EPR investigations of silicon carbide nanoparticles functionalized by acid doped polyaniline

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ABSTRACT

Nanocomposites (SiC-PANI) based on silicon carbide nanoparticles (SiC) encapsulated in conducting polyaniline (PANI) are synthesized by direct polymerization of PANI on the nanoparticle surfaces. The conductivity of PANI and the nanocomposites was modulated by several doping levels of camphor sulfonic acid (CSA). Electron paramagnetic resonance (EPR) investigations were carried out on representative SiC-PANI samples over the temperature range [100–300 K]. The features of the EPR spectra were analyzed taking into account the paramagnetic species such as polarons with spin $S=1/2$ involved in two main environments realized in the composites as well as their thermal activation. A critical temperature range 200–225 K was revealed through crossover changes in the thermal behavior of the EPR spectral parameters. Insights on the electronic transport properties and their thermal evolutions were inferred from polarons species probed by EPR and the electrical conductivity in doped nanocomposites.

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1. Introduction

Hybrid nanomaterials have been extensively developed during the last decade. The interest is motivated by the creation of original architectures and their applications as functional materials. Thus, conduction properties were investigated in nanocomposites associating silicon carbide nanoparticles and polymer media such as (DGEBA/EMI-2,4) [1] or doped polyaniline [2]. Electrical or optical properties were also investigated for SiC nanoparticles embedded in SiO2 [3] or for TiO2 nanoparticles incorporated in MEH-PPV or PVK host matrixes [4]. The latter architectures are particularly promising for the photovoltaic conversion. In the same context, the optical properties of the hybrid semiconducting nanomaterials [5] have been a subject of several studies in Core-Shell configurations and when a particular alignment of electronic band structures is realized.

Silicon carbide (SiC) as a wide band gap semiconductor was used in several nanostructures including hybrid nanocomposites associating SiC nanoparticles and polymers as guest–host or in core-shell configurations. The electronic and optical properties were investigated [6,7] to clarify the role of interfaces on the physical responses of the nanocomposites. Thus, SiC nanoparticles as isolated objects or associated with suitable polymers were investigated including their vibrational [8], dielectric [9–11] and transport properties [12] emphasizing the critical role of the interfaces.

In this work, we consider nanocomposites' Core-Shell of SiC nanoparticles encapsulated by thin layer of polyaniline. Their synthesis is based on the direct polymerization of the polyaniline on the surface of SiC nanoparticles. The composition of the polymer chains is made from tetramer (–Ph–NH–Ph–NH–Ph–N=Q=N) associated with CSA acid groups used as doping agents. The rate of CSA groups with respect to tetramers defines the doping ratios. Thus, the ratios about (0.0833, 0.25, and 0.5) correspond respectively to (1:3, 1:1, and 2:1) CSA molecule per tetramer groups.

The acid doping (CSA) of the polymer contributes to the protonation of the polymer chains and creates the charge carriers for the electronic conductivity of the doped polymer and composites. The charge carriers in the hybrid composites consist in polarons and bipolarons with concentrations depending on the doping rates and the thermal activation energies. The transport phenomena are governed by the nature of the charge carriers and their dynamics in the network (mobility, exchange interactions, excited states, etc.).

To characterize the features of the polarons in the doped polymers alone or associated to the SiC nanoparticles, electron paramagnetic resonance (EPR) technique is used with the experimental CW-EPR setup. The concentration of polarons and their dynamics can be probed from the spectral parameters (g-tensors,

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line width, paramagnetic susceptibilities) determined by the analysis of the EPR spectra and their evolution in the temperature range [100–300 K]. Particularly, the thermal variation of the spin susceptibility can be marked by the eventual interactions between the polarons. However, when the conditions of doping and thermal treatments are realized in order to create bipolarons in the nanocomposites, the EPR technique is no longer informative because such particles are spinless. However, for moderate doping, the polarons are present in the nanocomposites and contribute to probe the charge carrier mobility versus the temperature in close relation with the physical characteristics of the conducting media.

2. Experimental details

2.1. Core-shell nanocomposites

The investigated samples were synthesized by direct polymerization of camphor sulfonic acid (CSA) doped polyaniline (PANI) in the presence of 30 nm sized SiC nanoparticles. The main steps to achieve the synthesis are hereafter outlined. An appropriate amount of SiC nanoparticles is added to a solution made from distilled water and CSA. Ultrasonic stirring is performed in order to disperse the nanoparticles leading to a homogeneous suspension. The aniline is added to this solution followed by the use of a solution of ammonium persulfate with continuous magnetic stirring to homogenize the mixture. A decantation under 4 °C is performed on a day followed by dialysis, washing of the reaction products and drying under dynamic vacuum at temperatures 50–70 °C. The obtained composites are then characterized by Raman spectrometry (Fig. 1) for the as synthesized and also for those after heat treatments dedicated to test the stability of the nanocomposites at temperatures as high as 440 K. For all samples, the Raman spectra are dominated by the vibrational fingerprints of polyaniline [8,13]. This testifies the achievement of the PANI polymerization on the SiC nanoparticles surfaces which will be referred below as SiC-PANI. It is worth noting also that the nanocomposites exhibit good thermo-mechanical stability even when heating up to 440 K is performed.

