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Hopping conduction on PPy/SiO$_2$ nanocomposites obtained via in situ emulsion polymerization

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Abstract This work describes the preparation and electrical characterization of conducting polypyrrole (PPy) and silica nanocomposites. Four samples were investigated: (i) pure PPy, (ii) PPy-covered SiO$_2$ spherical nanoparticles, (iii) PPy-covered SiO$_2$ spherical nanoparticles modified with 3-aminopropyltriethoxysilane (APS), and (iv) PPy-covered SiO$_2$ fibers. Structural characterization was made by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The electrical conductivity was measured from 80 K to 300 K and three-dimensional variable range hopping conduction was observed. From the hopping parameter the mean hopping distance was obtained as well as the density of active center and the energy associated with it.

Introduction

The unique size dependent properties of nanoparticles, namely confinement effects and other advanced properties related to high surface area have been increasingly reported in literature for several types of inorganic materials [1].

The synthesis and characterization of new nanostructures, have been so far the main concern in this field. Therefore, processing details and possible applications for these materials have become imperative. The homogeneous dispersion of nanoparticles in polymeric matrices constitutes an excellent strategy of protection, support, and easy processing of these materials [2].

Polymerization of the monomers in the presence of inorganic nanoparticles leads to new organic-inorganic hybrid nanocomposites whose characteristic properties often depend not only on the particle size, but also on the particle shape [1]. Considerable efforts have been made on the synthesis of composite nanoparticles, since these nanostructured composites have many potential applications, such as in drug delivery [3, 4], gene therapy [5, 6], and catalysis [6, 7]. Amongst conducting polymers, polypyrrole (PPy) is one of the most studied conducting polymers because of its high electrical conductivity, environmental stability, and easy synthesis [7–9]. For that reason various contributions have been reported regarding the preparation of PPy-based nanocomposites using a variety of different types of inorganic oxides such as SiO$_2$, NiO, CuO, ZnO, and CeO$_2$ and their electrical characterization [9–12]. However, no single unanimous model is so far available that can properly describe the prevailing conduction processes occurring due to the presence of nonlinear excitations like solitons, polarons, and bipolarons.

As the conductivity of SiO$_2$ is very low compared to PPy, the change in conductivity of different PPy/silica nanocomposites and the associated conduction process is an important issue which may help clarifying the conduction processes in this type of materials. Therefore, in the present work four different samples have been studied: (i) pure PPy, (ii) PPy-covered SiO$_2$ spherical nanoparticles, (iii) PPy-covered SiO$_2$ spherical nanoparticles modified

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with 3-aminopropyltriethoxysilane (APS), and (iv) PPy-covered SiO_2 fibers. As described in the experimental part the synthetic procedures were similar to those reported in the literature with some modifications. In this work, we focus on the electrical and morphological properties of the nanocomposites. From the electrical measurements on the nanocomposites the dominant conduction process was identified as three-dimensional variable range hopping. Furthermore, the mean hopping distance, the density of active center and the energy associated with it have also been calculated.

Experimental

Silica synthesis

Spherical SiO_2 nanoparticles were prepared following the well-known Stöber method [13]. Surface modification of spherical SiO_2 nanoparticles with 3-aminopropyltriethoxysilane was carried out following the method reported by Foshiera et al. [14]. Surface modification was confirmed by FT-IR spectroscopy [15]. Hollow SiO_2 fibers were prepared following previous work of Mann et al. [16].

Polymer synthesis

The PPy/SiO_2 nanocomposites were prepared via in situ emulsion polymerization according to the synthetic path illustrated in Fig. 1. The polymerization process was carried out under the conditions previously reported by other authors [17–19]. Typically 10% w/w (relative to monomer mass) of SiO_2 nanoparticles were dispersed in an aqueous solution of methylcellulose (Aldrich, $\overline{M}_n = 86,000$) (0.7% w/vol of water) which was used as stabilizer. This suspension was transferred to a jacket glass reactor (100 ml capacity) equipped with a thermostat bath, condenser, mechanical stirrer, and nitrogen inlet. $FeCl_3.6H_20$ (8.3 g) was added to the suspension and the mixture was cooled to 9 °C and degassed under N_2 flow for 30 min. Pyrrole (Aldrich) (1 ml) was then added and the reaction was left stirring for 6 h. A black suspension was obtained which was submitted to various centrifugation/redispersion cycles using pure water until the supernatant conductivity was below 50 µS/cm. The powders obtained after the centrifugation cycles were dried and compressed into disk-shaped pellets for conductivity measurements.

