Photoluminescence of poly (N vinylcarbazole)/carbon nanotubes composites

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The photoluminescence (PL) of two types of poly (N-vinyl-carbazole)(PVK)/carbon nanotubes (CN) composites, prepared by chemical and electrochemical method, has been investigated. In comparison with the pure PVK, the chemically prepared PVK/NC sample shows a significant PL quenching and a shorter decay time. For the samples prepared electrochemically, PL increases in intensity, red shifts and gets longer decay time with the increase of voltammetric cycles number. In addition, the latter shows a change in emission from high-energy excimer to low-energy excimer after a treatment with NH_4OH.

1. Introduction

Combining carbon nanotubes with polymers one can obtain composites with new interesting properties. One of these is the compound PVK / CN, which due to a wide range of applications such as sensors, supercapacitors, advanced transistors, high-resolution printable conductors, electromagnetic absorbers, photocells, photodiodes and optical limiting devices, has received an increasing attention [1].

The PVK/CN composite obtained by bulk polymerization of N-vinyl-carbazole (VK) in the presence of CN was studied by photoluminescence (PL), Raman scattering, and Fourier transform infrared spectroscopy [2]. The presence of CN induces a reduction of the PL efficiency of PVK and the appearance of a new emission band at about 500nm whose intensity increases as the nanotubes weight grows into the synthesis mixture.

The mechanism of electropolymerization of VK on single-walled carbon nanotubes (SWNT) film was studied by Baibarac et al. [1, 3]. The difference between the product resulted from the electrochemical polymerization of VK on an alone Pt electrode and the product obtained on the same electrode covered with a SWNT film consists in a charge transfer complex that appears in the later case in the first stage of reaction, it being formed from a VK radical cation and a SWNT radical anion. Using IR and Raman spectroscopy, it was demonstrated that the electrochemical polymerization of VK onto CN electrode results in a covalent functionalization of CNs with PVK.

In this paper we report the studies of steady state PL and PL decay time in a series of PVK/CN samples prepared by chemical and electrochemical methods.

2. Experimental

The monomer VK, benzene, azo-bis-izobutyronitrile (AIBN) and methanol (CH_3OH) had Merck purity. For the chemical synthesis of PVK one used 2 g of NVK dissolved in 20 cm^3 of benzene to which 0.08g AIBN was added. Before starting the polymerization the reaction mixture was bubbled with argon for 5 min. The polymerization reaction took place at 80 C for 10 hours. The interruption of the polymerization reaction was performed by cooling at room temperature re-precipitating the synthesis mixture with 60cm^3 of CH_3OH. The obtained precipitate was then washed with 200ml of CH_3OH and then filtered. To remove the residual reactants, the synthesis mixture was re-dissolved in benzene and then reprecipitated with CH_3OH. The drying of PVK was carried out in vacuum for 5 hours.

In the case of the composites of PVK/SWNT a similar procedure was applied. The only difference was that in the volume of 20cm^3 of benzene were added ca 0.03g SWNTs (PVK/CN).

The electrochemical polymerization of VK was obtained by cyclic voltammetry in the potential range of (-0.8; +1.8) V vs Ag/Ag$^+$. For this purpose a conventional cell with three electrodes was used as follows: the working electrode was a blank plate of Pt with the aria of 1 cm^2 and respectively, covered with ca 100nm thick film of SWNT, an auxiliary electrode consisting of a spiral of Pt and a referential electrode of the Ag/Ag$^+$ type. The electrochemical cell was connected to a potentiostat/galvanostat of the VOLTALAB 80 type from Radiometer Analytical. The synthesis mixture consisted of 6 10^{-3} M VK and 10^{-1} M $LiClO_4$ in acetonitril (CH_3CN). The sweeping speed used for the potential range (-0.8; +1.8) V vs. Ag/Ag$^+$ was 100mVs^{-1}. Before starting the electrochemical polymerization, a bubbling with Ar for 20 min was carried out.

