

# Solventless Preparation of Thoria and Its Inclusion into SiO<sub>2</sub> and TiO<sub>2</sub>: A Luminescence and Photocatalysis Study

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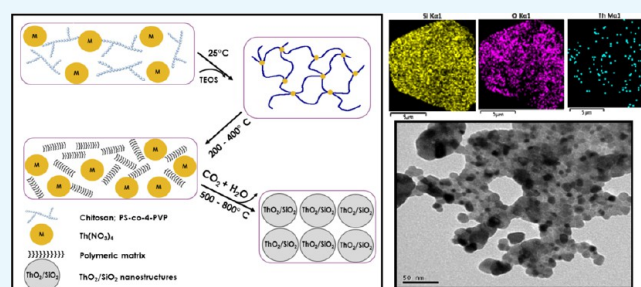


Article Recommendations



Supporting Information

**ABSTRACT:** Thoria was prepared using a solid-state method from the macromolecular precursor Chitosan·Th(NO<sub>3</sub>)<sub>4</sub> (chitosan) and PS-co-4-PVP·Th(NO<sub>3</sub>)<sub>4</sub> (PVP). The morphology and the average size of ThO<sub>2</sub> depend of the chitosan and PS-co-4-PVP polymer forming the precursor. Their photoluminescent properties were investigated, finding a dependence of their intensity emission maxima, with the nature of the precursor polymer. The photocatalytic activity of ThO<sub>2</sub> toward the degradation of methylene blue was measured for the first time, finding a degradation of about 66% in 300 min. The inclusion of ThO<sub>2</sub> into SiO<sub>2</sub> and TiO<sub>2</sub> was achieved by the solid-state pyrolysis of the macromolecular composites Chitosan·Th(NO<sub>3</sub>)<sub>4</sub>//MO<sub>2</sub> and PS-co-4-PVP·Th(NO<sub>3</sub>)<sub>4</sub>//MO<sub>2</sub>, MO<sub>2</sub> = SiO<sub>2</sub> or TiO<sub>2</sub>. The ThO<sub>2</sub> exhibits a homogeneous dispersion inside the silica, showing sizes of about 40 and 50 nm for the chitosan and PVP polymer precursors, respectively. The luminescent properties of the ThO<sub>2</sub>/SiO<sub>2</sub> and ThO<sub>2</sub>/TiO<sub>2</sub> composites were also studied, finding a decrease in intensity when introducing the SiO<sub>2</sub> or TiO<sub>2</sub> matrices. The photocatalytic behavior to methylene blue degradation of ThO<sub>2</sub> and their composites ThO<sub>2</sub>/SiO<sub>2</sub> and ThO<sub>2</sub>/TiO<sub>2</sub> was investigated for the first time, with them in the following order: ThO<sub>2</sub> > ThO<sub>2</sub>/TiO<sub>2</sub> > ThO<sub>2</sub>/SiO<sub>2</sub>.



## INTRODUCTION

Among actinides oxides, thoria is an important and promising material used in ceramic catalyst sensor solid electrolytes, catalysis and optical materials, and in the traditional nuclear industry.<sup>1–4</sup> In spite of this, few papers related to the preparation and properties of nanostructured ThO<sub>2</sub> have been reported. Among other methods, thermolysis, precipitation, sol–gel, or hydrothermal synthesis under supercritical conditions were proposed. Dash et al.<sup>5</sup> prepared ThO<sub>2</sub> by thermal decomposition of Th(CO<sub>3</sub>)<sub>2</sub>, while Tabakova<sup>6</sup> prepared thoria starting from Th(NO<sub>3</sub>)<sub>4</sub> and then precipitating the thorium hydroxide with K<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> followed by thermal treatment. A similar route was followed by Reibold et al.,<sup>7</sup> preparing thoria by hydrolysis of Th(NO<sub>3</sub>)<sub>4</sub> in the presence of ammonium hydroxide and propylene oxide. In another approximation, Moeini et al.<sup>8</sup> prepared ThO<sub>2</sub> by a hydrothermal process employing supercritical water. Most recently, Hudry et al.<sup>3</sup> used the oleyamine method to prepare ThO<sub>2</sub> of controlled morphology, while Shi and co-workers also prepared ThO<sub>2</sub> using a hydrothermal method starting from Th(NO<sub>3</sub>)<sub>4</sub> pentahydrate.<sup>9</sup> Recently, Pinkas<sup>10</sup> reports the preparation of thorium dioxide with nanofibrous morphology by the electrospinning method. Also, Romanchuk<sup>11</sup> reported that the facile chemical precipitation method and subsequent thermal treatment were shown to be suitable for preparation of

crystalline ThO<sub>2</sub> nanoparticles. Verma<sup>12</sup> has newly reported that ThO<sub>2</sub> nanoflowers can be successfully synthesized using thorium nitrate pentahydrate as the metal source along with two different capping agents.

