JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 5, May 2007, p. 1422 - 1425

Mechanico-chemical interaction of single-walled carbon nanotubes with ZnO evidenced by photoluminescence and SERS spectroscopy

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Mechanico-chemical interactions of single-walled carbon nanotubes (SWNTs) with zinc oxide (ZnO) were investigated by surface-enhanced Raman scattering (SERS) and photoluminescence (PL). We show that SWNTs dispersed into a ZnO host matrix and compressed non-hydrostatically at 0.58 GPa forms a new organic/inorganic hybrid material. The typical PL emission of nanometric size ZnO particles changes gradually with the increase of the SWNTs concentration in the SWNTs/ZnO hybrid material. As a result of the mechanico-chemical interaction with SWNTs, the “green” band at 2.8 eV, attributed to oxygen vacancies of ZnO nanoparticles, decreases continuously until its complete disappearance.

(Received November 14, 2006; accepted April 12, 2007)

Keywords: Carbon nanotubes, Zinc oxide, Raman spectroscopy, Photoluminescence

1. Introduction

The possibility of combining inorganic and organic components in a more intimate way by means of covalent or non-covalent bonds has widely opened the fields of applications of inorganic/organic hybrid materials [1]. Two main approaches used to prepare composites consisting of organic materials and semiconductor crystals. The former involves the in-situ generation of crystals in the presence of organic compounds such as, for example, conducting polymers or carbon nanotubes (CNs) [2-4]. The latter consists in the dispersion of previously prepared micro and nano-crystals in organic materials [5]. In the present work, using a solid-phase mechanico-chemical reaction a new synthesis route for the preparation of a SWNTs/ZnO hybrid material is reported. The interest of using ZnO in the achievement of hybrid materials based on SWNTs is determined by the potential application of the ZnO-coated CNs as novel photoactive material [4]. Generally, a solid-phase mechanico-chemical reaction changes the phonon spectrum of the two constituents and Raman spectroscopy is then suitable to characterize it. Particularly, surface-enhanced Raman scattering (SERS), which induces enhanced Raman signals due to the resonant excitation of surface plasmons [6], is appropriate for such investigations. Different reaction products have been reported for the solid-phase mechanico-chemical reactions between SWNTs and compounds as KOH, KI, Ag and aromatic hydrocarbons with isolated and condensed phenyl rings [7, 8]. Often, a non-covalent, covalent and/or ionic functionalization of CNs has been invoked. This paper demonstrates by photoluminescence (PL) and SERS spectroscopic studies the production of mechanico-chemical interactions between single-walled carbon nanotubes (SWNTs) and zinc oxide (ZnO).

2. Experimental

SWNTs were produced by the electric arc technique [9]. ZnO was purchased from Aldrich. CNs dispersed in ZnO powder were compressed non-hydrostatically for 5 min. at 0.58 GPa. The resulted samples, in form of pellets, were ultrasonically dispersed in toluene. Films of 150 nm thickness were prepared by evaporation of toluene from a known amount of solution spread on the rough Au substrate. SERS studies were performed in a backscattering geometry, under laser excitation wavelengths 1064 and 676.4 nm, using a RFS 100 FT Raman Bruker and a Jobin Yvon T64000 Raman spectrophotometer, respectively. Photoluminescence (PL) spectra were obtained on the SWNTs/ZnO pellets in a right angle geometry using a Jobin Yvon Fluorolog-3 spectrometer under a 265 nm light excitation.

3. Results and discussion

Fig. 1 shows the variation of PL spectrum of SWNTs/ZnO composites as a function of the SWNT concentration in the mixture. We notice that in all cases the PL spectra are dominated by the emission of ZnO. The PL spectrum of the ZnO platelets without addition of SWNTs consists in two main bands. A narrow one, peacking at about 3.26 eV, is generated by a radiative recombination of excitons [10]. Another one, broader, with a maximum at 2.2 eV is a complex band which reveals by decomposition two Gaussian components whose spectral width is about 0.6 eV FWHM. The two components labeled as “orange” and “green” bands are detected at 2.2 and 2.8 eV. The former is associated with a local oxygen excess while the second one is attributed to local oxygen vacancies [11-13]. These two bands in the general concept of ZnO luminescence, are associated with the surface fluorescence centres.

