

Nanocomposites Based on Polyelectrolytes-Multiwalled Carbon Nanotubes Coated with a Silica Shell

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This work reports a simple and reproducible method for silica-coated multiwalled carbon nanotubes (MWCNTs) nanostructures by the sol-gel method using tetraethoxysilane and 3-aminopropyltriethoxysilane as organosilicon precursors of silica. The synthetic method is based on a noncovalent functionalization of the MWCNTs by the adsorption of the monolayers of different polyelectrolytes, such as poly(allylamine hydrochloride) and poly(sodium 4-styrene sulfonate), which are positively and negatively charged, respectively. The role of these polyelectrolytes is the dispersion and interaction with both the nanotubes and the silicon precursors, influencing directly the silica shell growth. Two different morphology types of the silica-coated multiwalled carbon nanotubes composites were obtained on multiwalled carbon nanotubes. In both case the samples displayed uniformity in the silica layer. Finally, the investigation of the photoluminescence spectra of the samples suggested the presence of some incorrect oxygen bond, or vacancy of oxygen or even presence of nitrogen in the network, which is a typical feature of materials prepared by the sol-gel process at room temperature.

Keywords: *Nanocomposites, Carbon nanotubes, Sol-gel process, Silica shell.*

1. Introduction

Since the discovery of fullerene by Kroto, and carbon nanotubes (CNTs) by Iijima, the synthesis, characterization and theoretical studies of carbon nanostructures and related materials have been very active research fields¹⁻⁵. The CNTs consist of graphitic sheets, which are rolled up into a cylindrical shape, and are characterized by chemical inertness due to the strong covalent sp² bonds of the carbon atoms on the nanotube surface, a unique one-dimensional structure and nanometer size. These features impart unusual properties to the nanotubes, including exceptionally high tensile strength⁶⁻⁹, high flexibility, low mass density, high thermal conductivity and electronic properties ranging from metallic to semiconducting, depending on the arrangement of hexagonal rings along the tubular surface¹⁰⁻¹³. A tremendous amount of work has been done on different aspects of CNT technology⁶⁻⁸. However, manipulation and processing of CNTs has been limited by the formation of big bundles held strongly together via van der Waals interactions, and their hydrophobicity and poor solubility in organic solvents, preventing their application in various areas¹³⁻¹⁵. The application of CNTs in various composites, the fabrication of films and macrofibers from CNTs, and the production of electronic, optical and optoelectronic components and devices often requires surface modification through functionalization

of CNTs to overcome such difficulties of the chemical processability^{4,13-15}. Different strategies have been suggested to overcome these problems of processability by surface modification, and can be divided into two main categories involving either noncovalent functionalization or covalent functionalization^{16,17}. Noncovalent CNT modification concerns the physical adsorption of aromatic molecules and/or wrapping of polymers to the surface of the CNTs, allowing them to be dispersed into water efficiently¹⁷. Noncovalent functionalization methods are mainly based on supramolecular complexation using various adsorption forces, such as van der Waals forces, π - π interactions and charge-transfer interactions¹⁸. Covalent functionalization occurs by using a highly reactive reagent¹⁸⁻²⁰. The main strategies used for covalent functionalization have included halogenation²⁰, cycloaddition^{21,22}, radical addition²³, ozonolysis²⁴ and oxidation processes^{4,8}. For several years, the oxidation process by mixed acids has been the standard method to break down and functionalize carbon nanomaterials^{3,4,25}. One typical example of covalent functionalization is the carboxylation of CNTs, which usually requires a tedious reaction process under strongly acidic conditions. The carboxylic acid group (COOH) is considered the prototype chemical group for such purpose because it can either serve as an anchor group for further functionalization, or be created by the covalent attachment of further groups^{10,11,17}. However, covalent functionalization causes fragmentation and defects in the hexagonal lattice of

