Rice Husk Reuse in the Preparation of SnO$_2$/SiO$_2$ Nanocomposite

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In this study, biogenic SiO$_2$ of high purity and high surface area obtained from rice husk was used for prepare a nanostructured SnO$_2$/SiO$_2$ composite. The predominantly amorphous silica was extracted in an acidic route and then the nanocomposite was done via sol-gel route using ethylene glycol and citric acid followed by heat treatment. SiO$_2$ content of the rice husk was determined by X-ray fluorescence (XRF) and its specific surface area determined by nitrogen adsorption. The composite nanostructured SnO$_2$/SiO$_2$ was structurally characterized by the techniques of X-ray diffraction (XRD), Raman and Fourier transform infrared (FT-IR) spectroscopy. The morphological characteristics were revealed by scanning electron microscope (SEM).

Keywords: biogenic SiO$_2$, rice husk, SnO$_2$/SiO$_2$ composite, Pechini method

1. Introduction

Agroindustry has generated a large content of residues and a necessity of utilization of these residues might reduce pollution and increase energy savings. Among these residues, rice husks have received attention due to its large volume production and high content of amorphous silica, approximately 21%$^{12}$. SiO$_2$ can be obtained by direct calcination followed by calcination chemical treatment, and by sol-gel route. Silica from rice husk is considered as an alternative to commercial silica$^1$ due to low cost and wide application, such as to obtain silicon carbide$^2$, catalysts$^3$, adsorbents$^4$, zeolites$^5$, silicates$^6$ and cement$^7$.

Compared to conventional materials, nanomaterials have interesting physical and chemical properties, besides several areas of application, and relative easy production carried out by different methods such as microemulsion$^{10}$, hydrothermal$^{11}$ and sol-gel$^{12}$.

Tin oxide (SnO$_2$) is an important semiconductor oxide in the industry$^{13}$, but despite its wide usage$^{14-17}$ has low thermal stability and tendency to aggregation$^{18}$, that can be overcome by incorporating the amorphous SiO$_2$ to SnO$_2$ $^{19}$, generating the SnO$_2$/SiO$_2$ nanocomposite. There are several studies using SnO$_2$/SiO$_2$, like composite$^{20}$, xerogel$^{11}$, nanotubes$^{22}$ and films$^{23}$, which application can be in photocatalysis$^{21}$ and sensors$^{25}$.

This work aims prepare and characterize SnO$_2$/SiO$_2$ nanocomposites from amorphous biogenic silica of high purity extracted from rice husk by Pechini method$^{26}$, as an alternative to TEOS (tetraethoxysilane). Silica from rice husk was characterized by X-ray fluorescence (XRF) and by physical adsorption of nitrogen. The SnO$_2$/SiO$_2$ nanocomposite was characterized by scanning electron microscopy (SEM), by X-ray diffractometry (XRD) and Raman spectroscopy and Fourier transform infrared spectroscopy (FT-IR).

2. Experimental

2.1. Extraction of SiO$_2$ and Preparations of nanocomposite

Extraction of silica was made by grinding of the rice husk (RH) followed by chemical treatment with HCl (10% v/v), in the ratio RH:HCl 1:3, for one hour with constant stirring to solubilize organic matter. The solubilized RH was washed with ultrapure water and it was filtered under vacuum, obtaining a pulp (PRH) which was treated with a solution of H$_2$SO$_4$ and H$_2$O$_2$ in the ratio of 1:2:1 (w/v/v) - PRH:H$_2$SO$_4$:H$_2$O$_2$ - under constant stirring for one hour to promote the oxidation of organic matter. Finally, the oxidized PRH was washed with ultrapure water and the biogenic SiO$_2$ was obtained by vacuum filtering and calcinations in an oven for 4h at 600 °C.

SnO$_2$/SiO$_2$ nanocomposite was prepared by adding biogenic silica and SnCl$_2$:2H$_2$O to a solution of nitric acid (NA)/ethylene glycol (EG), obeying the following proportions 1:3:12 (SnCl$_2$:2H$_2$O: CA: EG) and 1:4 (w / w) - (SiO$_2$#: SnCl$_2$:2H$_2$O). This mixture was stirred for 1h at 60 °C with subsequent heat treatment at 250 °C for 2 hours, followed by calcination at 400 °C during 1 hour. All steps of calcination and heat treatment were performed without heating rate.