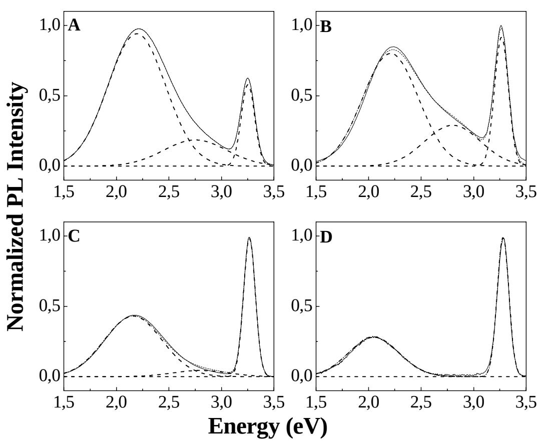

Fig. 1. PL spectra of ZnO (a) and the SWNTs/ZnO hybrid materials. SWNTs concentration in hybrid material is of: 0.1 (b), 1 (c) and 10 wt% (d).

By adding different masses of SWNTs to the ZnO host matrix (0, 0.1, 1 and 10%, Figs. 1a, b, c and d, respectively), a systematic change of the relative strength of the band-edge PL peak is seen in Fig. 1. This is noticed by the modification of the ratio between the intensity of the broad band at 2.2 eV and the UV band (3.26 eV) from 1.5 to 0.36 when the SWNT concentration in the ZnO matrices varies in the range 0-10 wt%. Recently, a similar variation of the PL spectrum has been reported both for ZnO films with different layer thicknesses, i.e. between 0.16-0.95 μm [14], and poly(vinyl pyrrolidone)-modified ZnO nanoparticles [15]. Besides, increasing the SWNTs amount in the SWNTs/ZnO mixture, we remark a gradual decrease in the intensity of the “green” band until to its complete disappearance. It is worth noticing that the same PL spectrum, illustrated in Fig. 1 d, has been reported for different ZnO nanoparticles of the type whiskers [16] and nanowires [17]. In the latter case, a dependence of the variation of luminescence peak intensity ratios as a function of the average wire radius was established, too [18]. In our case, when by charge transfer process is formed of a new hybrid material, the modification of the typical luminescence of ZnO by interaction with SWNTs is due to the change of the nature and density of lattice defects involved in the excitonic recombination. Besides, additional information are obtained by SERS spectroscopy. We remind that when there is no interaction between both constituents, the Raman spectrum appears as a modulated sum resulting from the separate contribution of ZnO and SWNTs. Raman lines at 376, 438 and 581 cm^{-1}, observed in Fig. 2, belong to ZnO [19]. The Raman line at 438 cm^{-1} is attributed to the ZnO non-polar optical phonon E_2 mode, which is typical of one Raman active branch. The peak at 376 cm^{-1} corresponds to an A_1 mode and the Raman line with maximum at 581 cm^{-1} is associated to a ZnO E_1 (LO) mode. Having a fast look on Fig. 2 and 3, SERS spectra recorded on SWNTs/ZnO films show significant changes as a function of the SWNTs concentration used for the preparation of these samples.