In this work four samples have been prepared: PPy, PPy/SiO_2 nanospheres, PPy/APS/SiO_2 nanospheres, and PPy/SiO_2 fibers and henceforth they will be designated by P1, P2, P3, and P4, respectively.

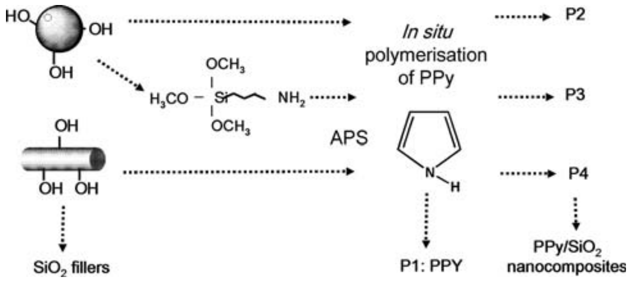

Fig. 1 Synthetic route for PPy/SiO_2 nanocomposites preparation

Characterization

SEM was obtained using a Hitachi-SU70 operated at 25 kV. TEM was carried out on dilute dispersions dried onto carbon-coated copper grids using a Hitachi H-9000 microscope operating at 200 kV. For the SEM characterization, the powder samples were carbon sputtered prior to measurements.

The temperature-dependent d.c. conductivity was measured on disc-shaped pellets which were prepared by using a uniaxial load of 2 ton to shape them in 8-mm diameter and 1-mm thick discs. After that, contacts were fabricated at top and bottom facets with silver epoxy contacts. The conductivity measurements were carried over the temperature range of 80–300 K. An exchange gas cryostat was used to control sample temperature and a Keithley 617 electrometer with an internal voltage source that was used for the electrical measurements.

Results and discussion

TEM and SEM

Figure 2a, b present TEM images of P2 and P3, respectively. Figure 2c, d present SEM images of P1 and P4. The TEM microscopy was applied to samples P2 and P3 in order to evidence how the PPy and APS attach to the spherical SiO_2 nanoparticles. The choice of SEM images for samples P1 and P4 was due to the large size of the SiO_2 fibers which turn out to be inadequate for TEM. P1 image is shown in the same scale of P4 image in order to evidence how PPy attach to the fibers.

However, further TEM characterization of the samples P2 and P3 proved the presence of the spherical SiO_2 nanoparticles covered with PPY for both samples P2 and P3 (Fig. 2a, b, respectively). The diameter of the particles was estimated to be within the range of 150-180 nm. For sample P4 SEM characterization showed that the SiO_2 fibers were covered with PPy (Fig. 2d).

The fact that all the SiO_2 particles are covered with PPy is thought to be due to the presence of methylcellulose which was used as stabilizer in the in situ emulsion

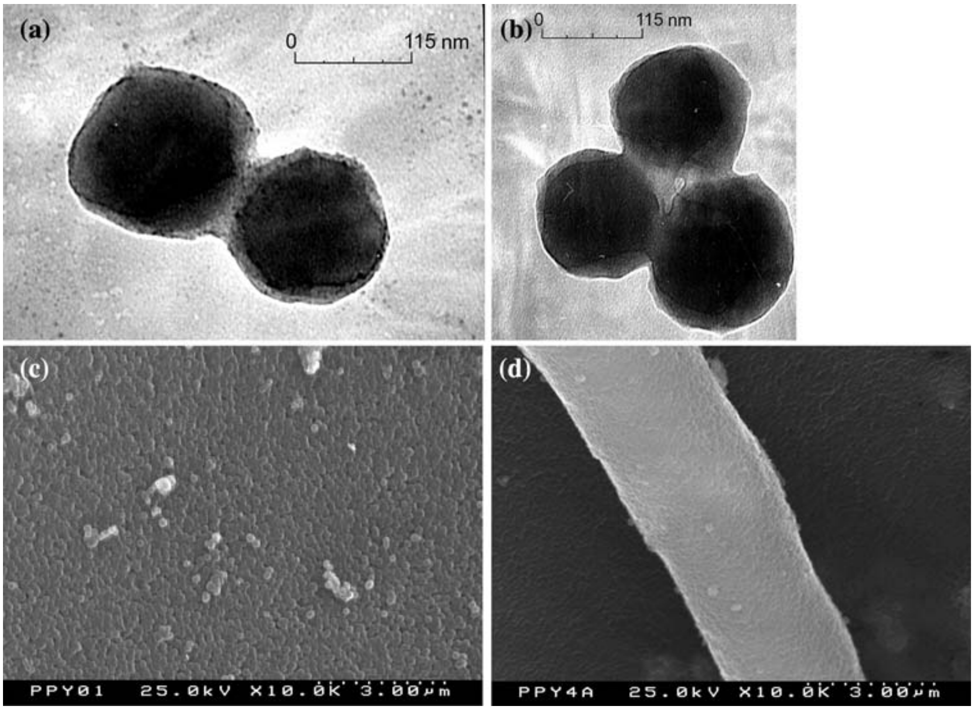

Fig. 2 TEM images of: (**a**) P2, (**b**) P3, and SEM images of: (**c**) P1 and (**d**) P4

