

Research Article

Surface Modification of SnO₂ with Phosphonic Acids

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Received 16 November 2016; Revised 2 January 2017; Accepted 4 January 2017; Published 22 January 2017

Academic Editor: Jean-Marie Nedelec

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The aim of the present work was the study of phosphonic acids grafting on the surface of SnO₂ at different molar ratios. In this paper we describe the functionalization of SnO₂ surfaces with phosphonic acids RPO(OH)₂. The surface modification process was achieved by using phenyl-phosphonic acid (PPA) and vinyl-phosphonic acid (VPA). The synthesized materials were investigated by using FT-IR, TGA (in air and in nitrogen), EDX, ESEM, and TEM methods. This synthetic approach has many advantages: films with optical quality and controlled thickness can be obtained using low temperatures and cheap raw materials, by using “green chemistry” synthetic routes. The hybrid materials have structures diversity and fascinating applications, attracting attention for a long time, due to their potential.

1. Introduction

Metal or metal oxide nanoparticles have unique characteristics compared to larger scale materials. For applications, it is necessary to stabilize or to give a particular function to such nanoparticles. Surface grafting of nanoparticles is an important challenge in chemistry [1] and is of great interest for optical and electric applications, but especially for their use in medicine.

Synthesis of organic-inorganic hybrid materials leads to combining physical and chemical properties of organic and inorganic components. Hybrid organic-inorganic films are an ideal material for those applications in which transparency and homogeneity are of primary concern, such as in optics and photonics [2, 3]. The synthetic methods have a central role in the development of new materials [4]. Recent development in the field of nanoscience and nanotechnology has set a focus on synthetic approaches to complex assemblies of nanoparticles with applications in optics, electromagnetism, bioimaging, and pharmaceuticals [5, 6].

Titanium dioxide nanomaterials are known for their numerous and diverse applications, which range from common

products, as sunscreens, to advanced devices, as photovoltaic cells, and include many environmental and biomedical applications (photocatalytic degradation of pollutants, water purification, biosensing, and drug delivery). The importance of these applications increased the interest for the fabrication and characterization of TiO₂ nanomaterials in the last decades [7–10].

The addition of tin oxide or zirconium oxide typically serves to increase the refractive index of the photocurable hybrid material and to control the synthesis conditions: this is important for applications in optics [11, 12]. This synthetic approach has many advantages: films with optical quality and controlled thickness can be obtained using low temperatures and cheap raw materials. Nanoparticles of a broad variety of main group and transition metal oxides form exceptionally stable surface complexes with the ligands incorporating phosphate or phosphonate moiety [13].

Organic-inorganic hybrids appear as a creative alternative to obtain new materials with unusual features. These materials are considered innovative advanced materials and promising applications are expected in many fields: optics, electronics, mechanics, membranes, protective coatings, catalysis,

sensors, biology, catalysis, elaboration of solid phases for chromatography, organic synthesis on solid phases, and the modification of the surface properties of solids [14–26].

The nanostructure, the degree of organization, and the properties that can be obtained for such materials depend evidently on the chemical nature of their components, but they also depend on the synergy of these components. The design of organically modified surfaces is a rapidly expanding field of research in materials science in which the central purpose is access to materials possessing tunable properties in diverse areas (derivatization of substrates with reactive end groups for further modification, protective layers, analytical or biological sensors, catalysis, biomedical devices, solar batteries, etc.). The most commonly applied approach to the stabilization of metal oxide nanoparticles dispersions is based on grafting of organic molecules on their surface [27, 28].

This modification can be performed using traditional polymer coatings or layer by layer deposition of ionic species [29], but the next-generation technologies increasingly involve grafting onto the surface using appropriate functional molecules, thus providing a better control of the density and orientation of the organic component at the surface.

Titania-based adsorbents can be surface modified for potential uses in various applications using organic monolayers carrying a wide range of organic functionalities [30]. Surface modification allows TiO₂ nanoparticles to be stabilized in both aqueous [13] and hydrocarbon [31, 32] media. They have also been converted into hybrid organic-inorganic materials with a lot of potential applications in several fields [33, 34].