The steady state PL emission and excitation spectra were taken with the Horiba Jobin Yvon Fluorolog, model FL-3.22 and the PL decay measurements were performed using the time correlated single photon counting (TCSPC) accessory of the Fluorolog. All the PL decay measurements were done at the excitation wavelength of 281nm.
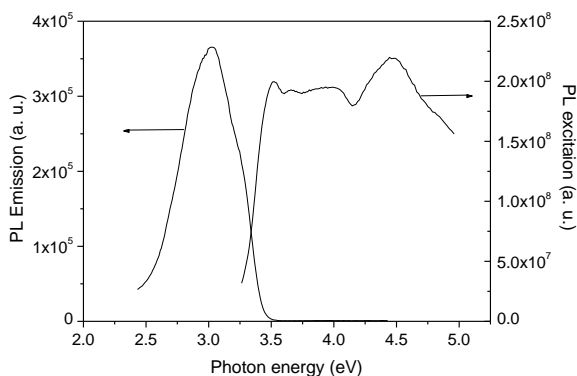

Fig. 1. PL of pristine PVK at room temperature (left) and the PL excitation spectrum of pristine PVK at the emission wavelength of 400nm (right).

3. Results and discussion

As shown in Fig. 1, the PL of the pristine PVK powder excited at 260nm (4.77 nm) exhibits a single structureless band peaking at 3.018 eV (410 nm), that we assign to the low energy excimer [4, 5]. "An excimer is a dimeric or heterodimeric molecule formed from two species, at least one of which is an electronic excited state"[6]. It is well known that in PVK two types of excimers can be created: one of low-energy and the other one of high-energy. The low-energy excimer has a sandwich structure formed from two fully overlapped carbazole groups and the high-energy excimer is a specie involving two partially overlapped carbazole groups [5].

Fig 1 shows also the PL excitation spectrum of PVK recorded at the emission wavelength of 400nm. It shows several distinct bands located at; 4.48 eV (277 nm), 3.94 eV (315nm), 3.66 eV (339nm), and 3.51 eV (353nm). PL emission is 0.37 eV Stokes sifted in comparison with the band gap edge revealed by the associated excitation spectrum.

Fig. 2a presents the PL of PVK/CNs powder obtained by bulk polymerization of VK in the presence of CNs compared to the PL of pristine PVK. Exciting the composite at 260nm, only the polymer is excited and the PL spectrum of the composite show similar emission features with that of the pristine PVK, indicating that the luminescence predominantly results from low-energy excimer. However, the intensity of the PL emission of the composite decreases substantially, fact which shows that less PVK excimers are formed in the presence of CNs or a

charge separation occurs at the interface between the two materials.

The steady state PL of the samples obtained by bulk polymerization of PVK in the absence and presence of the SWNT was studied in ref [2]. It was shown that the PL efficiency of PVK reduces and a new band around 500nm (2.48 eV) appears when CNs is added to the synthesis mixture.

In Fig. 2b the PL spectra of the electrochemically prepared samples are displayed. The strongest PL band (curve 1) corresponds to PVK deposited on a blank Pt electrode after 100 voltammetric cycles were carried out in the VK/LiClO$_4$ /CH$_3$CN solution. It discloses a maximum at 3.18 eV (389nm), a shoulder at 3.05 eV (407 nm) and a low energy tail which extends up to around 2.04 eV (600nm). The rest of the PL bands belong to the PVK/SWNT/Pt samples which were synthesized during different number of voltammetric cycles (100 cycles (curve 2), 50 cycles (curve 3) and 25cycles (curve 4)) on the Pt electrode coated with a SWNT film. Their peaks are located as follows: 3.25 (382 nm), 3.29 eV (377 nm), and 3.33 eV (372 nm) for the band 2, 3, and 4, respectively. Taking into account the positions of the PL maxima of the electrodeposited samples, we are tempted to say that the PL originates mainly from the high energy excimer of PVK, fact which could be related to the short length of the polymer chain in the composite. One can also notice that the PL intensity increases and the PL peaks shift toward lower energies when the number of voltammetric cycles rises.