polymerization. Therefore, it might contribute to the adsorption of pyrrole on the surface of the fibers.

Variable range hopping conductivity

A three-dimensional variable range hopping conduction (VRH) is observed in all the samples. The Mott's VRH formalism for phonons or small polarons for conductivity of disordered semiconductor materials [20–22] will be described here in summary. Depending on the dimensionality of the system, i.e., $d = n - 1$, the temperature-dependent VRH conductivity is given by

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{\frac{1}{n}}\right] \tag{1}$$

where σ_0 is the high temperature limit of conductivity and T_0 the Mott's characteristic temperature associated with the electronic wave function localization degree . The exponent n assumes 4, 3, and 2 for three-, two- and one-dimensional systems, respectively. In this work, a three-dimensional system is considered and we will assume $n = 4$ in Eq. 1 and all other equations will be presented for this condition.

The 3D characteristic Mott temperature T_0 can be expressed in terms of

$$T_0 = \frac{\lambda}{k_B \eta(E_F) a^3} \tag{2}$$

where λ is a dimensionless constant ($\sim$18.1) [23–26], k_B the Boltzmann constant, a the wave function localization radius, and $\eta(E_F)$ the density of states at the Fermi level. T_0 can be obtained from the experimental data through fittings to Eq. 1 usually in a linearized form. From T_0 we can calculate $\eta(E_F)$, which is used to determine the mean hopping distance R [26], the mean density of hopping carriers N, and the mean energy necessary for a hop E [27],

$$R = \left\{\frac{9a}{[8\pi k_B T \eta(E_F)]}\right\}^{\frac{1}{4}} \tag{3}$$

$$N = \frac{3}{4\pi R^3} \tag{4}$$

$$E = \frac{N}{\eta(E_F)} \tag{5}$$

Figure 3 presents σ as a function of $(k_B T)^{-1}$ in a logarithmic scale for samples P1, P2, P3, and P4. The nonlinear functional dependence indicates that all samples show temperature-dependent activation energy. This suggests that band conduction, or nearest neighbor hopping models, is not sufficient to explain the conduction processes in these composites.

Figure 4 presents σ versus $T^{-1/4}$ plotted in a logarithmic scale for the different samples. The similar temperature dependence for the electric conductivity shown by sample P1 and P2 indicates that silica has negligible influence on the electric conductivity of P2. Sample P2 (PPy/SiO$_2$) has slightly lower conductivity than sample P1 (pure PPy). Considering that the conductive polypyrrole chains adsorb onto the surface of the silica particles as very thin layers, as illustrated by the TEM image in Fig 2a, and the covered particles make contact with each other, the conduction