The modification of metal oxides surfaces (SnO₂, TiO₂, or ZrO₂) with phosphonic acids is currently attracting growing interest in different areas as self-assembled monolayers [35] and ceramic membranes [36]. The balance between surface complexation (grafting) and surface phase transformation (metal phosphonate phases) [37] depends strongly on the experimental conditions. The use of aqueous solutions of phosphonic acids may result in the formation of phosphonate phases instead of the simple grafting, depending on the conditions [36, 37].

This paper is focused on the synthesis of hybrid materials by grafting of SnO₂ surfaces with phenyl-phosphonic acid and vinyl-phosphonic acid.

2. Experimental

2.1. Materials and Methods

2.1.1. Materials. SnO₂ (Carlo Erba), phenyl-phosphonic acid (PPA)-C₆H₅P(O)(OH)₂ (Fluka), vinyl-phosphonic acid (VPA), C₂H₅PO₃ (Merk), and water were used as purchased.

2.1.2. Methods. There were carried out four syntheses (S1–S4). The first three syntheses were performed with phenyl-phosphonic acid at different molar ratios SnO₂:PPA (1:1, 2:1, and 3:1). In the case of S4, vinyl-phosphonic acid was used at molar ratio SnO₂:VPA 2:1.

In a Berzelius flask containing 50 ml water, tin oxide was dispersed. The amount of SnO₂ used was 0.5 g for S1, 1 g for S2, and S4 and 1.5 g for S3, respectively. Then, 0.55 g phenyl-phosphonic acid for S1, S2, and S3 (resp., 0.4 g vinyl-phosphonic acid for S4) was dissolved in 50 ml water and was added dropwise to the mixture, over a period of time of 20–30 minutes. The reaction mixture was left under stirring for 32–35 hours.

The reaction mixture was filtered in vacuum, resulting for all compounds in a light grey precipitate, while the filtrate is very clear. The precipitate was left to dry for 2–3 days to dryness, resulting in synthesis of S1@PPA, S2@PPA, S3@PPA, and S4@VPA.

2.2. Equipment

- (i) Jasco FT-IR 4200 Spectrometer, KBr support, was used for recording the spectra.
- (ii) Thermal analysis TGA-DTG-DTA (thermogravimetry) was carried out by changing the temperature between 20°C and 900°C, by using an 851-LF 1100-Mettler Toledo apparatus in airflow. It has a sensitivity of 1 µg. The maximum amount of the sample, which could be measured, is 5 g.
- (iii) SEM and EDX characterizations were made using a Jeol JSM 6400 Scanning Microscope coupled with an X-ray microanalyzer EXL II System Link Analytical with a detector of 133 eV.

3. Results and Discussion

The modification of SnO₂ surfaces with phosphonic acids is attracting growing interest because of the applications of such hybrid materials in different fields. This work describes the study of phosphonic acids grafting on the surface of SnO₂ at different molar ratios.

The surface modification process was achieved using phenyl-phosphonic acid (PPA) and vinyl-phosphonic acid (VPA). The synthesized materials were investigated by using FT-IR, TGA (in air and in nitrogen), EDX, ESEM, and TEM methods.

In (Figure 1) characteristic FT-IR spectra for phenyl-phosphonic acid (S1) and vinyl-phosphonic acid (S4) of synthesized grafting of the SnO₂, there are intense absorption bands at $\nu_{(P=O)} = 1145.47\text{--}1239.12\text{ cm}^{-1}$. In each of these spectra, we can clearly see the presence of important bands overlapping in the $987.37\text{--}997.01\text{ cm}^{-1}$ region, corresponding to the different vibration modes of the phosphonic acid confirming the grafting of the molecules on the surface. Unfortunately, the absorption bands in this region are too poorly defined to clearly identify them and eventually determine the way the bifunctional molecules bind the surface. In the $\nu_{(C-H)} = 3735.4\text{--}3736.4\text{ cm}^{-1}$ region of the spectra, very weak C–H asymmetric and symmetric stretching vibrations bands are observed around 3064.30 cm^{-1} . The bands in the regions of $987.37\text{ cm}^{-1}\text{--}997.01\text{ cm}^{-1}$ and $1646.91\text{--}1647.88\text{ cm}^{-1}$ were attributed to stretching and vibrations of the –Sn–O–Sn– group and at 3853.08 cm^{-1} were attributed for Sn–O–P