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graphite, which affect the intrinsic structural properties of the nanotubes, including mechanical, thermal and electrical properties, thus the performances of CNT hybrid materials do not reach the goal level²⁶. Another important strategy toward obtaining composites involving heterostructures of CNTs is the noncovalent functionalization of CNTs. The main advantage of noncovalent functionalization compared with covalent functionalization is that it does not destroy the conjugated system of the CNT walls, and therefore it does not affect the final structural properties of the material¹³. Functionalization of the CNTs was used successfully to assemble silica-coated gold nanoparticles and gold nanorods^{27,28} as well as CdTe QDs^{13,29} and CdSe/ZnS³⁰ onto the surface of CNTs. The interest in the preparation of nanocomposites of polymers, nanoparticle or/and silica and carbon nanotubes (CNTs) has increased tremendously in recent years due to the synergistic effects resulting from the combination of these two classes of materials³¹. Combinations of nanomaterials that exhibit different properties, highly desirable for simultaneous and efficient technological applications, can be performed by assembling “building blocks” of several materials into nanocomposites, thereby providing bi-, tri- or multifunctionality³². Recently, silica-coated CNT composites are of interest because they are useful for the advancement of nanoscale sensors and electric devices as well as optical²⁹, mechanical reinforcement⁹ and templates for fabrication of silica nanotubes³³. The silica-coated multiwalled carbon nanotubes (MWCNTs) show the ability to prevent charge transfer and improve the nanomechanical properties of polymeric composites because the bending strength of CNTs is improved by the silica shell^{29,30}. Several methods have been explored to fabricate silica-coated CNT nanocomposites, such as synthesis of silica on noncovalently (using π - π interaction) or covalently (by forming a σ bond) functionalized¹⁶. However, despite using the techniques of functionalization of CNTs, many studies did not obtain composites with coated carbon nanotubes individually, with a homogeneous layer of silica, and some methods are comparatively complicated, or even are not suitable for large-scale production^{16,34}.

In this paper, we report on SiO₂ deposition on MWCNTs by the combination of noncovalent functionalization and sol-gel method to generate nanocomposites consisting of CNTs coated with a SiO₂ shell. Our approach is based on the noncovalent functionalization of CNTs, which has led to a high level of dispersion of the resulting products. The use of different polyelectrolytes, positively or negatively charged, allows us to investigate the influence of reagent order on the morphology of the resulting CNT-SiO₂ hybrid nanocomposites.

2. Experimental

2.1 Materials

MWCNTs (95% purity) were purchased from CNT Co. Ltd, Incheon, Korea, polyelectrolyte poly(sodium 4-styrene sulfonate) (PSS; MW ~70 000) (PSS) and the polyelectrolyte poly(allylamine hydrochloride) (PAH), tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APS) were obtained from Sigma-Aldrich.

2.2 Preparation of MWCNTs/Polyelectrolyte Suspension

In this study, we have produced composites based on the silica coating of MWCNTs. The synthetic process required initial nanotube functionalization for the dispersion in water of the MWCNTs, which were prepared by noncovalent functionalization using the polymer-wrapping technique by the adsorption of the monolayers of polyelectrolytes. The first composite prepared was based on functionalized MWCNTs with a cationic polyelectrolyte. The previous reported route was adapted²⁹, changing the reagent concentrations. In the second one, we employed the coating by using an anionic polyelectrolyte, PSS, for the subsequent growing of the silica shell.

The dispersion of MWCNTs by functionalization using cationic polyelectrolyte was performed using 0.045 g PAH as a polymer-wrapping agent for 0.030 g of the nanotubes in 50 mL of water under sonication for 4 h. For purification, the excess PAH was removed by several centrifugation/redispersion cycles, and then the supernatant was filtered in a microporous membrane and redispersed in distilled water by brief sonication. PAH provides stable dispersions of CNTs with amine functionalities. The material was labeled as PAH-MWCNTs.

The functionalization using anionic polyelectrolyte was performed using 0.030 g of MWCNTs in 50 mL of 1.0 mol L⁻¹ NaCl solution, where it was sonicated (40 kHz) for 3 h. Then, 0.100 g of PSS was added, and the resulting solution was stirred for 6 h. The dispersion was centrifuged for 1 h (3600 rpm), and the supernatant was discarded. The MWCNTs were redispersed in distilled water, filtered in microporous membrane and diluted in 50 mL of distilled water, to afford the material labeled PSS-MWCNTs¹³.

2.3 Coating of SiO₂ on MWCNTs

Silica coating using PAH-MWCNTs as template was carried out according to a modified version of the method described by Giersig et al.²⁷. In a typical procedure, 400 mL of ethanol containing 84.5 μ L TEOS was added to 100 mL of an aqueous solution of PAH-MWCNTs containing citric acid (1.85 \times 10⁻³ mol⁻¹ pH 3) under sonication for 1 h. Finally, APS (7.2 μ L) was added and the mixture, and homogenized by magnetic stirring for 30 min. After that, a solution of NH₄OH (4.2%) was added dropwise until pH 8 was reached. Subsequently, the solution was aged for 10 h at room temperature, obtaining the silica coating. The products were separated by centrifugation (3600 rpm), and

the precipitates were vacuum-filtered, washed in ethanol and redispersed in 50 mL of absolute ethanol.

