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Composites of Polyindole nanowires within Silicate and Aluminosilicate hosts with distinct conductive properties

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Abstract. Nanostructured silicate SBA-15 and aluminosilicate AlSBA-15 were synthesized in order to prepare polyindole composites. The Silica mesoporous materials were prepared by sol-gel method and alumination using post-synthesis technique and analysed by different methods (XRD, BET, TEM, and FTIR). Polyindole/host composites were prepared by in situ oxidative polymerization of pre-adsorbed indole, employing Cl₂Fe as oxidant. TG, FTIR, BET, XRD, SEM and TEM were used to characterize the resulting composites. These studies show that the porous structures of the materials are preserved after polymerization, and polyindole is found within the porous channels. The composites have an electrical conductivity range between values higher than those of the pure chemically synthesized polyindole, close to those of the pure electrochemically synthesized polymer and lower than those of the pure chemically synthesized polymer, in the order of 10⁻⁸ S/cm.

1. Introduction

Nanostructure materials through an unvarying nanopores array structure, with great precise surface area have been widely studied in the last decades because of its possible usage as catalytic materials, adsorbents of great carbon-based compounds or host as chemical supports. Among the nanoporous materials are found amorphous or polycrystalline solids and modified layered materials. A significant amount of work has been devoted to synthesizing, within the nanoporous range, materials characterized by a consistent and well-defined pore assembly [1, 2].

SBA-15 and Na-AlSBA-15 are crystalline mesoporous molecular frameworks with an ordered and precise mesoporous system. These materials possess regular networks and its pore diameter fluctuate thoroughly among 1.5 to 10 nm depending on the template, supplementary chemicals and different reaction environments. Because of their pore building and form, they have often been subject to study as a probe material as an absorbent for a variety of gases and vapours [3, 4].

In recent years they have aroused great scientific interest studies of electro activity of polypyrrole (PPi) polyaniline (PANI), polycarbazol and its derivatives (conductive polymers with N₂ heterocycles), together with the great possibility of industrial applications [1, 3].

Polypyrrole displays good environmental stability and high electrical conductivity, and is good to prepare films of PPi by electrodeposition. In this way Poly (paraphenylene) also shows suitable thermal stability. As Indole is a compound that contains aromatic linked with heterocycle no basic pyrrole ring, therefore, it is possible that PInd and the by-products have the characteristic that depict both polymers (poly(paraphenylene) and PPi). Nevertheless, from amongst the different characteristic of nanowire
conducting polymers, research on PInd and its by-products has been sparse at best, in spite of close similarities observable with the other polymers [5].

The electroactive polymer polyindole (PInd) was synthesized electrochemically, or by oxidative process of indole (C$_8$H$_7$N$_7$).

Polyindole and derivatives are suitable for use in scientific and industrial areas including electrocatalysis, electronics and pharmacology. When doped, polyindole is green, its electrical conductivity lying between 5.10$^{-4}$ and 8.10$^{-2}$ S cm$^{-1}$, a variation range which depends slightly on the nature of the counterion [6]. Polyindole films have also been reported to show good thermal stability, great reduction/oxidation performance and slow degradation proportion compared to PPI and PANI [7].

The aim of this work is to synthesize PInd-SBA-15 and PInd-AlSBA-15 composites by means of in situ polymerization, to produce novel nanostructured composite showing both conductive behaviour as possible materials with catalytic properties for electrocatalytic developments. In this way, we expect to make an appreciated impact to the synthesis and applications of nanostructured composite materials.

2. Material and methods

2.1. Synthesis of Si-SBA-15 and Na-AlSBA-15

Well-organized nonporous SBA-15 silicates were produced employing P123, a triblock copolymer EO$_{20}$PO$_{70}$EO$_{20}$ as template and TEOS as silica basis. The procedure was the following: 20 g of template in solution on chloridric acid pH <1 (400 ml), stirring at 323 K. Later, TEOS (40 g) was incorporated under stirring at 323 K for a day. The product, white in appearance, was removed to a PP flask and subject to aging during 72 h and 373 K. The material was filtered, with Millipore water to achieve pH ~6.

The molecular mixture was Si: 0.018 EO$_{20}$PO$_{70}$EO$_{20}$: 2.08 HCl: 112 H$_2$O. The template was removed by first immersing the material under ethanol reflux for 6 h and dried at 363K [8], after being filtered and washed. To ensure the elimination of the structure-directing agent, the product was heated under N$_2$ flow at 573K, calcined at 823 K in air during 6 h. In order to prepare AlSBA-15, we used post-synthesis alumination with sodium-aluminate at room temperature; the procedure has already been described [9].