Almost all of these preparation methods involve solution procedures. However, several of the abovementioned practical applications require the incorporation of ThO<sub>2</sub> into solid-state devices. Generally, the incorporation of metal-oxide nanoparticles into solid devices is problematic when those have been produced via a solution phase method because the solid-state isolation could cause nanoparticle agglomeration.<sup>13–16</sup> In this regard, the synthesis of nanoparticles directly from a solid-state approach might represent a more reliable method to achieve the incorporation of metal oxides into practical applications.

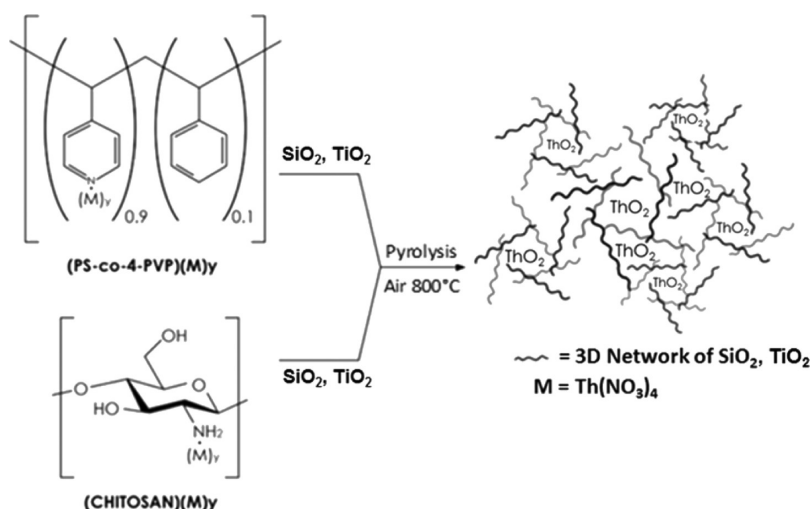
In addition, various practical applications—for instance, catalysis—involving solid-state devices are formed by nanoparticles and/or nanostructures inside a solid matrix, such as

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Scheme 1. Schematic Representation of the Preparation of the Composites ThO<sub>2</sub>/SiO<sub>2</sub> and ThO<sub>2</sub>/TiO<sub>2</sub>

SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, glasses, and so on.<sup>17,18</sup> For this reason, we will show results about the incorporation of thoria inside SiO<sub>2</sub> and TiO<sub>2</sub> matrices. This solid-state route synthesis method to prepare nanostructured metal and metal oxides materials from thermal treatment of the Chitosan·(MLn)<sub>n</sub> and PS-co-4-PVP·(MLn)<sub>n</sub> precursors under an air atmosphere was developed recently.<sup>19–21</sup>

In this paper, we have applied this methodology to prepare nanostructured ThO<sub>2</sub> from the chitosan and PVP precursors. We also present an easy alternative procedure to prepare nanostructured thoria and their inclusion inside SiO<sub>2</sub> and TiO<sub>2</sub>, as seen in Scheme 1. Their photoluminescent properties and the photocatalytic activity toward the degradation of methylene blue were also investigated.

This novel and original work includes the first systematic study of the effect of different matrices—SiO<sub>2</sub> and TiO<sub>2</sub>—in a metal oxide such as thoria, determining their optical and photocatalytic properties. There are very limited studies regarding ThO<sub>2</sub> photocatalytic activity and more especially regarding its combined effect with different matrices.

The inclusion of thoria will be performed by a novel solid-state thermolysis of different chitosan and PVP precursors, ensuring a regular distribution of thoria with the different Ti and Si oxides.

## METHODOLOGY DESCRIPTION

**Reagents.** Th(NO<sub>3</sub>)<sub>4</sub>, TEOS (tetraethylortosilicate), chitosan, and poly(styrene-co-4-vinylpyridine) PS-co-4-PVP were purchased from Sigma-Aldrich and were used as-received.