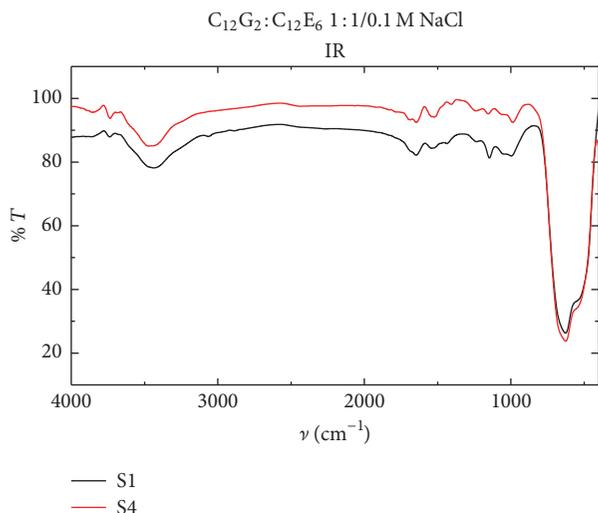


FIGURE 1: The characteristic IR spectra for the representatives synthesized compounds by grafting phosphonic acids on the SnO_2 .

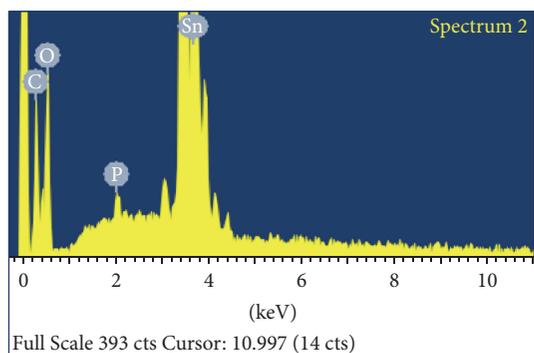


FIGURE 2: EDX spectrum of SnO_2 @ phenyl-phosphonic acid (S1).

indicating the formation of the grafting of acid phosphonic the SnO_2 . The band ascribed to superficial Sn–O vibrations appeared at 625.78 cm^{-1} . In addition, the FT-IR spectrum of the phosphonic acid grafted on SnO_2 shows bands at $\nu_{(\text{P-O})} = 997.01\text{ cm}^{-1}$, $\nu_{(\text{OH})} = 3736.4\text{ cm}^{-1}$. These values are indicative of weakly organized monolayer. These results confirm the presence of the grafting of phosphonic acids on the SnO_2 . From the values obtained, it results that the functionalization of tin oxide surface occurred with a higher yield with phenyl-phosphonic acid (S1–S3) relative to vinyl-phosphonic acid (S4).

In order to fully characterize the synthesized hybrid materials EDX analysis was also performed. Based on this analysis, the presence of all the elements could be confirmed for all the samples, including the presence of the phosphorus, which proves that the hybrid material containing SnO_2 and the phosphonic acid was indeed obtained.