The PVK layers deposited electrochemically result in a doped form irrespective if they are deposited on a blank electrode or on an electrode covered with a CN film. To undope PVK, the samples were treated with an aqueous solution of NH$_4$OH. After the treatment, the peaks of the PL bands (see Fig. 2c) shift to: 2.82 eV (440 nm) for the sample PVK/Pt obtained during 100 cycles (curve 1) and to 2.94 eV (421 nm) (curve 2), 2.96 eV (419 nm) (curve 3) and 2.99 eV (415 nm) (curve 4) for the PVK/SWNTs/Pt samples obtained during 100, 50, 25 cycles, respectively. All the PL spectra of the treated samples shift their peaks to higher wavelengths by approximately 43 nm with respect to untreated ones. The new locations of the PL peaks indicate that luminescence originates mainly from low-energy excimer. The PL bands of the treated samples exhibit also a considerable broadening (especially the PVK/Pt sample), which could be caused by the formation of some conglomerates in the samples as a result of the basic chemical treatment. The same reduction of the PL intensity can be seen as the PVK/SWNT ratio decreases in the composites.

Former PL studies carried out on the PVK film electrochemically deposited on the Pt electrode [7] showed an emission band with the maximum at 415 nm which was assigned to low energy excimer. A similar PL band is also observed when the cyclic voltammetry is applied to a CN film immersed in the VK/LiClO$_4$/CH$_3$CN solution [7]. In ref [3] it was shown that the electropolymerization of VK on the CN film gives rise to a vibronic structure in the high energy side of the PL spectrum of PVK. The intensity of

the vibronic structure decreases by the achievement of 20, 50, and 100 voltommetric cycles. The existence of the vibronic structure was explained by the appearance of additional defect sites in the PVK structure where excitation energy is trapped or by the dopant role of CNs [3].
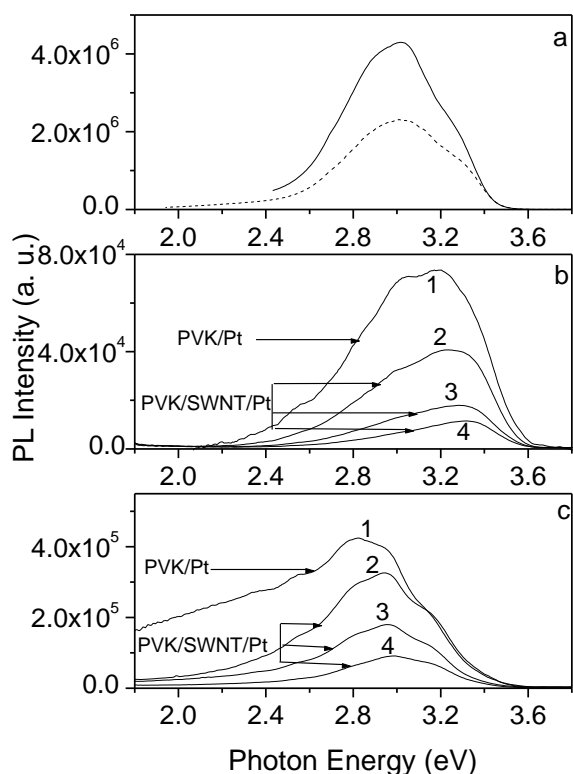

Fig. 2. PL of PVK (solid line) and PVK/NC composite chemically prepared (dotted line) (a). PL of the electrochemically prepared samples; PVK/Pt obtained during 100 cycles (curve 1), PVK/SWNT/Pt obtained during 100 (curve 2), 50 (curve 3), and 25 cycles (curve 4) (b). PL of the electrochemically prepared samples after the treatment with NH₄OH solution; PVK/Pt obtained during 100 cycles (curve 1), PVK/SWNT/Pt obtained during 100 (curve 2), 50 cycles (curve 3), and 25 cycles (curve 4) (c).

An important contribution to understand the mechanisms of photoluminescence is obtained by the decay time studies. In this context we have measured the PL decay time of the pure PVK powder at different energies within the PL band (see Fig.3a). The decay profiles of the PVK decay curves can be well fitted with a double-exponential function: $I(t) = A_1*exp(-t/t_1) + A_2*exp(-t/t_2)$, where t_1 and t_2 are the time constants of the fast and the slow processes and A_1 and A_2 are the intensities of the corresponding processes, respectively. The fitting parameters are used to calculate the average decay time: $t_{ave} = (A_1*t_1 + A_2*t_2) / (A_1 + A_2)$ [8]. Employing the above formula, we got for the average decay times of the pristine PVK the following values: 11.84, 18.32, 22.67 and 24.30 ns, which are associated with the decay curves measured at: 3.10, 2.95, 2.75 and 2.61 eV, respectively. It can be

noticed that the PL decay time increases monotonically across the emission band, from high energies to lower energies fact that reveals a deep and continuous distribution of the traps.