**Preparation: Synthesis of the Precursors.** Chitosan·Th(NO<sub>3</sub>)<sub>4</sub> and PS-co-4-PVP·Th(NO<sub>3</sub>)<sub>4</sub>. The typical procedure is described as follows: in a Schlenk flask, an appropriate amount of Th(NO<sub>3</sub>)<sub>4</sub> and chitosan or PS-co-4-PVP were added into CH<sub>2</sub>Cl<sub>2</sub> at different [polymer/Th(NO<sub>3</sub>)<sub>4</sub>] molar ratios (1:1; 1:5). The heterogeneous mixture was stirred at room temperature for a given reaction time (reaction time and additional details for each Th(NO<sub>3</sub>)<sub>4</sub> reaction are explained in Table S1 of the Supporting Information). After removing the supernatant solution by decantation, the remaining solid was dried under reduced pressure to give a white solid.

Chitosan·Th(NO<sub>3</sub>)<sub>4</sub>/SiO<sub>2</sub> and PS-co-4-PVP·Th(NO<sub>3</sub>)<sub>4</sub>/SiO<sub>2</sub>. SiO<sub>2</sub> was prepared according to the following literature procedure.<sup>21</sup> Briefly, tetraethoxysilane (TEOS), ethanol, and

acetic acid in a molar ratio of 1:4:4 were mixed with water (nanopure), and the mixture was stirred for 3 days. The obtained gel was dried at 100 °C under reduced pressure in a vacuum furnace.

**Pyrolysis of the Precursors.** Pyrolysis experiments were performed using 0.05–0.15 g of the metallic Chitosan·Th(NO<sub>3</sub>)<sub>4</sub> and PS-co-4-PVP·Th(NO<sub>3</sub>)<sub>4</sub> precursors, as well as their composites with SiO<sub>2</sub>. The samples were placed in alumina boats and heated in a furnace (Daihan oven model Wise Therm FHP-12) under an airflow up to 200 °C and then to 800 °C, followed by annealing for 2–4 h. The heating rate was fixed at 10 °C min<sup>-1</sup> for all experiments.

**Characterization of the Pyrolytic Products.** The solid pyrolytic samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM), Fourier transform infrared (FT-IR) spectroscopy, and thermogravimetric and differential scanning calorimetric analysis. SEM images were acquired with a Philips EM 300 scanning electron microscope. Energy-dispersive X-ray analysis was performed on a NORAN Instrument microprobe attached to a JEOL 5410 scanning electron microscope. TEM data were acquired using a JEOL SX100 and a JEOL 2011 transmission electron microscope. HRTEM observations were performed using a JEOL 2000FX microscope at 200 kV. TEM samples were prepared by dispersing the pyrolyzed material onto copper grids in ethanol media and then dried at room temperature. XRD was conducted at room temperature on a Siemens D-5000 diffractometer with  $\theta$ -2 $\theta$  geometry. XRD data were collected using Cu K $\alpha$  radiation (40 kV, 30 mA). FTIR measurements were performed on a PerkinElmer FT-IR spectrophotometer model Spectrum BXII.

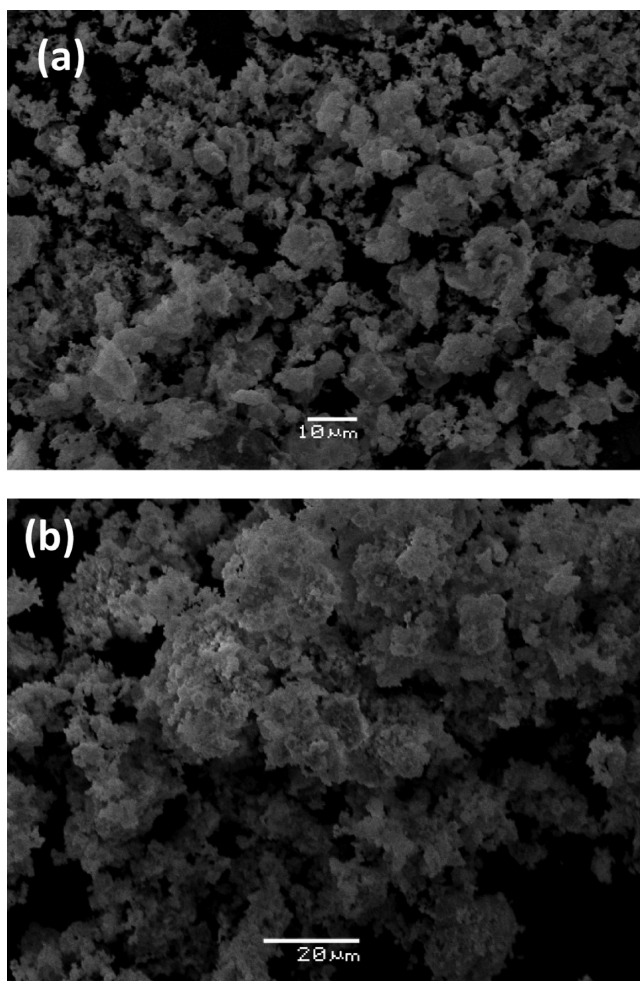
**Photocatalytic Measurements.** For the evaluation of the photocatalytic activity of the composites, 30 mL of a buffer solution at pH 7 of 1 × 10<sup>-5</sup> M methylene blue (AM) was used. To reduce the adsorption of the dye on the surface, a buffer solution of pH = 7 was used to reach a zero isoelectric point. The same amount of mass (5.6 mg) was added for the composites dissolved in 300  $\mu$ L of ethanol.