In a typical synthesis of silica coating using PSS-MWCNTs as template, 30 mL of water containing PSS-MWCNTs was sonicated for 1 h. The above mixture was added to 80 mL anhydrous ethanol, and further sonicated for 1.5 h to form a stable dispersion. Immediately, 1 mL of NH_4OH and 0.2 mL of APS were added to the as-prepared MWCNTs dispersion. After that, a TEOS solution (0.8 mL TEOS in 40 mL ethanol) was added dropwise under vigorous stirring. The reaction mixture was stirred for another 12 h. Finally, the CNTs solution was centrifuged and washed with ethanol and once more redispersed in water. The resultant hybrid materials were designed as PAH-MWCNT- SiO_2 and PSS-MWCNT- SiO_2 . The processes described above lead to the formation of a uniform and thick layer of silica on every individual MWCNT.

2.4 Characterization techniques

Ultraviolet-visible (UV-vis) spectra were registered on a diode array UV-2550 Shimadzu spectrometer. Photoluminescence (PL) spectra were obtained at room temperature using a Shimadzu RF-5301 PC spectrofluorophotometer. The spectrofluorophotometer is equipped with a 150 W xenon lamp. The absorption and fluorescence measurements were typically performed with 10 mm-quartz cuvettes (Shimadzu) using air-saturated solutions at room temperature. The Fourier-transform infrared (FT-IR) spectra were acquired

on a PerkinElmer spectrometer (Spectrum GX), in the transmission mode; 32 spectra with 2 cm^{-1} resolution. Transmission electron microscopy (TEM) was performed on a JEM 2100 FEG-TEM operating at 200 kV. The grid used was 300-mesh Lacey Formvar with ultrathin carbon film. The scanning electron microscopy (SEM) was performed on a FEI Inspect F50. The zeta potential values of the dispersions were determined at a pH of 10.0 using a Delsa Nano C apparatus from Beckman Coulter. The pH values of the MWCNTs dispersions were adjusted to 10 by dropwise addition of 0.1 mol L^{-1} NaOH solution.

3. Results and Discussion

A simple, efficient and reproducible method for silica coating of MWCNTs with different SiO_2 coating thicknesses was applied. We have used the sol-gel method starting with TEOS and APS as silicon precursors, and carbon nanotubes coated with polyelectrolytes bearing positive and negative charges. We produced two types of CNT- SiO_2 nanocomposites with different silica shell sizes, PAH-MWCNT- SiO_2 and PSS-MWCNT- SiO_2 . The two processes described above lead to the formation of a uniform layer of silica on individual MWCNTs. The morphological structures of the PAH-MWCNT- SiO_2 and PSS-MWCNT- SiO_2 composites were investigated by TEM and SEM observation. Figure 1 shows the electron microscopy images of the silica-coated MWCNTs. The MWCNTs' thickness after silica coating increased to