In order to dope the shell-polymer encapsulating the SiC nanoparticles with different protonation degree, a dedoping of the composites is performed initially. This procedure suppresses the CSA groups which can be retained by the polymer backbone.
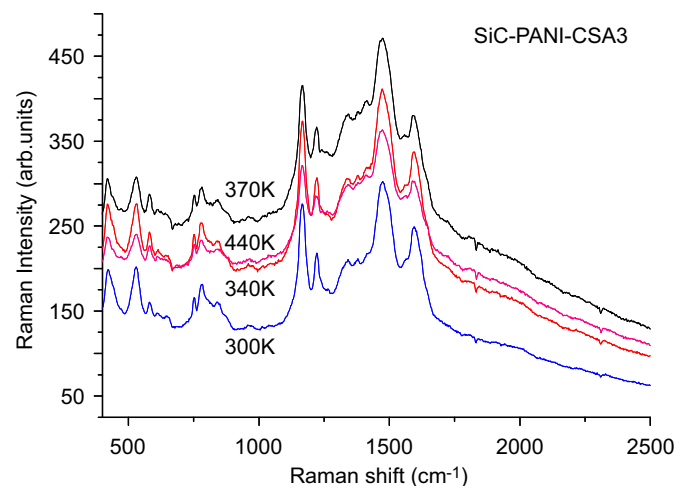
The experiment consists of an ammonia treatment of the composites followed by a dialysis and drying as described above.

In order to dope the composite SiC-PANI-CSA, a given CSA amount with respect to the dedoped composite was used in distilled water and added to the composite. A homogenization of the mixture is performed in ultrasonic bath accompanied by magnetic stirring. Filtration and drying under dynamic vacuum at 50–70 °C allow obtaining the final core-shell composite with the appropriate doping level. The same procedure is also used to synthesize PANI-CSA doped at the same levels. These samples serve as references to evaluate the nanoparticles effects and then the role of the microstructure on the charge carriers features (nature, thermal activation, mobility, etc.)

The investigated samples SiC-PANI-CSA are characterized by the protonation degrees [0.5], [0.25] and [0.0833] which correlate respectively to the compositions associating SiC nanoparticles, polyaniline from the tetramers –(Ph–NH–Ph–NH–Ph–N=Q=N)– and CSA groups as follows:

- 106.8 mg of SiC/PANI(CSA) [0.5] is constituted by 94.7 mg of SiC and 12.1 mg of PANI(CSA) [0.5] (emeraldine base (EM) 5.3 mg+6.8 mg of CSA),
- 103.4 mg of SiC/PANI(CSA) [0.25] is constituted by 94.7 mg of SiC, 8.7 mg of PANI(CSA) [0.25] (EM 5.3 mg+3.4 mg of CSA),
- 101.1 mg of SiC/PANI(CSA) [0.0833] is constituted by 94.7 mg of SiC, 6.4 mg of PANI(CSA) [0.0833] (EM 5.3 mg+1.1 mg of CSA).

When considering a total protonation a simple assignment can also be used such as a degree [0.5] corresponds to 2 CSA groups grafted on 1 –(Ph–NH–Ph–NH–Ph–N=Q=N)– tetramer. In a similar way, [0.25] is used when 1 CSA molecule is associated to 1 –(Ph–NH–Ph–NH–Ph–N=Q=N)– tetramer. As illustrated by numerical simulation of composites' structures in Fig. 2, the protonation degree [0.0833] defines the case of 3 tetramer fragments of –(Ph–NH–Ph–NH–Ph–N=Q=N)– associated to 1 CSA molecule. Thus, the ratio of protonation degrees of the three investigated samples is normalized as 6:3:1 instead of 0.5:0.25:0.00833.

An illustration of the features of the nanocomposites is realized by numerical modeling as shown in Fig. 2. The constituents were optimized by molecular mechanics using MM+ force field using a unit cell length about 3.5 nm. The SiC nanograin has a diameter about 1.5 nm and its crystal structure was fixed as in hexagonal 6H-SiC structure.
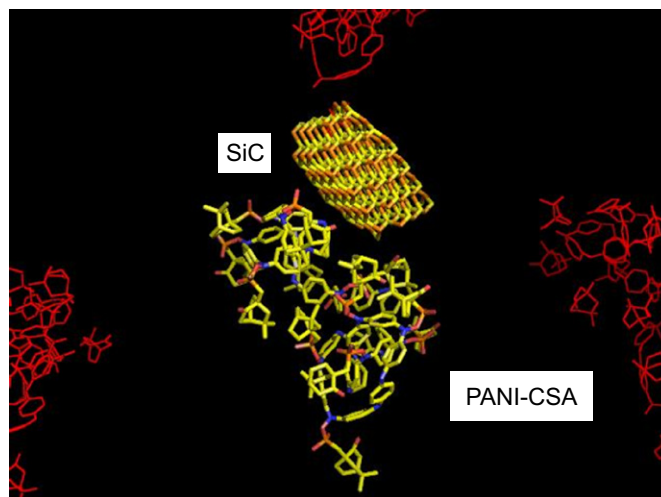

Fig. 1. Raman spectra of the core-shell nanocomposites made from SiC-PANI. Vibrational bands of PANI are well resolved indicating the correct polymerization of PANI on the SiC nanoparticle surfaces.

Fig. 2. Numerical modeling of the nanocomposites based on SiC nanoparticles, polyaniline groups and camphor sulfonic acid molecule used as doping agent.