Irradiation was performed with a 300 W xenon lamp model 6258, which presented an incident light intensity of 1250 mW/m<sup>2</sup>, measured with a pyranometer. The distance between the lamp and the suspension was 16 cm. The AM concentration

for each sample was determined by UV–vis spectrophotometry. Specifically, the intensity of the maximum absorbance corresponding to the lowest energy peak of the characteristic spectrum of methylene blue at 664 nm was measured. The photocatalytic efficiency of the products is expressed as the variation of the percentage of degradation with respect to the irradiation time.

## RESULTS AND DISCUSSION

ThO<sub>2</sub> was prepared by thermal treatment of the chitosan and PVP precursors. The XRD pattern shows the pure phase of ThO<sub>2</sub> arising from these two precursors (see Supporting Information S2), in concordance with the other XRD pattern reported from solution methods.<sup>1,4,5,8,9</sup> SEM images evidence a morphology composed of porous grains of ThO<sub>2</sub> particles arising from both macromolecular complexes (see Figure 1).



**Figure 1.** SEM image of ThO<sub>2</sub> from the Chitosan·Th(NO<sub>3</sub>)<sub>4</sub> precursor (a) and from PS-co-4-PVP·Th(NO<sub>3</sub>)<sub>4</sub> (b).

Similar morphology was observed for ThO<sub>2</sub> obtained by Moeini et al.,<sup>8</sup> in contrast with more densified grains observed from other solution methods.<sup>4,5</sup> The SEM–EDS analysis for ThO<sub>2</sub> from both precursors shows the expected presence of Th and O (see Supporting Information S3).

TEM images show nanoparticles of average sizes of 50 and 40 nm for ThO<sub>2</sub> from chitosan (Figure 2a) and PVP (Figure 2b) precursors, respectively. Similar particle sizes were observed for ThO<sub>2</sub> obtained by the hydrothermal method.<sup>8</sup>

