One-Pot synthesis and characterization of polythiophene and polythiophene/carbon nanostructures composite thin films

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Introduction

Conducting polymers are a class of materials that has been in wide research nowadays, mainly because of its low toxicity, optical and electrical properties and efficient electronic conjugation which gives to this material a special attention to technological applications. The polythiophene as a thin film is a conductive polymer which has interesting characteristics for use in organic photovoltaic devices, since it presents a band gap of 2.1 eV and has a high stability under irradiation.[1] The incorporation of carbon nanostructures for forming composites with polymers has proposed excellent results, with the improvement of the physical and chemical properties of these materials. Owing to obtainment of polythiophene as thin films are extremely complicated, the present study aimed to synthesize thin films of polythiophene and hybrids of polythiophene/graphene by interfacial method developed in the research group, as well as to characterize these materials.

Results and Discussion

The polythiophene films were prepared as follow: a dispersion of 500 mg of $FeCl_3$ in 20 ml of organic solvent was added to a round flask containing 20 mL of Milli-Q Plus water and 600 uL of thiophene. In each synthesis, three different organic solvents were used: n-hexane, chloroform and toluene, and the samples named PT-solvent. This mixture was stirred at 900 rpm for 3 h. Thereafter, the formed film was exhaustively washed with water and NH_4OH and then deposited on quartz, glass and silicon substrates. To obtain the polythiophene/graphene composite, the same methodology was used, but using benzene as the organic solvent. The characterization of the materials using the Raman spectroscopy technique shows the spectra of the films exhibiting bands near 1457 cm^{-1} related to the symmetric stretching C=C (A_g), 1370 cm^{-1} that is the stretch in the C-C ring, 1219 cm^{-1} related to the stretch across the C-C thiophene rings, 1045 cm^{-1} related to the C-H deformation and 701 cm^{-1} related to C-S-C deformation.[2] All the films prepared through this method performed as a thin film red-brown film. Using UV-Vis spectrophotometry, were observed the typical absorptions of polythiophene polymer conjugate bands, which generally occurs between 500 and 550 nm. However, the PT-benzene film showed increased conjugation with a corresponding absorption values nearby 540 and 602 nm, while the PT-hexane showed the lowest value at 451 nm. The lowest conjugation presented by the film synthesized with n-hexane is related to the torsion between the rings in the structure of the polythiophene, which reduces the orbital overlap and hence their conjugation. The SEM images show the morphology of the polymer, which it is possible to observe some plane structures uniformly spread in the PT-benzene film, whereas in PT-hexane and PT-chloroform films is observed only aggregates of polymer. These planar structures in PT-benzene film could be typical structures of graphene. To confirm this purpose, an interfacial film was prepared by the same method, in the absence of thiophene. This film showed characteristics of graphitic structures such as bands nearby 1346 cm^{-1}, 1592 cm^{-1} and 2695 cm^{-1} in the Raman spectroscopy, which is typical of composite materials carbon sp^2.[3] Thus, it appears that the synthesis using benzene may have produced a hybrid material polythiophene/graphene in which both are synthesized simultaneously.

Conclusions

The liquid-liquid interfacial method proposed proved to be effective in the synthesis of complex structures such as polythiophene and the hybrid polythiophene/graphene. The prepared materials have characteristic of a transparent thin film, in which studies of its optical-electronic properties will be studied posteriorly.

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