2.2. Indole adsorption and polymerization

The water contained in all the samples employed as hosts was eliminated at 673 K at 10$^{-3}$Torr during 1 h. Afterwards, indole was adsorbed into the host in gas phase for a day and at 333 K obtaining indole-SBA-15 following the technique described earlier [9]. In this way, the indole/host saturation ratio was attained.

The Polyindole were polymerizes whiting the host (PInd-AlSBA-15 and PInd-SBA-15) by in situ oxidation in a similar way reported by us [9], using FeCl$_3$ as oxidant. 30 ml of FeCl$_3$ 0.1M was added to the Indol/Hosts in a bottle during 24 h and static conditions. Then, the materials were extracted by filtration, cleaned using an ethanol/water solution. After this were dried at 333 K for 72 h.

3. Results and discussion

3.1. XRD, TEM and Structural studies of hosts and composites

Low-angle XRD analyses of samples employed as hosts was displays in Figure 1. The XRD analysis of SBA-15 and AlSBA-15 samples reveals a strong (1 0 0) reflection signal, as well as small signals, showing a high regularity at long range resultant from (1 1 0) and (2 0 0) diffraction planes, which are typical of SBA-15 material [8].

The aluminated sample suggests that the SBA-15 structure is preserved after Al has been incorporated by post-synthesis: the (1 0 0) reflection signals of Na-AlSBA-15 produced by post-synthesis broaden only slightly, and the (1 0 0) peak shifts marginally to higher 20 values and lower d-
The uniformity of the pores (hexagonal arrangement) of these composites is indicated by the good resolution of individually XRD peaks. Moreover, the persistence of the hexagonal-ordered structure of the hosts after in situ polymerization is demonstrated for PInd-composites by X-ray results (Figure 1). A shift for different composites diffraction plane (1 0 0), distinctive of SBA-15, to higher 2θ angles can also be observed, which is an indicator of the successful integration of the polymer nanowire and the hosts, and has more orderly and uniform [10].

The composites surfaces are considerably minor in size than the hosts; nevertheless, its representative nanostructure is preserved with the PInd polymer within it, according to XRD analysis, (Table 1).

**Figure 1.** XRD of Si-SBA-15, AlSBA-15 and composite PInd-AlSBA-15 and PInd-SBA-15.

Moreover, the persistence of the hexagonal-ordered structure of the hosts after in situ polymerization is demonstrated for PInd-composites by X-ray results (Figure 1). A shift for different composites diffraction plane (1 0 0), distinctive of SBA-15, to higher 2θ angles can also be observed, which is an indicator of the successful integration of the polymer nanowire and the hosts, and has more orderly and uniform [10].

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| Sample          | Area m²/g | Vₚ (cm³ g⁻¹) | BJH Pore diameter (nm) |
|-----------------|-----------|--------------|------------------------|
| SBA-15          | 1040      | 1.38         | 8.9                    |
| PInd-SBA15      | 550       | 1.14         | 5.1                    |
| AlSBA-15        | 960       | 1.05         | 8.6                    |
| PInd-AlSBA-15   | 736       | 0.89         | 5.0                    |

TEM of composite images (Figures 2-3) show narrow pore size distribution indicating that the host structure is retained after the inclusion of the polymer. Images also show that no bulk polymer clusters are synthesized outside the channel hosts and we can observe the filling of pores with PInd.
Figure 2. TEM images of PInd-Na-AlSBA-15 composite.

Figure 3. TEM images of PInd-SBA-15 composite.

3.2. FTIR characterization

FTIR spectra of polymer and composites can be seen in Figure 4. The FTIR absorption signals of pure PInd made it possible to detect detailed composite bands.

Figure 4. FTIR of pure polyindole and composites in the range of 1300-1700 cm$^{-1}$.
The bands observed at approximately 1574-1560, 1508, 1493, 1454-1460, 1383 cm$^{-1}$ were assigned according to previous research [9].

The indole polymerization mechanism occurs by two main routes, 1,3 position or 2,3 position. The peak at 1564 cm$^{-1}$ could be ascribed to N-H interactions in the pure PInd [11]. The composites have a small band at about the same vibration of pure polymer (1560 cm$^{-1}$). These results suggest that the N-H bond is perturbed or diminishes in both composites. This indicates that polymerization occurs mainly in 1,3 position, marked by a small band of N-H bond vibrations. The polymerization process does not affect the benzene ring. In addition, new stretching signals due to the polymer chain appears at around 1460 and 1383 cm$^{-1}$. The bands observed at 1427 cm$^{-1}$ in pure polymer are assumed to C-N stretching. The shift of this band in PInd-AlSBA-15 and PInd-SBA-15 (1420 cm$^{-1}$) shows that this bond is perturbed, confirming that polymerization in these composites occurs in 1,3 position. PInd-host interaction origins that PInd signals move to different absorption frequency than the pure PInd.