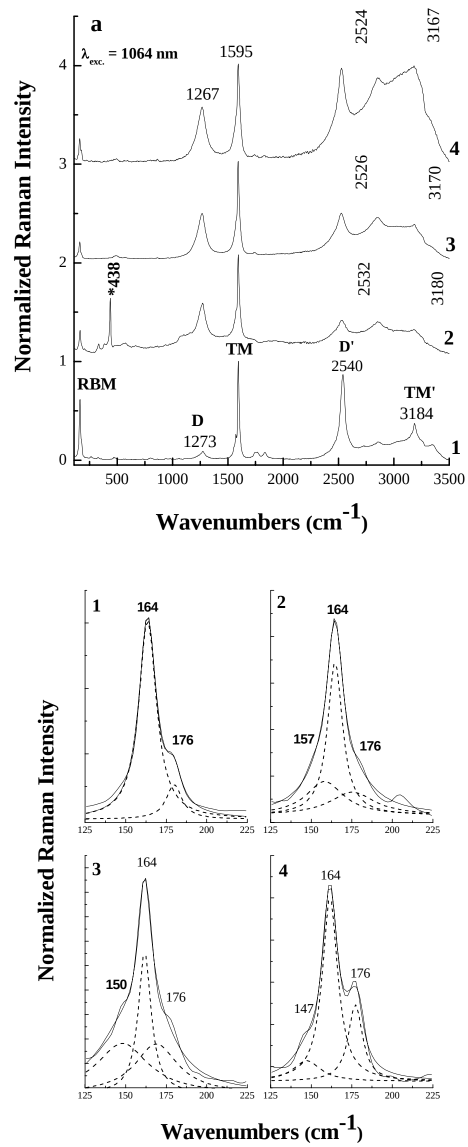

Fig. 2. SERS spectra ($\lambda_{exc.}$=1064 nm) of SWNTs (curve 1) and the SWNTs/ZnO hybrid materials with a SWNTs concentration of: 0.1 (curve 4), 1 (curve 3) and 10 wt% (curve 2).

To illustrate the chemical transformation of SWNTs, two Raman spectral ranges are of interest: 50-250 and

1100-1700 cm^{-1}. In the former interval, one finds bands associated to radial breathing modes (RBM) [20,21] whose peak position is sensitive to the excitation wavelength. Radial bands at 164 and 176 cm^{-1}, under 1064 and 676.4 nm excitations, indicate a resonance effect occurring over a narrow range of diameters around 1.35-1.30 nm, identified with transitions between the Van Hove singularities E_{22}^{S} and E_{11}^{M} in the valence and conduction bands of semiconducting and metallic tubes, respectively [21]. In the range 1100-1700 cm^{-1}, the bands, labeled TM and D, are displayed with changes in frequency, line-shape and intensity under various excitations. The former, with a maximum at 1595 cm^{-1} attributed to tangential mode (TM) vibration is also present in the Raman spectrum of other graphitic materials, like HOPG, glass carbon, etc. [22]. A specific signature of the metallic tubes is found under laser energies between 1.5-2.2 eV. Thus, at λ_{exc}. = 676.4 nm, the Raman spectrum contains in a broad TM band asymmetrical in its lower energy side with a Breit-Wigner-Fano profile, peaking around 1540 cm^{-1}, that indicates an electron–phonon interaction [23]. The D band whose peak position depends on the excitation energy, found both in SWNTs and graphite compounds, is frequently associated with a disorder in the graphitic lattice or defects in nanotubes [22]. Another group, located in the high frequencies range from 1700 to 3500 cm^{-1}, corresponds to the second-order Raman spectrum. As a rule, the most intense bands are those detected at approximately twice the frequency of the D and TM bands. Like their first-order counterparts, they behave resonantly when the excitation wavelength is changed. The decrease of the CNs concentration in the SWNTs/ZnO hybrid material (10, 1 and 0.1 %wt) induces the following changes in the SERS spectra recorded at the 1064 nm excitation light (curves 2, 3 and 4, respectively in Fig. 2): i) a gradual increase in the intensity of the D band, which is accompanied by a shift of its peak to lower energy, i.e. from 1273 at ca. 1267 cm^{-1}; ii) a down-shift of the D' and TM' bands of ca. 16 cm^{-1}; and iii) a decrease in the intensity of the bands situated at 164 and 176 cm^{-1} and the appearance in the RBM range of a new line situate at ca. 157 cm^{-1}.