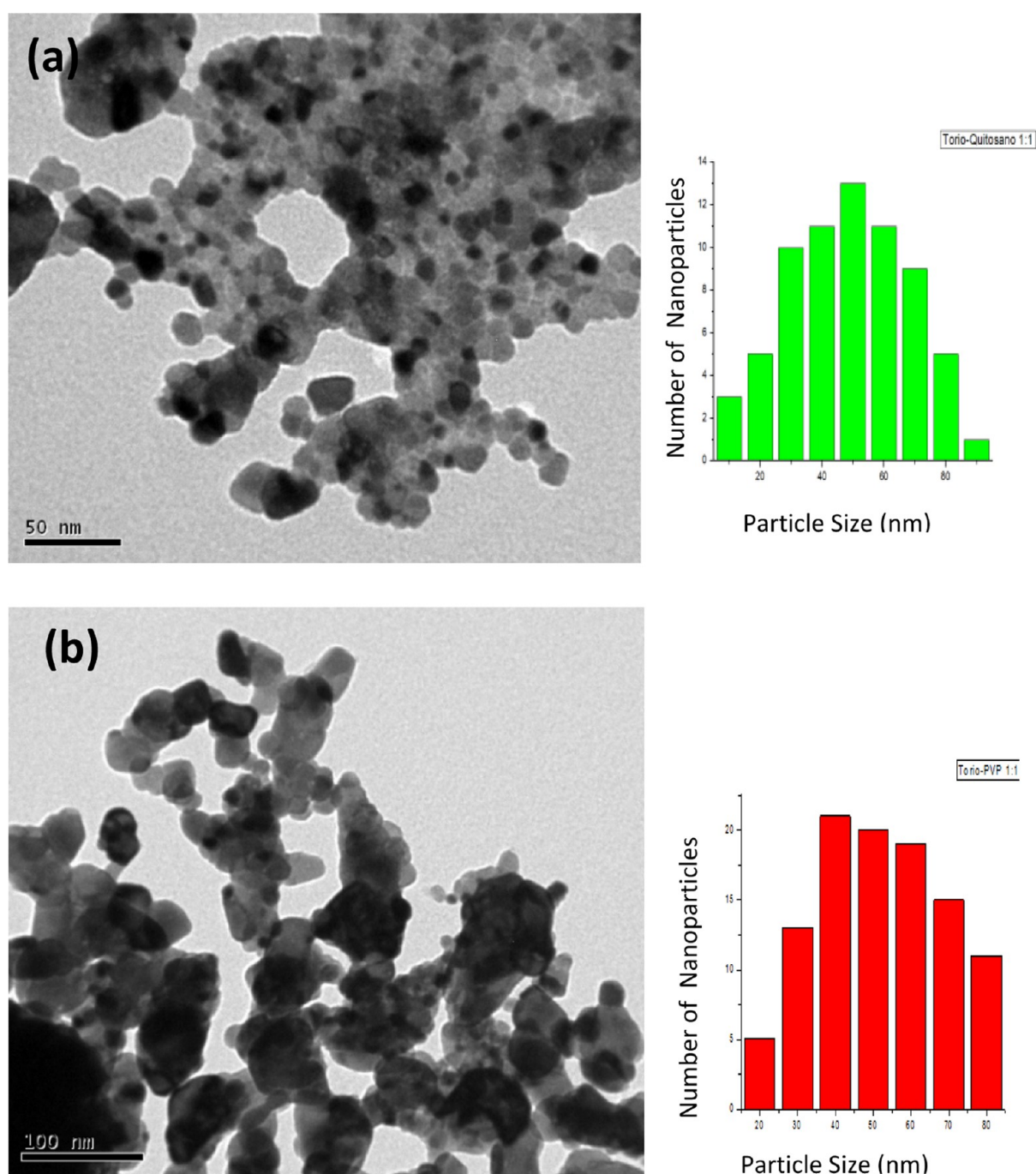
In Figure 3, HR-TEM images are shown for ThO<sub>2</sub> obtained from the chitosan precursor. Nanoparticles of ThO<sub>2</sub> with sizes of about 10 nm (Figure 3a,b) are observed, which are typically concatenated. Several interplanar distances were indexed, such as 0.32 and 0.28 nm, which correspond to the (111) and (200) interplanar spacings, respectively. Similar results were obtained for the ThO<sub>2</sub> obtained from PVP, as observed in Figure 4a, with a mean size of about 45 nm. An interplanar distance of 0.31 nm corresponding to the (111) interplanar spacing of the ThO<sub>2</sub> was measured (Figure 4d).

In terms of their photoluminescence properties, a very few studies have been reported for ThO<sub>2</sub>.<sup>22–26</sup> Our photoluminescence study for the obtained ThO<sub>2</sub> particles is shown in Figure 5. The excitation spectra (not shown), which reveal one broad band at 366 nm, produce an emission wavelength at 697 nm. The position of the band at 366 nm is attributed to absorption of charge transfer Th<sup>IV</sup>/Th<sup>III</sup> → Th<sup>III</sup>/Th<sup>IV</sup> under nonstoichiometric conditions (ThO<sub>2-x</sub>).<sup>24</sup> The two main emission peaks, around 400 and 420 nm, have been assigned to the Th<sup>4+</sup> typical center,<sup>22,24</sup> while those at 680 and 710 nm could be ascribed to the formation of oxygen vacancies on the ThO<sub>2</sub> surface, which could be occupied by either oxygen or other impurities.<sup>22,26</sup> Nevertheless, the exact origin of these emissions is not fully clear.<sup>22–26</sup> Additionally, an effect on the emission intensity depending on the nature of the polymer and the metal/polymer ratio of the precursor was also observed (see Figure 5). The ThO<sub>2</sub> prepared from the PVP precursor using a 1:1 metal/polymer ratio exhibits the most intense emission of the maxima peaks at 400 and 420 nm, while that for the PVP precursor using the 1:5 metal/polymer ratio exhibits the most intense emission in the emission at 680 and 710 nm.