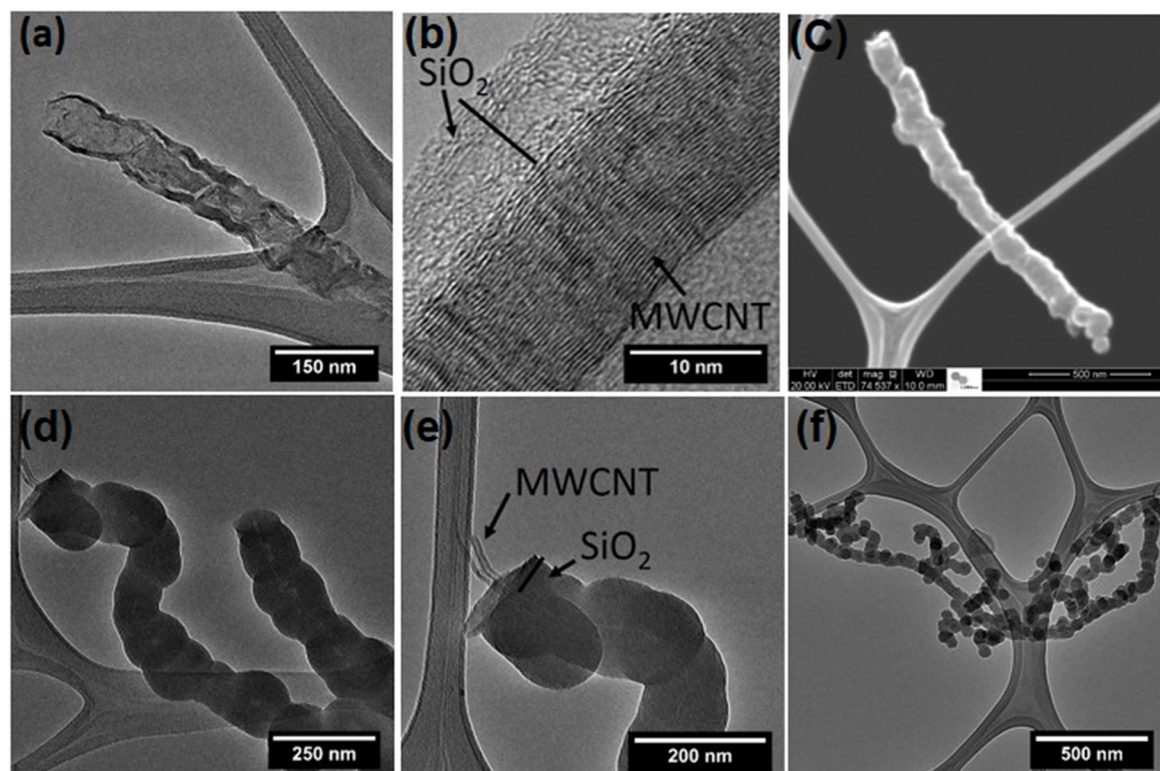


Figure 1. TEM (a) and (b) and SEM (c) images of PAH-MWCNT- SiO_2 ; TEM image (d), (e) and (f) of PSS-MWCNT- SiO_2 .

around 5 nm, as presented in Fig. 1 (a) and (b), for the PAH-MWCNT-SiO₂ and 50 nm for the PSS-MWCNT-SiO₂, as presented Fig. (d) and (e). The SEM image in Fig. 1(c) and the TEM image in Figure 1(f) clearly show that the SiO₂ layer is homogeneously coated on individual MWCNTs for the two methods used. The presence of roughening of the surface observed in some regions of the shells in Fig. 1 (a), (b) and (d) resulted from the coalescence of nanoparticles that originated at different nucleation sites on the carbon nanotube surface.

In the sol-gel process, the acidic or basic catalysts have a significant role in the formation of the final morphology^{35,36}. The reactions presented in Figure 2 can be used to explain the morphologies of the PAH-MWCNT-SiO₂ and PSS-MWCNT-SiO₂. The silica shell in the PAH-MWCNT-SiO₂ is thin because in the acidic catalyst the condensation of the silanol groups occurs more rapidly, which may result in the formation of a smaller silica layer on the surface of the carbon nanotubes, due to lower aggregation, Figure 2a. The acid/base catalysis incorporated more atoms in the structure, increasing the silica layer. The silica shell in the PSS-MWCNT-SiO₂ is formed by basic catalyst, in which the silica sol is based on spherical particles, Figure 2b. The synthesis in this condition produces a thicker layer formed by numerous spherical particles on the surface of carbon nanotubes due to the slower condensation.

The differences in the silica shell can also be related to the acid catalyst, which promotes the protonation of ethoxy groups, while in basic catalysis, the amino (-NH₂) basic group reacts preferentially with the silanol, affecting the condensation of these groups. In this case, growth is hindered and the particles formed will be smaller in size³⁶.

Figure 3 shows a scheme that represents the two different methods of applied functionalization of MWCNTs with the polyelectrolytes, PAH and PSS, as well as the coated silica layer. Surface modification by noncovalent functionalization using the self-assembly layer-by-layer technique allowed us to obtain PAH-MWCNT-SiO₂ and PSS-MWCNT-SiO₂ via electrostatic interactions between the charged surface

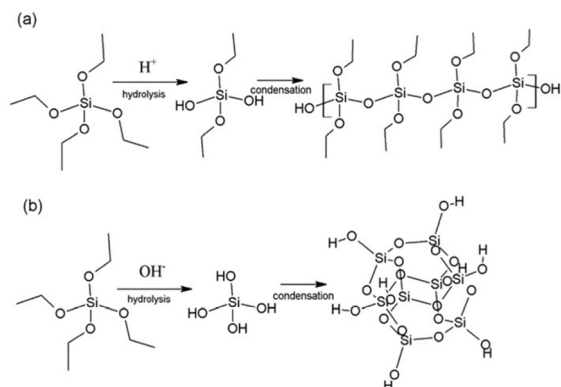


Figure 2. Schematic representation of the sol-gel reaction using (a) acid and (b) basic catalyst.