2.2. Characterization

Biogenic silica was characterized by x-ray fluorescence (XRF) using an Epsilon 3XL spectrometer. Specific surface area was determined by nitrogen gas adsorption using a
Quantachrome Autosorb-iQ equipment by multipoint BET method (Brunauer Emmett Tell) and the average diameter of the silica particles was estimated using the following equation for spherical particles

\[ d_{\text{BET}} = \frac{6}{A_{\text{BET}} \rho_{\text{TEO}}} \]

where \( \rho_{\text{TEO}} \) is the theoretical density for the amorphous silica, having a value of 1.92 g cm\(^{-3}\) and \( A_{\text{BET}} \) is the specific surface area.

Morphology of SnO\(_2\)/SiO\(_2\) nanocomposite was determined by scanning electron microscopy (SEM) using a JEOL model JMS6360-Lv microscope. The crystallinity of the material were characterized by X-ray diffraction (Shimadzu/XRD-7000) with CuK\(\alpha\) radiation (\( \lambda = 1.542 \) Å), 40 kV and 30 mA. Vibrational spectra were recorded on a Bomem MB-series spectrophotometer (Model B100) and Raman spectra were obtained using Confocal Raman equipment model T64000 Jobin-Yvon with laser excitation at 532 nm. Composition of the biogenic silica and the nanocomposite were identified by XRF, and the crystallite size was determined by Debye-Scherrer equation:

\[ d = \frac{K \lambda}{\beta \cos \theta} \]

where \( d \) is crystallite size, \( K \) is shape factor (typical value of about 0.89 for spherical crystalline solids with cubic unit cells), \( \lambda \) is CuX-ray wavelength (1.542 Å), \( \theta \) is Bragg diffraction angle and \( \beta \) is the peak width of the diffraction peak profile at half maximum height.

3. Results and Discussion

3.1. Amorphous SiO\(_2\)

Composition of the biogenic silica is shown in Table 1. According to the percentage values of the components, the methodology used to extraction provided SiO\(_2\) with purity of approximately 98.6\%, higher than commercial SiO\(_2\)\([28]\). The analysis of the surface area by BET method showed an approximated value of 450 m\(^2\) g\(^{-1}\) and a mean particle size of 7 nm, given by Equation 1.

3.2. Structural study of SiO\(_2\) and nanocomposite

XRD diffractogram of the biogenic SiO\(_2\) is presented in Figure 1a and shows a broad peak located approximately at 2\( \theta = 22.5^\circ \), that suggests an amorphous characteristic of the sample and agrees with the reported JCPDS data (card No. 01-086-1561).

XRD pattern for the nanocomposite is shown in Figure 1b and reveals a small shoulder at 2\( \theta = 21.7^\circ \) that can be attributed to amorphous SiO\(_2\) and other peaks assigned to crystalline SnO\(_2\). All values of diffraction peaks are in accordance with JCPDS pattern (card No. 00-041-1485). The main diffraction peaks observed for SnO\(_2\) are centered approximately at 2\( \theta \) values of 27.1\(^\circ\), 34.2\(^\circ\) and 52.1\(^\circ\). In addition, the crystallite size based on the major diffraction peak is 27.8 nm for the nanocomposite.

3.3. Morphology of nanocomposite

Surface morphology of the nanocomposite is presented in Figure 2. SEM micrographs reveal formation of a heterogeneous mixture of agglomerates with irregular shapes and sizes.

3.4. FTIR and Raman analyses

FT-IR and Raman spectra for the SnO\(_2\)/SiO\(_2\) nanocomposite are shown in Figure 3a and 3b, respectively. Comparisons between wavenumber obtained in this work with literature values are exhibited in Tables 2 and 3.

Table 1. Composition of SiO\(_2\) determined by XRF.