In addition to the previous described measurements, EDX analysis was also studied (Figures 2–5). Based on this, in the cases of phenyl-phosphonic acid and vinyl-phosphonic acids grafted on the tin oxide magnetic nanoparticles, the

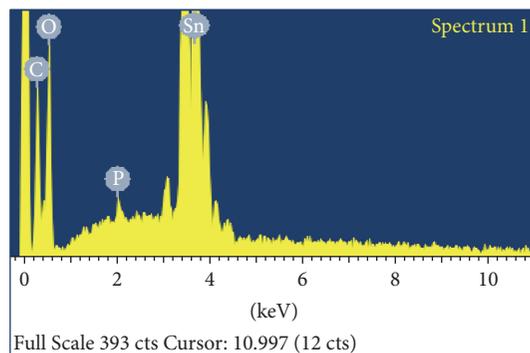


FIGURE 3: EDX spectrum of SnO_2 @ phenyl-phosphonic acid (S2).

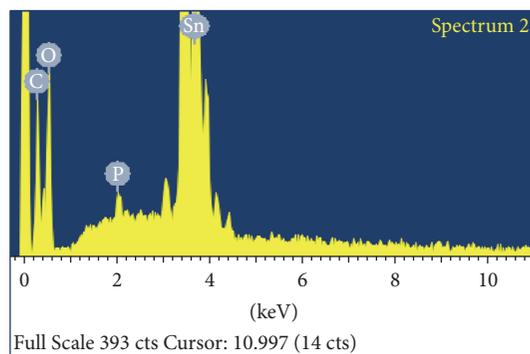


FIGURE 4: EDX spectrum of SnO_2 @ phenyl-phosphonic acid (S3).

presence of phosphorus can be observed in all analyzed samples.

The presence of phosphorus was confirmed for all the obtained samples (Figures 2–5). Based on this analysis, the presence of the combined material can be confirmed by the presence of Sn, P, O, and C in the spectra.

From ESEM results (Figure 6(a), S1, Figure 6(b), S2, Figure 6(c), S3, and Figure 6(d), S4), we can observe no differences in morphology for all analyzed samples because the structures are very similar. The different radicals from their structures could not influence ESEM images at this resolutions.

The TEM images (Figure 7(a), S1, Figure 7(b), S2, Figure 7(c), S3, and Figure 7(d), S4) confirmed the findings from ESEM measurements, in the way that all the samples showed similar morphology. This is expected because the samples' structures were not very different. Only the radicals (phenyl, vinyl) could not change the morphology significantly, according to TEM resolutions.

The TGA curves recorded for all samples are presented in Figures 8 and 9.

It is obvious that the TGA curves show small weight loss in the temperature range $25\text{--}800^\circ\text{C}$, lower than 5% weight (Table 1).

Because the weight loss up to the temperature of 130°C is under 0.5% wt, the physically adsorbed water or trapped solvent was missing or was totally removed, due to the prior drying step. Over 200°C in the all samples a monotonous

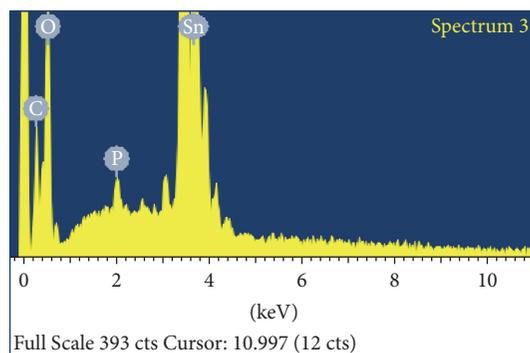


FIGURE 5: EDX spectrum of SnO_2 @ vinyl-phosphonic acid (S4).