The result of the PL decay time measurement of the chemically prepared PVK/CN composite comparative to that of the pure PVK is shown in fig 3b. The measurements were done at the emission energy of 2.95 eV (420nm). The decay curve was also fitted with two exponentials function and the average decay time obtained was 16.47 ns. Comparing the values of the average decay times of the two samples, a reduction of the average PL lifetime (16.47 ns) in the composite with respect to the average PL lifetime (18.32 ns) in the pure PVK can be seen. The decrease of the PL decay time of the composite reveals an increase in the nonradiative decay rate of the PVK excimers in the presence of CNs.
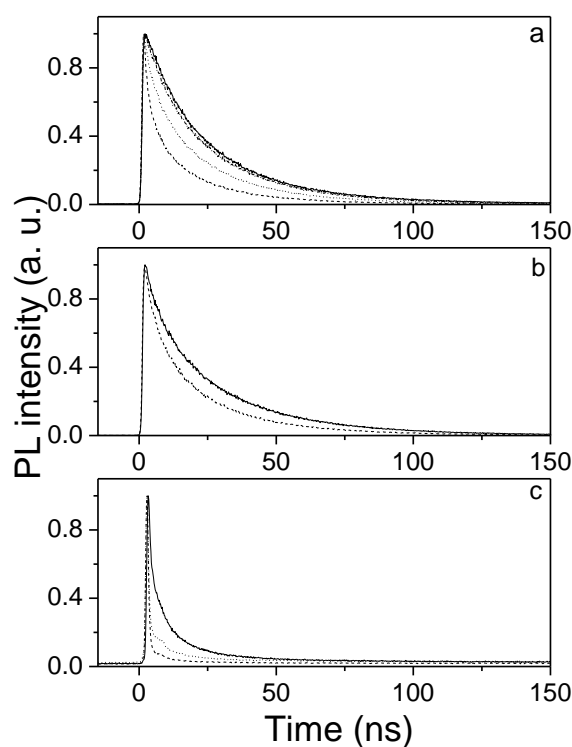

Fig. 3. The PL decay curves of pristine PVK sample at different emission energies; 3.10 eV (dashed line), 2.95 eV (dotted line), 2.75 eV (dashed-dotted line), and 2.61 eV (solid line) (a). The PL decay curves of PVK (solid line) and PVK/NC composite chemically prepared (dotted line) (b). The PL decay curves of electrochemically prepared samples; PVK/Pt synthesized on a blank Pt plate during 100 cycles (solid line), PVK/SWNT/Pt synthesized on a CN film during 100 cycles (dashed line), PVK/SWNT/Pt synthesized on a CN film during 50 cycles (dotted line) (c).

The PL decay curves of the electrochemically prepared samples (before being treated in aqueous solution of NH₄OH), measured at the emission wavelength of 420nm (2.95 eV), are displayed in Fig 3c. Using the same

fitting function as above, we found the following values for the average decay times: 1.16, 2.42 and 5.54 ns, being associated with the PVK/SWNT/Pt samples obtained by 50, and 100 cycles and PVK/Pt sample obtained by 100 cycles, respectively. It can be seen that in the samples containing carbon nanotubes, PL decays faster than in the samples without CNs. Moreover, the average PL decay time of the PVK/SWNT/Pt samples rises when the number of voltammetic cycles increases.

4. Conclusions

We used steady state PL and PL decay time measurements to investigate PVK/CN composites synthesized via chemical and electrochemical routes. In comparison to the pure PVK, we found that in the chemically prepared PVK/NC composite, the PL quenches and the PL decay time shortens, revealing a charge transfer between PVK and CN. In the PL spectra of the PVK/SWNT/Pt samples, an increase in intensity and a red shift of the maximum can be noticed as the number of voltammetric cycles grows. Additionally, their PL decay times augment when the number of voltammetric cycles carried out during the deposition increases. We also observed a change from an emission originating from high-energy excimer to an emission coming from low-energy excimer, after the electrodeposited samples were treated in a solution of NH_4OH. The PL average decay times of the samples were calculated using the fitting parameters that result from the fit with a double exponential function.

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