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
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<tr>
<td>SiO(_2)</td>
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<tr>
<td>P(_2)O(_5)</td>
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<tr>
<td>Al(_2)O(_3)</td>
<td>0.390</td>
</tr>
<tr>
<td>CaO</td>
<td>0.130</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>0.020</td>
</tr>
<tr>
<td>Ag(_2)O</td>
<td>0.011</td>
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<tr>
<td>MnO</td>
<td>0.007</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.003</td>
</tr>
<tr>
<td>Cl</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Figure 1. XRD obtained for (a) biogenic SiO\(_2\) from rice husk and (b) SnO\(_2\)/SiO\(_2\) nanocomposite.
Infrared spectrum shows a broad band at 3455 cm$^{-1}$ attributed to O-H stretching from hydroxyl groups presents on surface of the material and the band at 1628 cm$^{-1}$ is associated with bending H-O-H bond groups of adsorbed water molecules\textsuperscript{29}. Bands at 467, 807 and 1097 cm$^{-1}$ are assigned respectively to vibrational modes of O-Si-O bending, to symmetric stretching of Si-O-Si group and to the asymmetric stretching of Si-O-Si structural bond of siloxane\textsuperscript{30}. Vibrations in the range from 500 to 700 cm$^{-1}$ are assigned to Sn-O-Sn group as result of condensation reactions\textsuperscript{33}. The bands characterized by the peaks 548 and 664 cm$^{-1}$ are assigned to the Sn-O stretching vibration and Sn-O-Sn asymmetric vibration, respectively\textsuperscript{32}. 

SnO$_2$ has a tetragonal rutile crystalline structure with point group D$_{4h}$\textsuperscript{35}. According to Li et al.\textsuperscript{4}, there are three typical modes to SnO$_2$, in Raman spectrum (474 cm$^{-1}$ (E$_g$), 631 cm$^{-1}$ (A$_{1g}$) and 775 cm$^{-1}$ (B$_{2g}$)). When the particle size decreases, A$_{1g}$ and B$_{2g}$ modes of SnO$_2$ are shifted to lower wavenumbers and E$_g$ mode is shifted to higher wavenumber\textsuperscript{36}. Obtained results have shown that mode at 475 cm$^{-1}$ is assigned to translational mode (E$_g$) of the oxide. On the other hand, mode
at 620 cm\(^{-1}\) is assigned to symmetric O-Sn-O stretching (\(A_{3g}\)) and the third mode at 752 cm\(^{-1}\) is assigned to asymmetric O-Sn-O stretching (\(B_{3g}\))\(^{17}\).

The position of SnO\(_2\) peak in Raman spectrum is dependent of particle size and a fourth vibrational mode (\(B_{1g}\)) peak appears only to nanomaterials. Thus, in the Raman spectrum the presence of an intense peak centered at 125 cm\(^{-1}\) is associated to non degenerated B\(_{1g}\) mode of SnO\(_2\) and is assigned to rotation of the oxygen atoms, with all oxygen atoms participating in the vibration at tetragonal unit cell of rutile\(^{36}\). All modes and assignments are presented in Table 3.

The effects of particle size and disorder in the material lead to a relaxation of the Raman selection rule, and some modes that are usually inactive in Raman become active. Furthermore, the peaks at 242 cm\(^{-1}\), 347 cm\(^{-1}\), 540 cm\(^{-1}\) and 681 cm\(^{-1}\) were assigned to optical phonon modes of SnO\(_2\), \(E_\text{g}(1)\) TO, \(E_\text{g}(2)\) LO, \(A_\text{g}(1)\) TO and \(A_\text{g}(2)\) LO of SnO\(_2\), where LO and TO are longitudinal and transverse optical phonons, respectively\(^{38-40}\).

Peaks at 1354 and 1587 cm\(^{-1}\) are termed D and G bands, respectively\(^{41}\), and confirm the presence of amorphous carbon that is typical of the temperature and of the sol-gel route used for obtain the nanocomposite.

4. Conclusion

Biogenic SiO\(_2\) extracted from rice husk and the SnO\(_2\)/SiO\(_2\) nanocomposite were characterized by XRF, XRD, SEM, FTIR and Raman. The method used in SiO\(_2\) extraction was efficient to obtain amorphous biogenic SnO\(_2\) of high purity in nanometer scale. SnO\(_2\)/SiO\(_2\) nanocomposite behaved as a solid mixture of SnO\(_2\) of low crystallinity and crystalline SnO\(_2\). Therefore, from rice rusk is possible obtain biogenic SnO\(_2\) of high purity that added to SnO\(_2\) provide the SnO\(_2\)/SiO\(_2\) nanocomposite.

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References