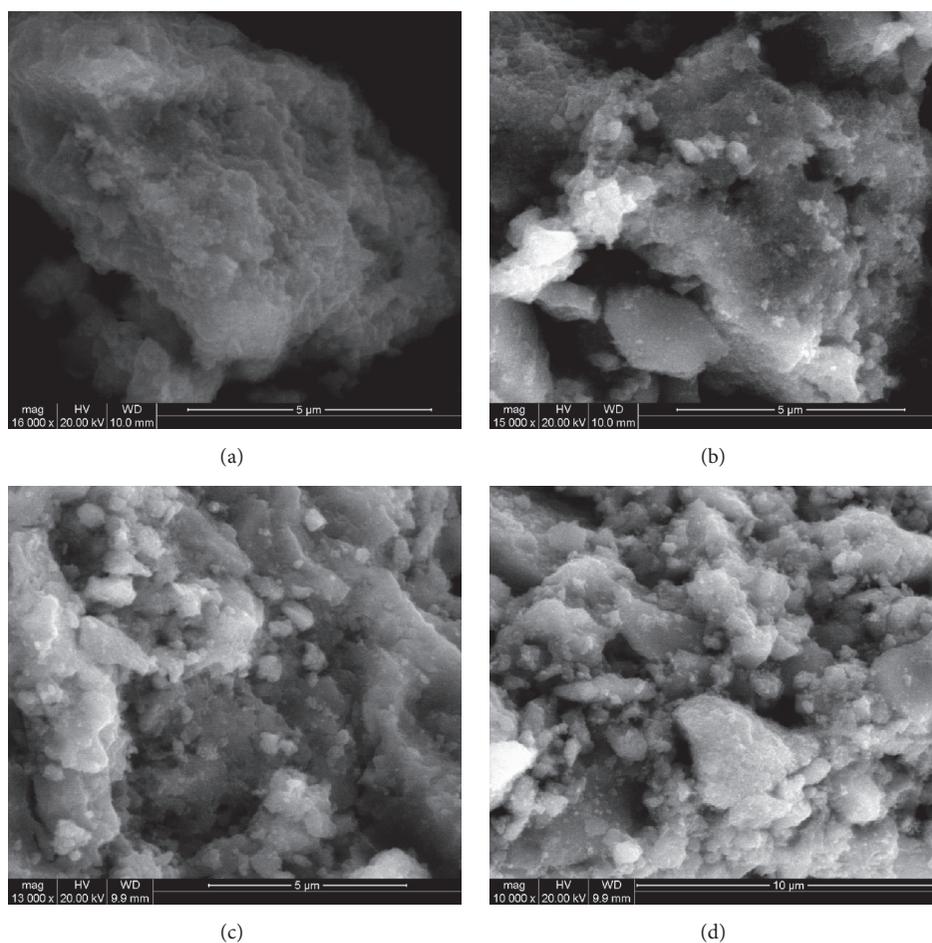


FIGURE 6: ESEM images for S1–S4 compounds.

TABLE 1: TGA data for S1–S4 compounds.

Sample	Weight loss, % 25–130°C		Weight loss, % 130–550°C		Total weight loss till 800°C in air, %
	Air	Nitrogen	Air	Nitrogen	
S1	0.33	0.30	4.10	3.03	4.31
S2	0.47	0.26	3.01	2.41	3.40
S3	0.45	0.30	2.63	2.24	3.09
S4	0.54	0.42	2.45	1.98	2.89