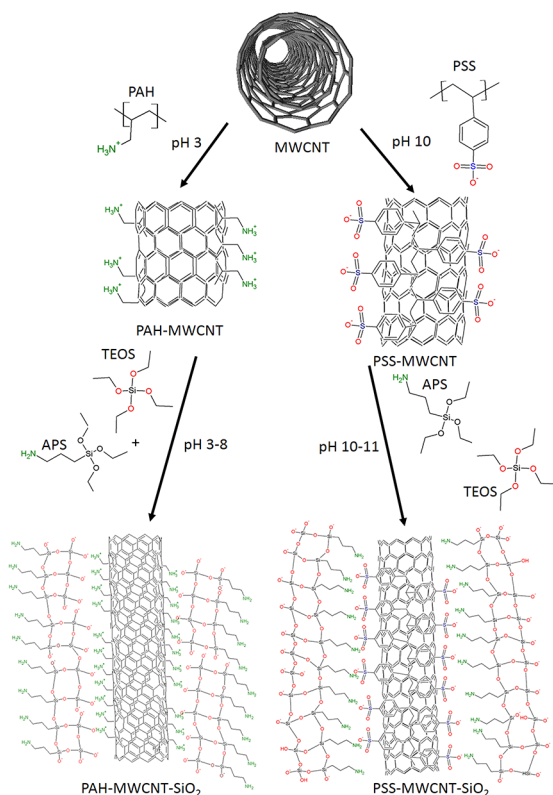


Figure 3. Schematic representation of the two synthetic routes used for the preparation of the PAH-MWCNTs-SiO₂ and PSS-MWCNTs-SiO₂, including the functionalization with polyelectrolytes PAH and PSS.

of the functionalized carbon nanotube and the charge of prehydrolyzed alkoxide precursor (TEOS and APS). These methods involved the dispersion of MWCNTs in water using two different functionalizations with the cationic and anionic polyelectrolytes, PAH and PSS, as polymer-wrapping agent, furnishing a stable dispersion (Figure 4). The dispersion stability is due to thermodynamic preference between polyelectrolyte and MWCNTs, as compared in the interaction between water and MWCNTs³⁰. This process suppressed the MWCNTs'

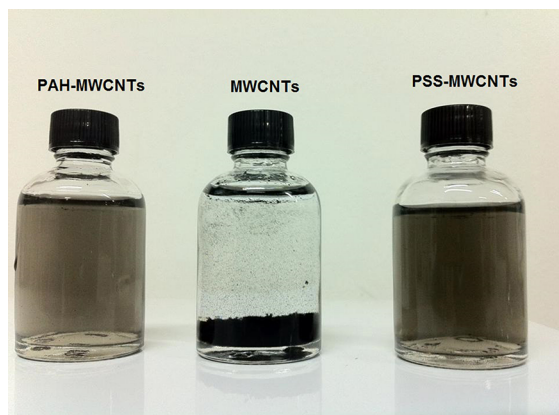


Figure 4. Photographs of aqueous dispersions of MWCNTs, PAH-MWCNTs and PSS-MWCNTs.

hydrophobic surface and generated a positive charge when functionalized with the PAH and negative charge with PSS. PAH-MWCNTs with positive charge at pH 3 can be formed via donor-acceptor interactions between MWCNTs and PAH, a weak polyelectrolyte. Indeed, in water at pH = 3 the PAH-MWCNTs materials displayed a positive charge (zeta potential (ζ) = +50 mV). PAH has an effective pK_a of ca. 8-9, being fully protonated in neutral and acidic solutions but partly deprotonated in slightly basic solutions. Multilayers can also be deposited in acidic or neutral aqueous solutions (pH of the PAH solution is 3.1 or 6.5), in which the amino groups of PAH are fully protonated, indicating the prevalence of the positive charge⁶. The high density of sulfonate groups in PSS confers a negative charge to this polyelectrolyte¹⁹ that, as a polyacid, is fully ionized above pH 3.5³⁷ Indeed, in water at pH = 10 the PSS-MWCNTs materials displayed a negative charge (zeta potential (ζ) = -49 mV). The high zeta potential values indicated that the colloidal dispersion was stable. These values are presented in Table 1.