A similar behavior is observed for the SWNTs SERS spectra recorded at 676.4 nm excitation light (Fig. 3). Independent of the SWNTs weight in the CNs/ZnO mixture, we remark a sudden disappearance of the asymmetric profile of TM band, the abrupt increase in the intensity of the D band and a gradual decrease in the intensity of the RBM band. In our opinion, these results highlight that the BWF profile is extremely enhanced in bundles and almost non-existent in isolated SWNTs, as predicted theoretically [24, 25] and previously reported [25-27].

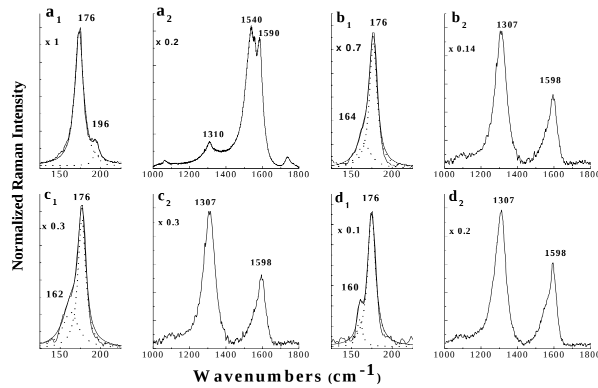

Fig. 3. SERS spectra ($\lambda_{exc.}$= 676 nm) of SWNTs (curves a_1, a_2) and the SWNTs/ZnO hybrid materials with a SWNTs concentration of: 10 wt% (curves b_1, b_2), 1 (curves c_1, c_2) and 0.1 (curves d_1, d_2).

The presence of a great number of isolated SWNTs in the SWNTs/ZnO samples as result of the mechanico-chemical reaction is also confirmed of the spectral modifications in the RBM range. As it is well-known, for $\lambda_{exc.}$ = 676.4 and 1064 nm, in the 125-250 cm^{-1} spectral range, the two bands at 176/196 cm^{-1} and 164/174 cm^{-1}, respectively, have been attributed to the RBM of CNs in the isolated and bundled states [28]. For $\lambda_{exc.}$ = 676.4 nm, we observe almost in totality the disappearance of the band at 196 cm^{-1} and the appearance of another one situated at 164 cm^{-1}. For the moment, a clear explanation for the presence of the Raman bands at 164 and 157 cm^{-1} in the SERS spectrum recorded at both 676.4 and 1064 nm excitations, respectively is difficult. However, the appearance of these bands in the hybrid material has to be considered as a result of a solid-phase mechanico-chemical interaction between ZnO and SWNTs. Depending of the SWNTs concentration in the hybrid material, a down-shift of the RBM bands with the maximum at 157 and 164 cm^{-1} to 147 and 160 cm^{-1} is observed in Figs. 2 and 3, respectively. We note that, a rather similar down-shift was reported in the case of alkali-doped SWNTs [29]. This fact suggests that a chemical interaction between SWNTs and ZnO involves a charge transfer process. Understanding this particular behavior should involve further research. However, the data presented here are more than sufficient to show that the solid-phase mechanico-chemical reaction between SWNTs and ZnO involves in the first stage a housebreaking of bundle into individual CNs and afterwards a charge transfer between individual CNs and ZnO, similar with those reported for alkali-doped SWNTs, which results in an ionic functionalization of SWNTs.

4. Conclusions

This paper reports new results obtained by photoluminescence (PL) and SERS spectroscopy concerning the synthesis of a SWNTs/ZnO new hybrid material. Our results allow to draw the following conclusions: i) the solid-phase mechanico-chemical reaction between SWNTs and ZnO results in a new hybrid material consequence of a charge transfer between the two constituents; ii) the PL spectrum of the SWNTs/ZnO hybrid material is featured by a intense band at 3.26 eV associated to the radiative recombination of excitons and a weak band at 2.2 eV assigned to residual regions of ZnO with local oxygen excess.

Acknowledgements

This work was performed in the frame of the Scientific Cooperation between the Laboratory of Crystalline Physics of the Institute of Materials in Nantes and the Laboratory of Optics and Spectroscopy of the National Institute of Materials Physics in Bucharest. This work was supported by NATO reintegration grant RIG-981483.

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