ICAM2009
11th International Conference
on Advanced Materials
Rio de Janeiro Brazil
September 20 - 25

Nanowire-like structures consisting of mesoporous molecular sieves doped with 3,4,9,10-perylenediimide

S. Brochsztain[(1)*], F. J. Trindade[(1)] and D. Z. de Florio[(1)]

(1) Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas (CECS), Universidade Federal do ABC (UFABC), Rua Santa Adélia, 166, Santo André-SP, 09210-170, Brazil. E-mail: sergio.brochsztain@ufabc.edu.br.
* Corresponding author.

Abstract – Mesoporous molecular sieves MCM-41 and SBA-15 were covalently grafted with the organic dye 3,4,9,10-perylenediimide (PDI). The PDI-doped materials were studied by impedance spectroscopy. The obtained data indicate the formation of nanowire-like stacks of PDI within the channels of the molecular sieves.

The ordered channel array found in mesoporous molecular sieves is well suited for the supramolecular organization of dye molecules, allowing the assembly of advanced functional materials. Mesoporous siliceous materials, like the MCM-41 and SBA-15 families, are obtained by surfactant-templated synthesis, producing highly ordered hexagonal arrays of one-dimensional channels, with large surface area and narrow pore size distribution [1,2]. Owing to the large pore size, ranging from 1.5 to 10 nm in the case of MCM-41 and from 5 to 30 nm in the case of SBA-15, these materials have the ability to encapsulate large aromatic organic molecules. The 3,4,9,10-perylenediimides (PDI) are red dyes with high thermal and photostability, and are known as one of the best n-type organic semiconductors, which makes them very suitable for applications in optoelectronic devices. Our group has recently reported [3] the synthesis of solid state fluorescent materials obtained by the covalent grafting of PDI into the channels of MCM-41 and SBA-15. It was suggested in that report that the PDI molecules in these materials were stacked within the channels, resulting in nanowire-like structures (Figure 1).

In order to confirm that suggestion, impedance spectroscopy was employed. This technique allows one to access the conductivity of the organic dye within the insulating silicate framework, what would not be possible using regular DC measurements. For the impedance measurements, the powdered samples were pressed into ca 1 mm thick pellets. The pellets were placed between two CDtrodes, which are gold electrodes extracted from commercial CDs [4]. The CDtrodes were then connected to an Autolab III/FRA2 potentiostat, and the data were acquired using the frequency response analysis (FRA) mode. Figure 2 shows a typical impedance spectrum for SBA-15 doped with PDI (SBAPDI). It can be observed that the doped material is less resistive than non-doped SBA-15. The spectrum of SBAPDI is actually similar to those of model compounds, namely the commercially available 3,4,9,10-perylenetetracarboxylic dianhydride (PTCA) and *N,N'*-bis(2-phosphonoethyl)-3,4,9,10-perylenediimide, a typical PDI. These results point to the existence of a conducting path in the SBAPDI material, confirming the potential of these materials as conducting nanowires.

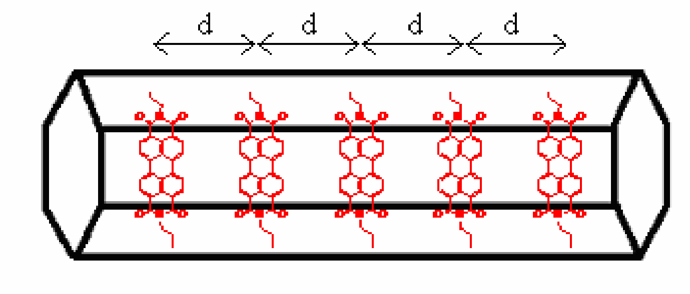

Figure 1: Nanowire-type stacking of semiconductor PDI molecules within the channels of mesoporous molecular sieves.

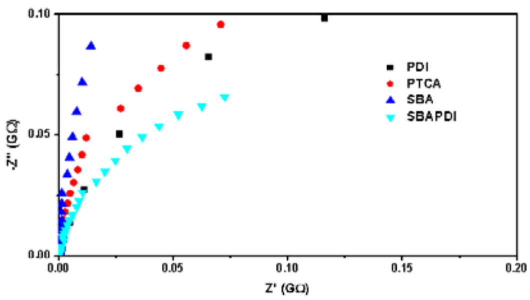

Figure 2: Impedance spectra of PDI-doped SBA-15 (▼), as compared to non-modified SBA-15 (▲) and to the reference compounds *N,N'*-bis(2-phosphonoethyl)-3,4,9,10-perylenediimide (PDI) (■) and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCA) (●).

References

[1] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, Nature 359 (1992) 710.
[2] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, Science 279 (1998) 548.
[3] F. J. Trindade, G. J. T. Fernandes, A. S. Araújo, V. J. Fernandes Jr., B. P. G. Silva, R. Y. Nagayasu, M. J. Politi, F. L. Castro and S. Brochsztain, Microporous Mesoporous Mater., 113 (2008) 463.
[4] L. Angnes, E. M. Richter, M. A. Augelli, G. H. Hume, Anal. Chem. 72 (2000) 5503.