When the cationic polyelectrolyte is used for wrapping the MWCNTs, a number of positive charges on the surface of the MWCNTs (see the zeta potential value in Table 1) can attract the silicate anions catalyzed by the hydrolysis of TEOS that will form uniform chains of silica on the surface of the nanotubes after condensation. Then, APS was added to the solution and the pH was adjusted to 8 to form more branched structures of SiO₂, increasing the thickness of the layer. However, the layer grows until ~5 nm. At acid pH, the composite PAH-MWCNTs-SiO₂ has a positive charge (zeta potential (ζ) = +19 mV) due to protonation of the amine group of the APS precursor. When the polyelectrolyte used to coat the carbon nanotubes has a negative charge, it will repel the silicate anions formed by the hydrolysis of TEOS; for that reason, the APS that has an amino group that can interact with the negatively charged nanotubes was used. Similar results have been reported by others¹⁴. On the other hand, using PSS-MWCNTs with a negative charge, the APS with the positive charge will interact with the SO₃⁻ groups from PSS (Figure 3) forming various nucleation centers for the growth of silica. The growth of the silica layer was performed using TEOS, which generates a negatively charged surface (zeta potential (ζ) = -12 mV) due the SiO⁻ groups. In this case, the thickness of the silica layer of the PSS-MWCNT-SiO₂ was 50 nm.

By analyzing the TEM images of the pristine MWCNTs (Figure 5), we can observe the morphology and tubular structure and that the carbon nanotubes have multiple walls, and that they agglomerate due to van der Waals interaction between the nanotubes. The MWCNTs did not contain impurities relative to the presence of catalysts employed during their synthesis; they did not present surface defects. The TEM images in Figure 5c and 5d showed that coating the MWCNTs with PAH and PSS not only dispersed the nanotubes without damaging their structure but also de-

Table 1. Zeta potential value (z) of MWCNTs coated with polyelectrolyte PAH, PSS and silica measured at different pH values.

Sample	Zeta potential (mV)	pH
PAH-MWCNTs	50	3
PSS-MWCNTs	-49	10
PAH-MWCNTs-SiO ₂	19	3
PSS-MWCNTs-SiO ₂	-12	10

agglomerated the MWCNTs bundles and showed an ultrathin polyelectrolyte layer as well as the absence of surface defects on the MWCNTs.

Figure 6(a) and 6(b) displays the FTIR spectra of commercially available PAH, PSS, MWCNTs and the prepared nanocomposites PAH-MWCNTs and PSS-MWCNTs. The pure MWCNTs do not exhibit absorption. The spectra of the MWCNTs coated with PAH and PSS are similar to the pure polyelectrolytes as well. In Figure 6(a), the absorption in the region 1600 cm⁻¹ is assigned to the stretching of the N-H bond. The band at 1069 cm⁻¹ is assigned to the stretching of the C-N bond of the polyelectrolyte (PAH). In Figure 6(b), the bands at 1228 and 1152 cm⁻¹ of the spectrum of PSS correspond to the SO₃ group asymmetric and symmetric vibrations, respectively. PSS-MWCNTs displayed all the typical absorption bands of commercial PSS, indicating successful functionalization of the MWCNTs.

The FTIR spectra of the PAH-MWCNTs-SiO₂ and PSS-MWCNTs-SiO₂ are shown in Figure 6(c). The absorbance band in the region 3400 cm⁻¹ is assigned to the stretching of the O-H bond, and the bands at 1100 and 950 cm⁻¹ are assigned to the asymmetric and symmetric stretching of the Si-O bond of silanol groups, which also confirms the successful coating of silica on MWCNTs. The characteristic bands related to the amino group appear at 1630 cm⁻¹ and 1550 cm⁻¹ and are assigned to N-H bonds. The absorption at 2854 and 2930 cm⁻¹ in Figure 6(a), (b) and (c) should be assigned to the C-H bonds from the CH₂ groups of the polyelectrolytes PAH and PSS. These bands suggest strongly that the MWCNTs were successfully encapsulated using the polyelectrolytes, and also with a silica shell, in the case of nanocomposites, because the absorption bands of these groups are present in the polyelectrolytes and nanotube-coated silica spectra.

An interesting property of organic and inorganic hybrid materials formed by the sol-gel process is the photoluminescence of these materials, which can serve as a probe for the quality of the silica network formed³⁸⁻⁴⁰. Figure 7 shows the PL spectra of the silica and the nanocomposites PAH-MWCNTs-SiO₂ and PSS-MWCNTs-SiO₂. The composite PAH-MWCNTs-SiO₂ presented an emission band at 426 nm (Figure 7a) while the silica nanoparticles synthesized under the same conditions without the use of functionalized nanotubes showed an emission at 434 nm. The emission spectra of