3.3. Thermogravimetric analysis

Figure 5 shows a TGA curve analysis for the samples. For pure PInd, the first mass elimination (300 - 373 K) was produced due to the water removal of polymer, which continue thermally constant nearby 430 K. Afterward, PInd begins to undergo a slow degradation until 700 K, when it commences to degrade quickly. MCM-41 and AlMCM-41 hosts, have a weight loss close 4% approximately 370 K and they become to stabilize; the complete mass loss being 7 % w/w at 770 K. SBA-15/AlSBA-15 hosts present a similar behavior to that of MCM-41, (total weight loss about 8 % w/w at 770 K).

The initial weight loss below 370 K of composites is likely to be caused by water loss and by adsorption of some gases. The composite is therefore fairly stable until around 770 K. Beyond this temperature, the weight loss rate of the composite materials (mainly polymer) increases.

Compared with the mass loss of PInd (16% w/w) and nanowire PInd whitin the composites about 770 K, the variance is extensive: 12% for PInd-AlMCM-41, 13% for PInd-MCM-41, 11% for PInd-SBA-15 and 9% for PInd-AlSBA-15 composites. The result is that PInd turn out to be stabilized when it is as nanowire within the hosts that make up the composites, preventing fast degradation of the polymer.

The mass loss ascribed to PInd in nanocomposites at 770 K is about 5% w/w for PInd-AlMCM-41, 6% for PInd-MCM-41, 3% for PInd-SBA-15 and 1% for PInd-AlSBA-15 composites. Note that the full mass loss for pure PInd was about 31%.

![Figure 5. TGA analysis for: Pure polyindole, hosts and Composites.](image)
3.4. Conductivity studies
Consistent with the results obtained by previous studies, chemically and electrochemically synthesized polyindole are characterized by an electrical conductivity of $1.10^{-4}$ and $5.10^{-2}$ S cm$^{-1}$ respectively [12].

The electrical conductivity of PInd-nanocomposites at 298 K (RT conditions) lay between $8.7\times10^{-4}$ (PInd-AlSBA-15) and $1.4\times10^{-8}$ (Pind-SBA-15) (Figure 6). When the conducting polymers are placed within the channels of nanostructured Al-SBA or Al-MCM, the conductivity of the composite is able to alter from ionic conductors to semiconductors, because the changing influencing for conductive polymers exhibits conductivity more than 10 orders of level [13].

The electrical conductivity of conductive polymers are susceptible to be affected by a diversity of aspects: polaron, conjugation and complete chain length combined with the charge relocation to close molecules. Thus, if the polymers are inside the nanostructured channels, a variation of the conductivity can be observed.

The electrical conductivity of the Plnd-AlMCM-41 composite is greater than pure polymer chemically synthesized, and approaches to the polymer produced by electrochemical methods [9].

The higher electrical conductivity of Plnd-Al-hosts is probably because aluminosilicates, instead of silicates, impact the electrical conductivity. This performance can be ascribed because Al-hosts increase the transmission of the electrical charges from side to side of Plnd chains in the nanopores. In this way, is possible that the host dopes polyindole.

![Figure 6. Conductive properties of Polymer/host composites (S/cm).](image)

4. Conclusions
SBA-15 and sodium aluminosilicate as NaAlSBA-15 host materials with longitudinal channel arrangement were prepared and characterized. All the nanostructured materials employed as hosts were analysed using a variety of methods (XRD, BET, TEM, and FTIR).

FTIR analysis were achieved to analyse the interaction of indole adsorbed onto the mesoscopic materials. Infrared spectroscopy allowed us to corroborate that polymerization occurs mainly in 1,3 position indicated by a small band of N-H bond vibrations with the same electron-acceptor sites (Na$^+$ and silanol sites). Furthermore the spectrum indicated the PInd polymerization can be attained inside the hosts with hexagonal pore systems. XRD analysis of the resulting nanocomposites showed that the nanochannels structure of the hosts subsist after polymerization. Polyindole is originated inside the nanostructured channels. Moreover, according with our corroboration by BET and TEM analysis, Plnd, is not on the external surface of the hosts.

These composites exhibit a wide range of desirable properties, with potential application in the field of electronics for developing e.g. electronic devices at a nanoscopic scale. The composites have
higher electrical conductivity range than those PInd, obtainable by chemical synthesis, close to those of the pure electrochemically synthesized polymer, and lower than those of the pure chemically synthesized polymer.

Hybrid composites of organic molecular wires within inorganic reservoirs were successfully developed. The final conductivity of the composites can be modified according to the requirements of the final product by varying the hosts (which implies altering the anchor sites of the nanowires to the host), and nanowires with “tailor made” conductivity behavior could so be developed.

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