Different composites of ThO<sub>2</sub> with SiO<sub>2</sub> were also prepared by pyrolysis at 800 °C under air of the Chitosan·Th(NO<sub>3</sub>)<sub>4</sub>//SiO<sub>2</sub> and PS-co-4-PVP·Th(NO<sub>3</sub>)<sub>4</sub>//SiO<sub>2</sub> precursors. The diffraction pattern of the different obtained products is shown in Supporting Information S4. ThO<sub>2</sub> is weakly observed by XRD due to the dilution of the precursors containing the thorium salts with respect to SiO<sub>2</sub> (1:100), as also previously reported for other metals<sup>27,28</sup> or metal oxides<sup>29</sup> with respect to the amorphous silica. The presence of ThO<sub>2</sub> inside silica was corroborated by SEM–EDS mapping by element analysis. This technique gives also information about the distribution of the thoria into SiO<sub>2</sub>. From Figure 6, ThO<sub>2</sub> agglomerated nanoparticles of about 250 nm were observed to be homogeneously dispersed into bigger silica particles. A similar distribution of the ThO<sub>2</sub> nanoparticles, but with bigger sizes of about 950 nm, was observed for ThO<sub>2</sub> inside SiO<sub>2</sub> obtained from the chitosan precursor (Figure 7). The representative SEM image of the ThO<sub>2</sub>/SiO<sub>2</sub> composites arising from both macromolecular precursors is displayed in Supporting Information S5. For the ThO<sub>2</sub>/chitosan sample, typical nanostructure morphology of that obtained from solid-state pyrolysis can be seen.<sup>13</sup> In some areas, a dense 3D morphology with several shapes joined between them with the presence of pores is exhibited, as shown in Figure S5a,b. On the other hand, sphered shapes were also observed, Figure S5c,d. For ThO<sub>2</sub> from the PS-co-4-PVP·Th(NO<sub>3</sub>)<sub>4</sub>//SiO<sub>2</sub> precursor, big agglomerates composed mainly of spheres of different sizes were observed, see Figure S5a.

XRD patterns of the ThO<sub>2</sub>//TiO<sub>2</sub> composites from the chitosan and PVP precursors are shown in Figure S6 of the Supporting Information. Again, the TiO<sub>2</sub> matrix presents more





**Figure 2.** TEM image of ThO<sub>2</sub> from the Chitosan·Th(NO<sub>3</sub>)<sub>4</sub> precursor (a) and from PS-co-4-PVP·Th(NO<sub>3</sub>)<sub>4</sub> (b).

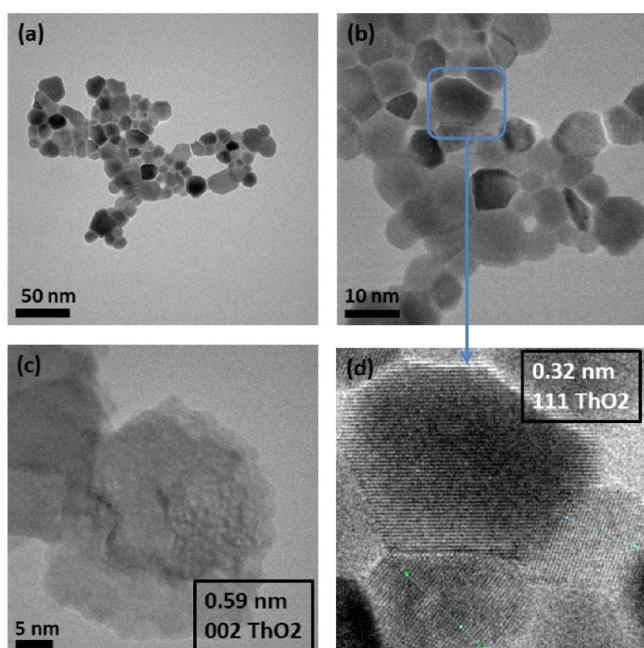
intensity than ThO<sub>2</sub>, for both cases. Nevertheless, the presence of ThO<sub>2</sub> was clearly identified from the SEM–EDS mapping image (see S7, [Supporting Information](#)). Several SEM images of the ThO<sub>2</sub>//TiO<sub>2</sub> composite obtained from the chitosan precursor are also shown in [Figure 8](#), where dense grains can be observed. Similar morphology was obtained for ThO<sub>2</sub>//TiO<sub>2</sub> composites arising from PVP precursors (see [Figure 9](#)).

