CORE-SHELL SiC BASED HYBRID NANOMATERIALS: SYNTHESIS AND EPR INVESTIGATIONS

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Introduction

Original synthesis routes were developed to obtain hybrid nanomaterials made from silicon carbide nanoparticles (nc-SiC) with the surface being functionalized by nanometric layers of polynaniline doped by camphor sulfonic acid (PANI-CSA). Electron paramagnetic resonance (EPR) experiments are performed on PANI-CSA and PANI-CSA-nc-SiC in order to probe the polaron features in such nanocomposites. Quite different EPR spectrum features are shown in the bare doped polynaniline compared to the core-shell composites. In one hand, efficient doping rates seem involved in the bare polymers through the saturation phenomena on the EPR spectra. In the hybrid core-shell composites no such saturation effects are shown even if similar features of the EPR spectrum contributions exist in both classes of samples. The thermal evolution of the EPR spectra show different behaviors suggesting that different transport phenomena are involved in the bare PANI-CSA compared to the core-shell composites.

Results and Discussion

The investigated samples were synthesized by using initial commercial products, namely PANI, CSA as dopant and nc-SiC nanoparticles. All the steps to realize doped PANI-CSA and the functionalization of nc-SiC surfaces to obtain the mentioned systems as core-shell structures (Fig. 1) were realized according to the procedure described in [1-3].

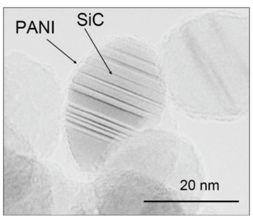

Fig.1. TEM image of nc-SiC functionalized at the surface by nanometric layer of PANI-CSA.

The X-band CW EPR measurements were performed as function of the temperatures (4 - 400 K) and the microwave (mw) power levels required for probing the saturation phenomena.

EPR spectrum features and saturation effects

1. SiC-PANI-CSA Core-Shell

Fig. 2 shows temperature evolution of X-band EPR spectrum for PANI-CSA-nc-SiC measured in the temperature range 6 - 250 K. Two EPR lines with very similar resonance positions were observed. They were resolved only because of their different thermal behavior in the temperature range 77 - 130 K. The EPR spectrum of PANI-CSA-nc-SiC sample consists in the EPR signal labeled as "SiC" superimposed to an EPR line named I3 line also revealed in PANI-CSA sample. According to reference [1], "SiC" EPR signal was attributed to the carbon vacancy located in the core of SiC nanoparticle [4]. In addition, the central "SiC" EPR line is accompanied by two weak satellites (A ~ 12 Gs) originating from hyperfine coupling of unpaired electron with the ^{29}Si nuclei in the neighborhood of the carbon vacancy. The second contribution to the EPR spectra such as "I3" line is related to the doping effect and corresponds to polarons.

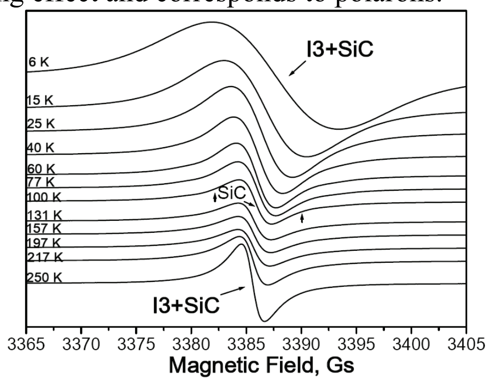

Fig. 2. The temperature evolution of X-band EPR spectrum measured on PANI-CSA-nc-SiC sample.

The intensity of the EPR signal ("I3" and "SiC" lines), increases with the mw power while no change was observed on the linewidth. This indicates that the EPR spectrum is no longer affected by the saturation phenomena.

2. PANI-CSA conducting Polymer

EPR experiments on PANI-CSA, reported in Fig.3 from 6 K to 40 K show only one EPR signal line I3*. Its thermal behavior is similar to the I3 EPR line obtained on the first set of experiments on hybrid composites. This seems to indicate that the I3 and I3* EPR lines are associated to the same paramagnetic species characterized by g~2.0023(2) at T = 300 K. Analysis of the saturation was also carried out in similar conditions as for the nanocomposite materials. For the I3* EPR signal, the intensity increases monotonically with the mw power while only slight decrease was observed on the linewidth. These experiments indicate the existence of saturation phenomena in the PANI-CSA samples. Thus, even if the doping of the polymer and of the nanocomposite were carried out in the same conditions, the saturation phenomena are more important for the bare conducting polymer. It can be suggested that the microstructure of the nanocomposite with more distant conducting islands can overcame the occurrence of saturation effects.

Comparative Temperature dependence of the spin susceptibilities

The temperature dependence of the double integrated intensities of the EPR signals, i.e. the spin susceptibilities, follow the Curie law in the temperature range from 6 K to 50 K. Above 50 K, a Pauli-like contribution and also thermally activated polarons dominates the paramagnetic spin susceptibilities (Fig. 4). This behavior is valid up to 195 K where a maximum of the linewidth was observed for I3 EPR signal. A Korringa like relaxation mechanism is also inferred from the EPR linewidths evolution with the temperature.

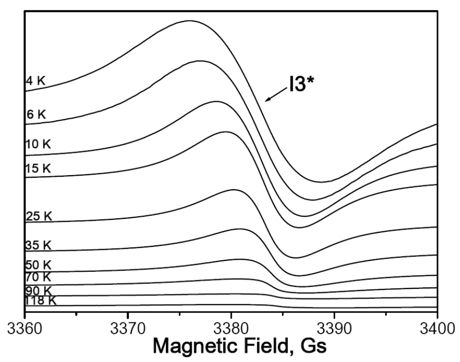

Fig.3. The temperature evolution X-band EPR spectrum measured on PANI-CSA sample heated from 6 K to 40 K and than cooled down to 6 K.

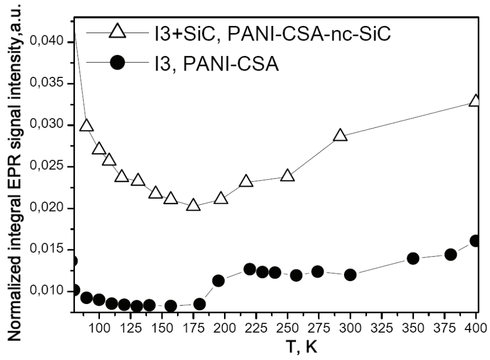

Fig. 4. The temperature dependence of the "I3" and "I3+SiC" EPR spectra integral intensities.

Furthermore, the transformation of the lineshape of the third paramagnetic center from Lorentzian to Dyson form indicates that hopping process of charge carriers occurs in PANI-CSA and PANI-CSA-nc-SiC samples in the temperature interval 60 K - 195 K.

Conclusions

The EPR experiments performed on PANI-CSA and PANI-CSA-nc-SiC samples point out common features connected with "I3" line induced by polarons. While the doping effect is performed in the same conditions, drastic saturation effects were observed only in the PANI-CSA samples. The microstructure of the nanocomoposite PANI-CSA-nc-SiC is thought to overcome a high doping level achievement. As common features on the transport phenomena it is worth noting the activation of polarons with similar energy (175 K) in PANI-CSA and PANI-CSA-nc-SiC. However, the density of polarons seems more high in the core-shell structure compared to the solely PANI-CSA.

References

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