase. Only 3 cm of deposition extension was achieved at 850°C, even increasing the N_2 flow. Figure 1(a2-d2) shows the morphology of SiO_2 surface that covers the fibers without interconnected them. At 10 min of deposition, a balls-like morphology is dominant. Figure 1(a3-d3) shows an analysis of the thickness of the SiO_2 layers. Although only a qualitative inspection has been done, it can be emphasized that the thickness does not follow a linear tendency. However what is truly important is that only 3 min of pirolysis is enough to cover completely the fiber.

The camphor/ferrocene pyrolysis yields high density aligned multi-walled CNT (MWCNT) forests on CF coated by SiO_2 layer. CNTs grow mainly on the surface CF, all around the CF but mainly pointing up from the cloth surface. Figure 4 shows the typical morphologies of CNTs grown on SiO_2 layer deposited at: (a) 1 min, and (b) 3 to10 min. The time of CNT growth was kept at 5 min for comparison. Notice that 1 min of SiO_2 deposition is not enough to prevent the iron diffusion and CNTs grows entangled (Figure 2(a1–a2)). The SiO_2 layers formed from 3min completely block the iron diffusion into CF, and CNTs films can grow vertically-aligned on CF (Figure 2(b1–b2)). The CNT films are 100 μm long (Figure 2(b2)), and CNT diameters range from 10 to 80 nm, as shown in the Figure 2c.

Spectroscopic analysis (Raman and FTIR) were performed on CF, SiO2 interlayer and vertically aligned CNTs. Figure 3a shows FTIR spectra of CF and CF coated by SiO_2, 1450 to 750 cm^1. The intense silicon–oxygen covalent bonds vibrations appear mainly in the 1200–1000 cm^{-1} range revealing the existence of a dense silica network, where oxygen atoms play the role of

bridges between each two silicon sites. The very intense and broad band appearing around 1050 cm^{-1} and the shoulder around 1200 cm^{-1} are assigned, respectively to the transversal optical (TO) and longitudinal optical (LO) modes of the Si-O-Si asymmetric stretching vibrations. The symmetric stretching vibrations of Si-O-Si appear at around 790 cm^{-1}. Furthermore, the Si-O in-plane stretching vibrations of the silanol Si-OH groups appear at around 934 cm^{-1}[8-10].

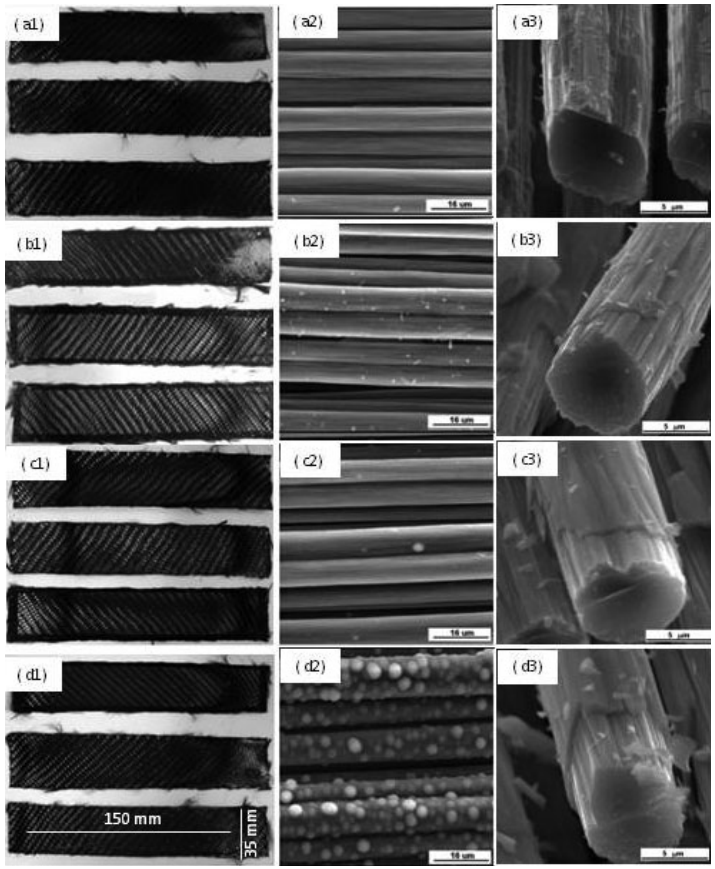

Figure 1: Silica layer deposited on CF at (a) 1min, (b) 3 min, (c) 5 min, and (d) 10 min. The numbers indicate: (1) photo of the 3 pieces of CF cloth with SiO_2 layer simultaneously deposited; (2) SEM image of SiO_2 on CF surface, and (3) the thickness of SiO_2 layers

