



Scheme 3. The photoconduction mechanism of PPV/RGO composite [36].

To estimate the time spent by the electrons, produced inside the PPV matrix, in the excited state and to identify the type of the RGO localized states, measurements of the photocurrent dynamics were performed.

The purpose of the study is to explain the observed fact that the composite samples remained charged for a while, after cessation of exposure, returning to the initial state after a certain time duration in the absence of light.

In this context the PPV/RGO composites were illuminated with optical pulses and, using the equations:

$$y = y_0 + A_1 e^{-\frac{(x-x_0)}{\tau_1}} + A_2 e^{-\frac{(x-x_0)}{\tau_2}} \quad (1)$$

for the charge process and

$$y = y_0 + (1 - A_1 e^{-\frac{(x-x_0)}{\tau_1}}) + (1 - A_2 e^{-\frac{(x-x_0)}{\tau_2}}) \quad (2)$$

for the discharge process, where y is the PC and y_0 its initial value, the time constants for the charge and discharge processes, τ_1 and τ_2 respectively, were calculated.

These time constants differ from each other through one order of magnitude ($\tau_1 = 10.2$ s and $\tau_2 = 145.8$ s, in the case of PPV with 0.01 % RGO) [36], fact which indicates the existence of two relaxation mechanisms, correlated with the different location of RGO energy states relative to the conduction band of PPV.

The RGO localized states delay the recombination of free carriers at the interface between the composite and the gold electrode, generating photocurrent.

Conclusions

As a result of the investigations presented in this thesis, we have concluded that:

1. The electrochemical reduction of TBPX in the presence of CNTs leads to the appearance of a shielding effect of S-SWNTs due to the full coverage of S-SWNTs with PPV macromolecular chains (PPV MC) and, respectively, an effect of isolation of the metallic carbon nanotubes from the bundle.

2. At the electrochemical synthesis of PPV in the presence of M-SWNTs a non-covalent functionalization process takes place.

As a consequence of the covalent functionalization of S-SWNTs with PPV, a steric hindrance effect appears in the case of PPV/S-SWNTs composites.

3. The luminescence quenching process is visible both in the case of PPV/SWNTs and PPV/RGO composites due to the charge transfer, which takes place from the PPV to SWNTs and, respectively, from the PPV to RGO.

4. The anisotropy values calculated for the PPV and its composites with RGO obtained through annealing conversion are very close to 0.4, which indicates that for a wrapping angle of almost 0°, the emission and excitation dipoles are aligned and parallel with the basal plane of RGO, suggesting that the PPV and its composite are preferentially oriented towards the support.

5. As indicated by Raman and IR spectroscopy, adding pyrene to the PPV matrix leads to a non-covalent process, which occurs through π - π interactions.

6. *The PC value is two orders of magnitude higher for PPV/RGO than for pristine PPV due to delaying of the recombination process at the PPV/electrode interface. This delay is caused by the RGO energy states localized in the vicinity of the PPV conduction band, which capture free electrons, keep them trapped, and release them after a while.*

This mechanism based on two processes of charge and discharge is described by two time constants, τ_1 and τ_2 , on the basis of which it can be said that there are two types of capture centers, situated differently with respect to the PPV conduction band.

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