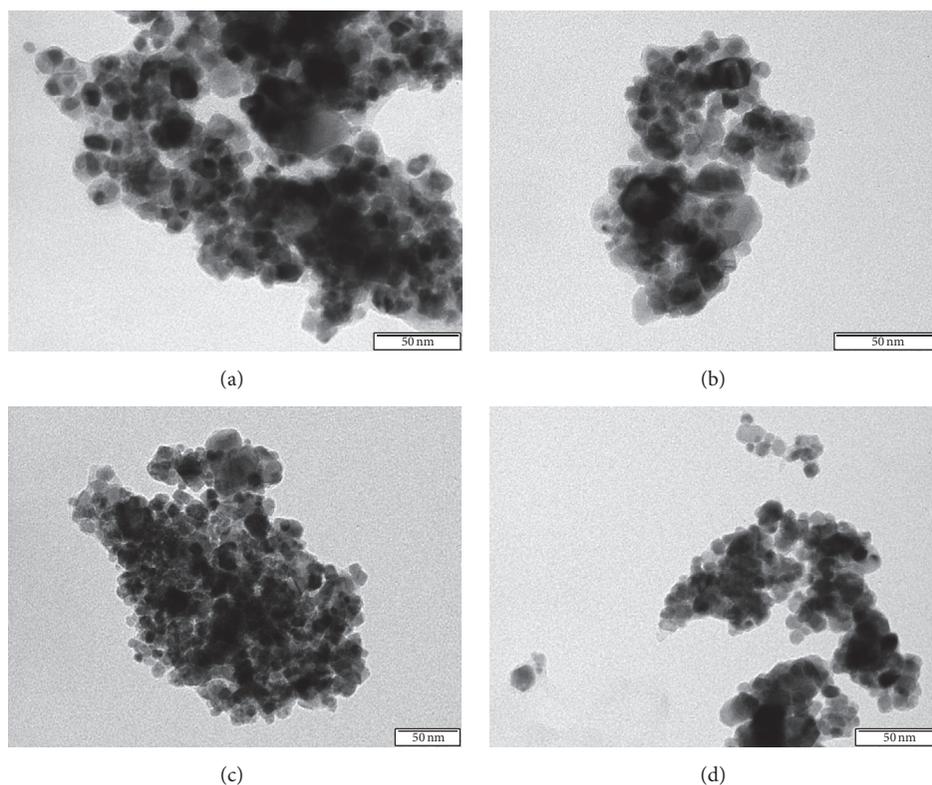


FIGURE 7: TEM results for S1-S4 synthesized structures.

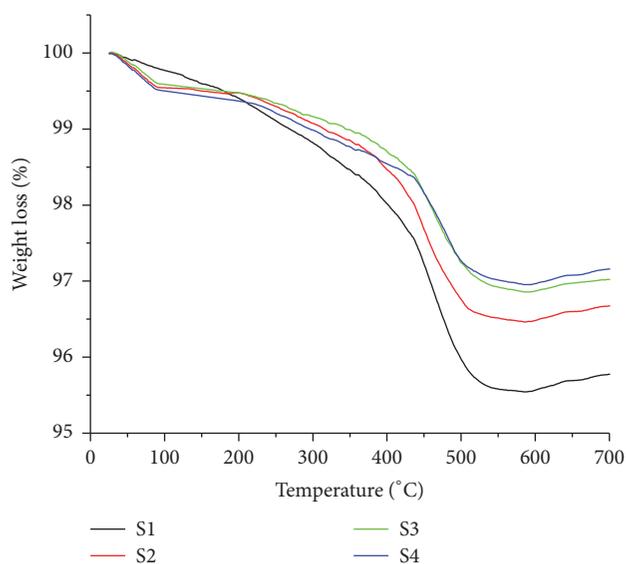


FIGURE 8: TGA curves of S1-S4 compounds in air.

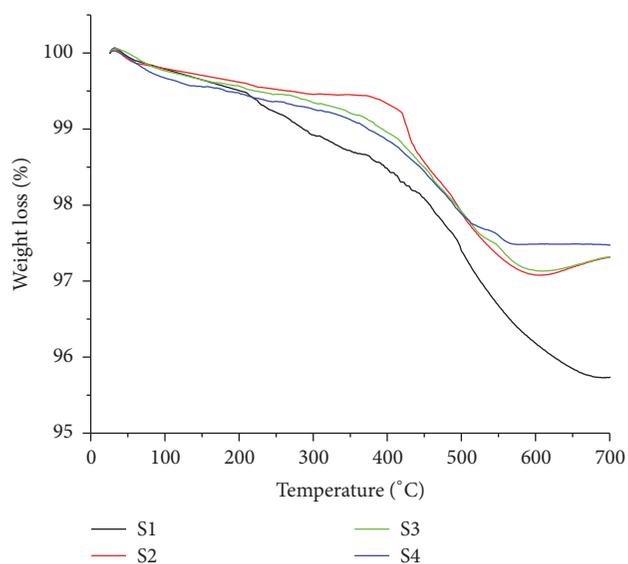


FIGURE 9: TGA curves of S1-S4 compounds in nitrogen.