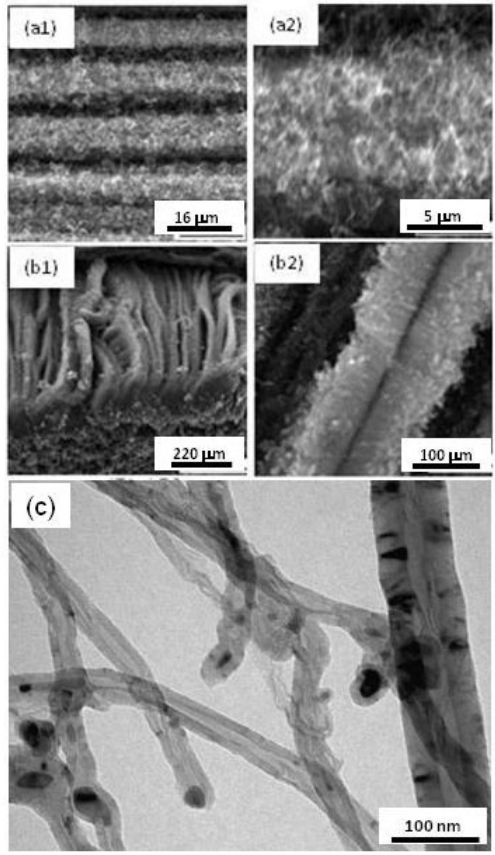

Figure 2: SEM images of typical morphology of CNTs grown at 5min on SiO_2 layer deposited at: (a) 1 min, and (b) 3 to10 min; (c) TEM image of internal structure of typical CNT. The numbers (1 and 2) indicate images with different magnifications.

The Figure 3(b) shows Raman spectra of CF and CNTs, both graphitic materials. The Raman spectra of graphite-like materials show four main bands: D (~1352cm^{-1}), G (~1582cm^{-1}), D' (~1600cm^{-1}) and G' (~2700cm^{-1}), analyzed by Ar laser (514.5 nm) . Usually, the relative intensity between D and G bands (ID/IG) indicates the crystalline degree of graphitic materials: as higher is this ratio, more disordered their chemical structure is [11-15]. Raman spectra of CF cloth from Texiglass are typical of PAN based CF, graphitized only to a 1000^{o}C, which implies

in a high I_D/I_G and $I_{G'}/I_G \sim 0$, i. e. a graphitic material with amorphous pattern. On the other hand, spectra with intensity of G' band compatible with the intensity of G band (IG'/IG ~ 1 or higher) indicate the presence of nanographite. Nanographites are composed or by few graphene sheets, either by turbostratic structures with distances among graphene sheets higher than at single crystals due to the curvature effects [16-18]. Therefore, high intensity G´ band is the signature of high quality multi-walled CNT.

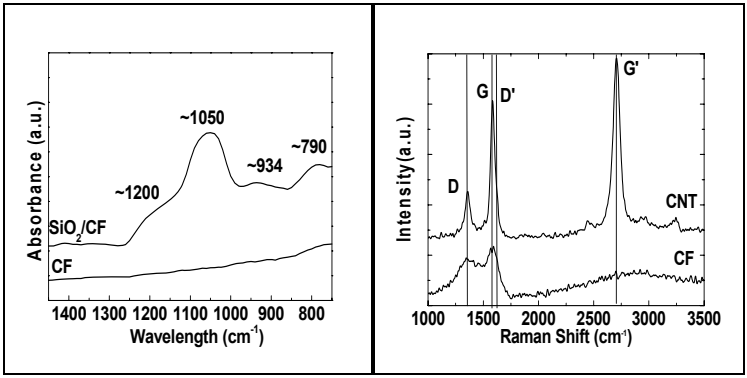

Figure 3: Spectroscopic analyses: (a) FTIR spectra of CF fabric and SiO_2 coating; (b) Raman spectra of the CF fabric and vertically aligned CNT film produced on SiO_2 layer.

CONCLUSIONS

There are two advantages of obtaining of SiO_2 by TEOS pyrolysis, besides the truly motivation of creating a diffusion barrier against Fe catalyst. The first one is its scalability, since CF cloths are submitted at the similar condition of CNT production. The other one is that the gas phase reactions warranty the formation of fiber coatings without interconnection among them, as occurs when liquid phase impregnation were used. This method also allows the thickness control of SiO_2 layer varying the deposition time. Silica depositions run at only 3 min already guarantee an uniform fiber coating , and vertically aligned CNTs on CF are successfully produced.

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