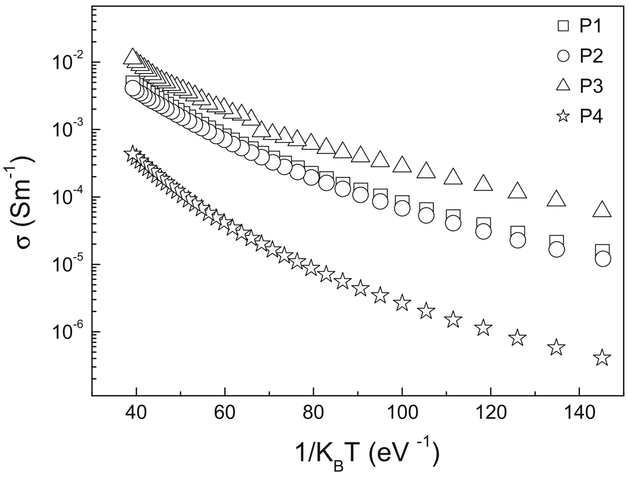

Fig. 3 Arrhenius plot of d.c. conductivity of the four samples

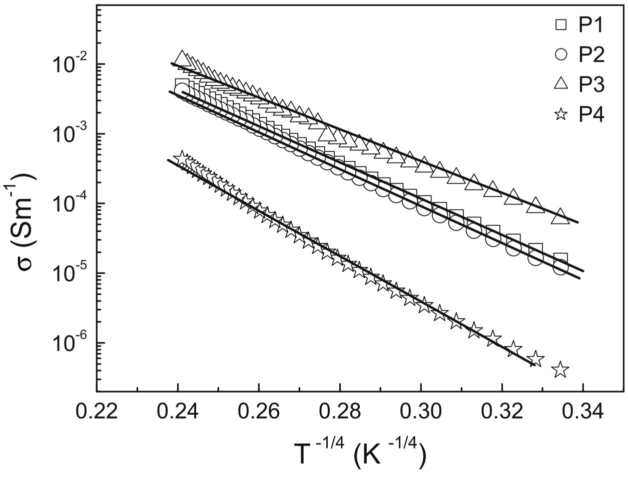

Fig. 4 Hopping characteristic plot for the d.c. conductivity of all the samples

process is defined by the PPy layers with negligible influence of the insulating SiO_2 particles. This accounts for the small difference between the conductivity of samples P1 and P2.

A different result is that of sample P3, which shows the highest conductivity due to the use of APS, which allowed better compatibility between the PPy and the SiO_2 nanoparticles. From the TEM it is possible to observe, like in the case of P2, that the silica particles are coated by PPy.

Lower conductivity was observed for sample P4 (PPy/SiO_2 fibers). In this case there is the effect of silica fibers size which contributes to the lowering of electric conductivity.

Concerning the conduction mechanism, since the best linear fittings to σ are obtained for the data presented in Fig. 4, we conclude that three-dimensional (3D) VRH charge transport occurs in our samples. In reference [28], from the calculations of the energy of polaron and bipolaron formation on pyrrole, a polaron radius of 1.82 Å was evaluated. To analyze the data using Mott's variable range hopping theory, it is assumed that the localization length a is 1.5 Å as proposed by Gangopadhyay et al. [26]. Table 1 presents the different parameters obtained by fitting the experimental results to the Mott's VRH theory. Combining Eqs. 2 and 3 we conclude that larger T_0 implies larger R. Therefore, the conductivity decreases with T_0. Also high T_0 implies larger hopping distances, and larger energies for a hop.

Comparing our results with those from the literature (Table 1), it can be seen that our samples have intermediate conductivities. In reference [25], the nanocomposites contain a core of Fe_2O_3, which is a well-known PPy doping agent, and explains the higher conductivity values of these samples. On the other hand, in reference [27] pure PPy and lower doping conditions are considered.

The composites have shown electrical characteristics close to those of the pure PPy (P1). Comparing PPy/APS/SiO_2 (P3) with PPy/SiO_2 (P2), we observed better compatibility between PPy and silica in the presence of APS. The lower conductivity of sample P4 is probably related to the effect of silica fibers size. In summary, we have prepared PPy/SiO_2 and PPy/APS/SiO_2 nanoparticles and studied the electrical conduction mechanism associated with them.

The present work can be extended to the design of novel materials for electroluminescent devices with the SiO_2 particles acting as cavity resonators to select specific wavelength ranges [29, 30].

Table 1 Parameters obtained by fitting d.c. conductivity data of the samples

Sample	$T_0^{1/4}(K^{1/4})$	R(Å) at $T = 300$ K	N (cm^{-3})	E (meV) $T = 300$ K
P1	57.6 ± 0.1	7.7	5.0×10^{20}	89
P2	59.8 ± 0.2	8.0	4.5×10^{20}	93
P3	49.6 ± 0.3	6.7	7.9×10^{20}	77
P4	67.4 ± 0.3	9.1	3.2×10^{20}	105
Ref. [25]	16.4 − 20.0	2.2 − 2.7	$(1.2 - 2.2) \times 10^{22}$	26 − 31
Ref. [26]	108 − 141	11.7 − 15.3	$(1.4 - 7.1) \times 10^{20}$	167 − 219

Conclusions

In summary, PPy/SiO_2 nanocomposites were prepared by in situ emulsion polymerization method. Electrical conduction in polypyrrole-silica nanocomposites is due to the conducting polymer. The conduction process is explained by a three-dimensional variable range hopping mechanism. For the PPy/APS/SiO_2 sample we observe better compatibility which results in highest conductive material. The results obtained have opened the possibility to exploit potential applications in electroluminescent devices with the SiO_2 particles acting as cavity resonators to select specific wavelength ranges.

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