decrease can be observed and mass loss curves indicate the decomposition of organic moiety and SnO_2 crystalline structure modifications. Each sample presents different weight loss over 200°C , associated especially with the nature of organic acids attached on the SnO_2 surface (Table 1). The second and more intense exothermic peak is related to the thermal decomposition of the organic matter, just as

observed in the TGA curves. This peak is attributed to the combustion of the organic material yielding basically CO_2 , P_2O_5 , and H_2O . Almost no weight loss is observed above 600°C , suggesting the formation of crystalline SnO_2 as a decomposition product. Tin oxides are stable between 500°C and 800°C .

In air, for sample S1 from 130°C to 435°C and 435°C to 550°C, there are two small exothermic peaks, which correspond to 2.10% and 1.99% relative weight losses. At about 435°C, the decomposition rate increases sharply.

For sample S2 from 130°C to 390°C and 390°C to 550°C, there are two small exothermic peaks in the air, which correspond to 0.96% and 2.06% relative weight losses. At about 460°C, the decomposition process takes place with the higher rate.

Sample S3, in air from 130°C to 365°C and 365°C to 550°C, shows two small exothermic peaks corresponding to 0.60% and 2.06% relative weight losses, respectively. At about 475°C, the decomposition process takes place with the maximum rate.

Two small exothermic peaks corresponding to 0.94% and 1.50% relative weight losses are observed for sample S4 in air from 130°C to 405°C and 405°C to 550°C, respectively. At about 475°C, the decomposition rate is maximum.

In nitrogen, the samples present two major weight losses, presented in Table 1. The first weight loss is associated with the release of moisture (90–130°C). The temperature range 130–550°C presents a weight loss mainly attributed to the release of the structural water resulting from the bonded hydroxyl groups and to the other process like degradation of P–C bonds.

TGA data showed a high thermal stability for all the obtained compounds. The mass losses were below 5%. According to Figures 8 and 9 and Table 1, due to the lowest mass loss, the most stable compound was obtained at molar ratio SnO₂ : PPA 3 : 1. On the other hand, at the same molar ratio of 2 : 1, the thermal stability was higher for the materials obtained with VPA, than in the case when PPA was used.

4. Conclusions

The grafting of the surface of SnO₂ under “green” conditions by using water as solvent was investigated by FT-IR, EDX, ESEM, TEM, and TGA (in air and in nitrogen). From FT-IR spectra, it results that the grafting of tin oxide surface occurred with a higher yield when phenyl-phosphonic acid (S1–S3) was used, in comparison with vinyl-phosphonic acid (S4).

From EDX determinations, the presence of phosphorus was confirmed for all the obtained samples, resulting in that the grafting process of SnO₂ on phosphonic acids took place. Based on this analysis, the presence of the combined material can be confirmed by the presence of Sn, P, O, and C in the spectra.

The images obtained with TEM and ESEM revealed the morphology of the synthesized nanoparticles and materials. From the images obtained with ESEM, we can observe no differences in morphology for all analyzed samples, because the structures are very similar. As expected, TEM images confirmed the findings from ESEM measurements, in the way that all the samples showed similar morphology.

TGA data indicate for samples S1–S4 a high thermal stability. For all samples the mass losses are under 5% wt and a monotonous decrease over 200°C takes place and indicates

the decomposition of organic moiety and SnO₂ crystalline structure modifications.

The types of inorganic surfaces which can be modified using phosphonic acid chemistry are summarized in the present paper, as well as the related mechanisms involved when attaching phosphonate groups onto these surfaces. This paper finally goes on to outline the richness of applications, which can be developed from the resulting functional materials. Indeed, grafting by phosphonic compounds would allow the introduction of more organic groups on the surface of SnO₂.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

The authors acknowledge the financial support of the ITN project 290248 part of the EU-ITN network Mag(net)icFun, FP7 Marie Curie Actions, and part of Research Program 2, Project 2.2, of Institute of Chemistry Timisoara of the Romanian Academy.

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