SYNTHESIS AND TERMAL BEHAVIOUR OF ZRO$_2$:AG NANOPARTICLES

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Abstract
Nanoparticles of ZrO$_2$ and ZrO$_2$ decorated with silver were synthesized through the advanced oxidative process and subsequent hydrothermal treatment. The samples were characterized using x-ray powder diffraction, middle infrared region spectroscopy, diffuse reflectance spectroscopy and thermogravimetry. All the samples shown zirconia tetragonal structure. It was possible to observe cubic silver peaks in the samples decorated. The presence of organic matter due to the butoxide precursor was confirmed through the thermogravimetry and infrared techniques.

Keywords: Nanoparticles, Thermal Behaviour, Silver.
Methods and materials

Synthesis (a): For ZrO₂ nanostructure synthesis, the zirconium–hydrogen peroxide complex was formed at room temperature by reaction between zirconium n-butoxide and hydrogen peroxide. Experimental details are as follows: to a Zr[(OCH₂)₃CH₃]₄ precursor agent deionized water solution, H₂O₂ was added under stirring in a 100 mL glass container reaction vessel. A white colloidal suspension of zirconium–peroxo complex was produced instantly. The solution was homogenized using a magnetic stirring bar for 24 h. Finally, the reaction vessel was heated to 200°C for 1 h in a closed stirred reactor system (hydrothermal treatment). After hydrothermal treatment, the system was cooled to room temperature naturally and the turbid suspension was centrifuged to collect a white powder that was five times washed with deionized water. The white product was dried in air at 100°C for 3 h and used for various characterizations. This sample was called Sample 1 (S1).

Synthesis (b): For ZrO₂:Ag nanostructure synthesis, the same methodology is followed, but AgNO₃ is added in concentrations of 1% and 10% by weight in a 100 mL glass container reaction vessel. In order to confirm the presence or absence of silver in the supernatant, it was subjected to a Argentometric method for quantitative analysis of silver. At the end of the titration no silver was detected. The white product which contains all the silver, was dried in air at 100°C for 3 h and used for various characterizations. The sample containing 1% and 10% of Ag was called Sample 2 (S2) and Sample 3 (S3), respectively.

X-ray powder diffractograms were collected on a Rigaku DMAX Ultima+ X-ray diffractometer using CuKα radiation (λ = 1.541 Å) and settings of 150 mA and 40 kV. Thermogravimetry curves were obtained with a STA 449 F3 Jupiter (Netzsch) thermal analysis equipment, under the following experimental conditions: open α-alumina crucibles, heating rate of 20 °C min⁻¹, air atmosphere at a 50 mL min⁻¹ flow and samples of about 5 mg. Middle infrared spectra (MIR) were collected on a Bomem FTIR MB100 spectrophotometer within the 4000-400 cm⁻¹ range, with KBr pellets, in transmittance mode. Solid UV-Vis spectra were collected on a Varian Cary 5000 spectrophotometer by diffuse reflectance within the 800-200 nm range.

Results and discussion

X-ray powder diffractograms of the zirconia and silver decorated zirconia was shown in Figure 1-a, and it is possible to seen the formation of well defined peaks of tetragonal zirconia in all the samples. Sample 2 and 3 shown the characteristics peaks of cubic silver. The crystal size was estimated by the Scherrer equation and the (111) peak of zirconia and the (111) peak of silver in XRD patterns were used in the calculations. The calculated values for zirconia were 7.37, 8.96 and 9.25 nm for samples 1, 2 and 3 respectively and the calculated values for silver crystal size were 33.80 and 43.91 nm for samples 2 and 3 respectively.
Fig. 1 – (a) XRD patterns of the samples after AOP/hydrothermal treatment; (b) Diffuse reflectance spectra and (c) f(R) plot of the samples.

Diffuse reflectance spectra of all three samples (Figure 1-b) shows the zirconia band that starts at 356 nm. Ploting the spectra as f(R) (Figure 1-c) and applying the Kubelka-Munk function the band gap was determined by the tangent and the values are 5.21, 5.16 and 5.18 for the Samples 1, 2 and 3 respectively, in agreement with the values found in literature for the zirconia band gap. In the spectra of the silver decorated particles a broad plasmon band appears at 405 and 424 nm for the sample 2 and sample 3, respectively.

Thermogravimetry curves are shown in Figure 2-a. The curves indicates two main steps of mass loss. The first is attributed to the loss of solvent molecules absorbed on the surface of ZrO$_2$ nanostructure and the second step is attributed to the decomposition of organic matter due to butoxide not oxidized in hydrothermal treatment. Sample 1, sample 2 and Sample 3 shows a first mass loss of 5.60, 4.71 and 5.89 % between 35-150 °C, respectively, and is attributed to the loss of water molecules used in the synthesis. For the sample 1 the second mass loss occurs in the interval of 150-790 °C and in the samples 2 and 3 this loss occurs in the interval of 150-650 °C and is 14.55, 2.77 and 2.43 % for the Sample 1, Sample 2 and Sample 3, respectively. The water content in the three samples quite similar, but the organic matter content is larger in sample 1, this is probably due to a smaller amount of butoxide used in the synthesis of sample 2 and 3 due to the presence of silver nitrate in these samples.

The presence of organic matter and the solvent molecules adsorbed in the surface of nanostructure was confirmed in the middle infrared region spectra (Figure 2-b). In the three samples the CH$_3$ and CH$_2$ assymetrical stretching appears as a little intense bands in the 2980-2910 cm$^{-1}$ region. The broad bands centered at 3430 and 1635 cm$^{-1}$ appears and is attributed to the OH stretching (symmetric and asymmetric) and HOH bending vibration of the water molecules, respectively. The band near of 1460 cm$^{-1}$ is assigned to the CH asymmetrical bending of CH$_3$ and CH scissoring of CH$_2$. The band near of 1125 cm$^{-1}$ and 1015 cm$^{-1}$ are assigned to C-C and C-O stretching of the butoxide, respectively. A large band in the 800-400 cm$^{-1}$ region are related to the Zr-O bond.
Fig. 2 – (a) Thermogravimetry curves of the samples and (b) MIR spectra of the samples.

Conclusions

Nanoparticles of ZrO₂ and ZrO₂:Ag were synthesized. Through XRD technique it was possible to observe a tetragonal structure of zirconia the samples and a cubic structure for silver in the decorated samples. The crystal size of ZrO₂ was estimated by the Scherrer equation and the values for zirconia were 7.37, 8.96 and 9.25 nm for samples 1, 2 and 3 respectively and the calculated values for silver crystal size were 33.80 and 43.91 nm for samples 2 and 3 respectively. The presence of silver in the two decorated samples was also confirmed by diffuse reflectance spectroscopy with the presence of the silver plasmon band in the spectra. The band gap was determined applying the Kubelka-Munk function in the diffuse reflectance spectra and the values found are 5.21, 5.16 and 5.18 for the Samples 1, 2 and 3 respectively. The organic matter presence in the samples was confirmed by TG curves and MIR spectra, which presents the characteristics bands of the butoxide precursor.

Acknowledgements

CNPQ, FAPESP and CAPES.

References