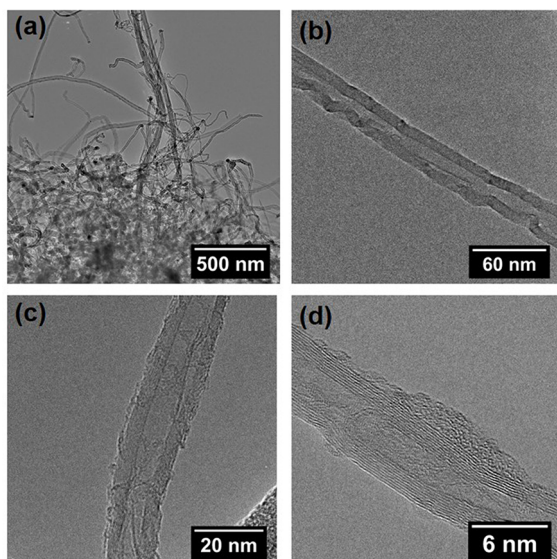


Figure 5. TEM images of the MWCNTs (a) and (b) PAH-MWCNTs, (c) and (d) PSS-MWCNTs.

the PSS-MWCNTs-SiO₂ (Figure 7b) presented an emission band at 392 nm while the nanoparticles synthesized under the same conditions showed emission 395 nm.

The origin of the photoluminescence in sol-gel derived silica has three possible mechanisms, defect mechanism, charge-transfer mechanism or the presence of carbon and nitrogen impurities³⁸⁻⁴¹. In addition, the sol-gel reaction used in these preparations can result in the formation of various defect centers, such as incorrect oxygen bond and the vacancy of oxygen that can form emission centers consisting of dioxasilirane =Si(O₂) and silylene, =Si: centers³⁹. The presence of the nitrogen atoms from the APS and PAH used for the synthesis of MWCNTs-SiO₂ can also have a similar effect as oxygen on the PL properties. In Figure 7, it can be seen that the PL spectra of the silica nanoparticles synthesized by the same method as the MWCNTs-SiO₂ are similar. However, the PL spectra of the PSS-MWCNTs-SiO₂ and PAH-MWCNTs-SiO₂ showed different maximum emission bands because of the local molecular environment, the number of nitrogen groups and pH used in the synthesis³⁸⁻⁴³. The PSS-MWCNTs-SiO₂ contains a larger number of nitrogen atoms in the silica layer than the PAH-MWCNTs-SiO₂, where the nitrogen atoms are on the surface of nanotubes, and in the outside part of the silica layer. These molecular environments are different because of the order of the reagents. Therefore, we can conclude that the silica shell was cross-linked as expected, with some incorrect oxygen bond, or vacancy of oxygen or even presence of nitrogen in the network detected from the analysis of PL spectra of these shells.

The study presented here shows that is possible to prepare nanocomposites based on MWCNTs covered with a thin SiO₂ shell that might be used in different fields of technological applications, such as support for catalysts or even as fillers

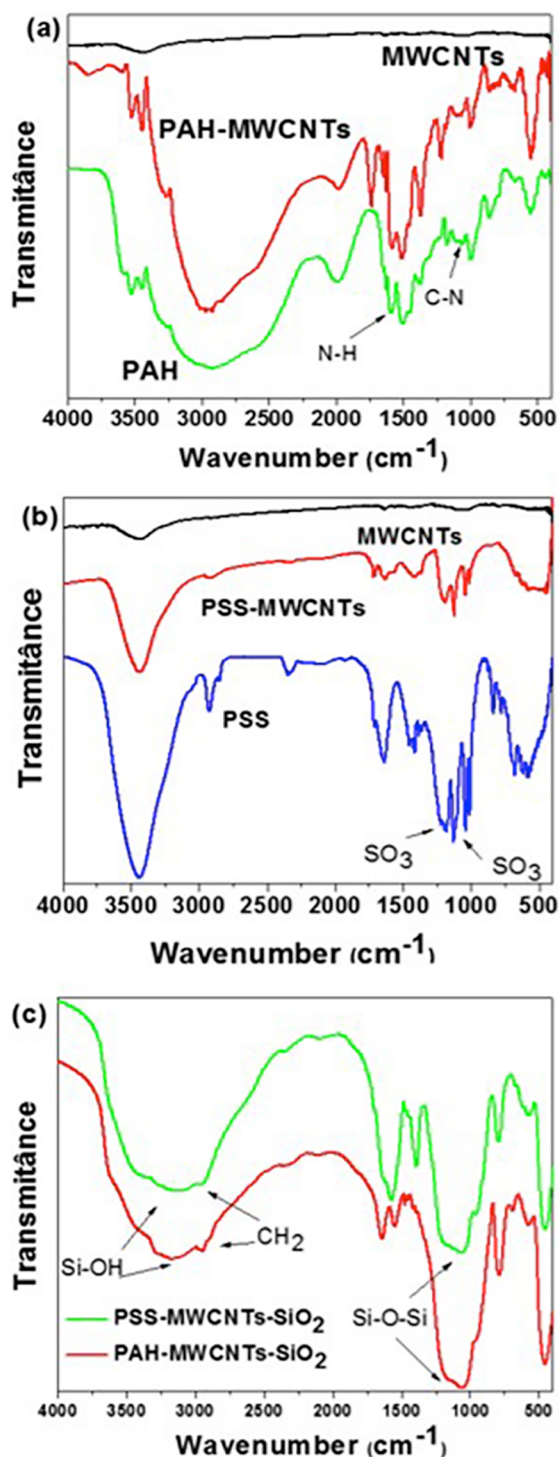


Figure 6. FTIR spectra of (a) MWCNTs, PAH and PAH-MWCNTs, (b) MWCNTs, PSS and PSS-MWCNTs and (c) PAH-MWCNTs-SiO₂ and PSS-MWCNTs-SiO₂.

in polymeric, ceramic or cementitious composites aiming to increase their mechanical properties.

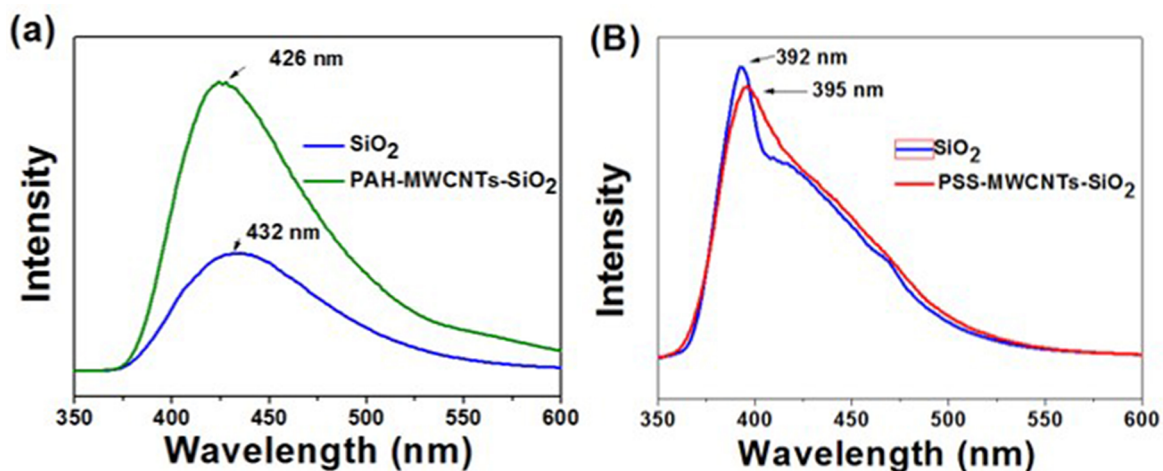


Figure 7. PL spectra ($\lambda_{\text{ex}} = 355 \text{ nm}$) of the silica nanoparticles and PAH-MWCNTs-SiO₂ and (b) silica nanoparticles and PSS-MWCNTs-SiO₂. The silica nanoparticles were prepared according to the specific procedures used to prepare the nanocomposites.

4. Conclusions

In this work, we have successfully synthesized MWCNTs-SiO₂ nanocomposites by simple methods using the self-assembly layer-by-layer technique on the basis of electrostatic interactions between MWCNTs and polyelectrolytes, and the sol-gel process to make a SiO₂ shell on the MWCNTs. The positively charged polyelectrolyte, PAH, and negatively charged, PSS, were used for the dispersion of MWCNTs and interaction with hydrolyzed silicon precursors, APS and TEOS, through electrostatic interactions with the charged surface of the carbon nanotube wrapped with the polyelectrolytes. The condensation of TEOS and APS on the carbon nanotube surface occurs due to the preferential nucleation through the electrostatic interactions, and guarantees a homogeneous deposition along the individual carbon nanotubes as shown by the TEM and SEM micrographs. The thickness of the nanocomposites, after silica coating, increased to around 5 nm for the PAH-MWCNT-SiO₂ and 50 nm for the PSS-MWCNT-SiO₂. The photoluminescence characterization of the resulting composites shows that although the SiO₂ shell well-fitted the MWCNTs, it might contain some incorrect oxygen bonds, or oxygen vacancy or even the presence of nitrogen in the network, which is a typical feature of materials prepared by the sol-gel process at room temperature.

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