Finally, SEM–EDS mapping (see [Figure S7](#)) exhibits a homogeneous distribution of ThO<sub>2</sub> inside the TiO<sub>2</sub> matrix for ThO<sub>2</sub>//TiO<sub>2</sub> composites produced from both precursors.

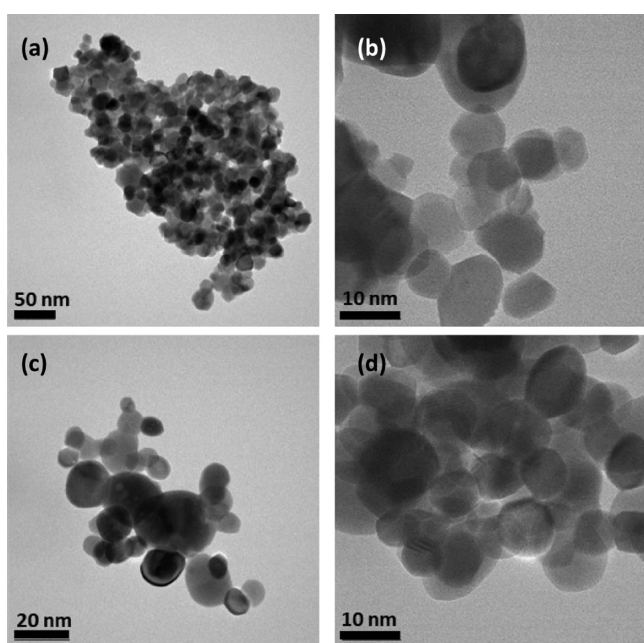
**Photoluminescence of ThO<sub>2</sub>/SiO<sub>2</sub> and ThO<sub>2</sub>/TiO<sub>2</sub> Composites.** In order to investigate the effect of the SiO<sub>2</sub> and TiO<sub>2</sub> matrices on the intensity of ThO<sub>2</sub> particles, the luminescence spectra of ThO<sub>2</sub>/SiO<sub>2</sub> and ThO<sub>2</sub>/TiO<sub>2</sub>

composites were recorded and compared with those of pure ThO<sub>2</sub>. The results are plotted in [Figure 10](#).

For the chitosan precursor ([Figure 10a](#)), it can be observed that the matrix inclusion produces a decrease in the emission intensity, showing the order ThO<sub>2</sub> > ThO<sub>2</sub>/SiO<sub>2</sub> > ThO<sub>2</sub>/TiO<sub>2</sub> for both main emissions. In the case of the samples produced from the PVP precursor, [Figure 10b](#), a similar trend was observed for the emission maxima at 680 and 710 nm but an inversion occurs for the emission at 400 and 420 nm, with the order ThO<sub>2</sub> > ThO<sub>2</sub>/TiO<sub>2</sub> > ThO<sub>2</sub>/SiO<sub>2</sub>. These variations of the maxima intensity at 680 and 710 nm could be related with the presence of surface oxygen or impurities generated in the SiO<sub>2</sub> and TiO<sub>2</sub>, leading to different morphologies and surface defects induced by these matrices. The detailed



**Figure 3.** HRTEM image of ThO<sub>2</sub> from Chitosan·Th(NO<sub>3</sub>)<sub>4</sub> precursors. 50 (a), 10 (b), and 5 μm (c,d).



**Figure 4.** HRTEM image of ThO<sub>2</sub> from PS-co-4-PVP·Th(NO<sub>3</sub>)<sub>4</sub>. 50 (a), 10 (b), 20 (c), and 10 μm (d).

mechanism of how this effect occurs is unknown. In this sense, it was reported that an increase in the emission intensity is normally associated with an increase in the surface defects on the ThO<sub>2</sub> which are occupied by oxygen.<sup>26</sup> As a consequence, according to Figure 10a, the oxygen absorbed on the surface of thoria decreased on the inclusion on SiO<sub>2</sub> and TiO<sub>2</sub>. A similar explanation for the observed intensity variation could hold for the ThO<sub>2</sub>/PVP sample.

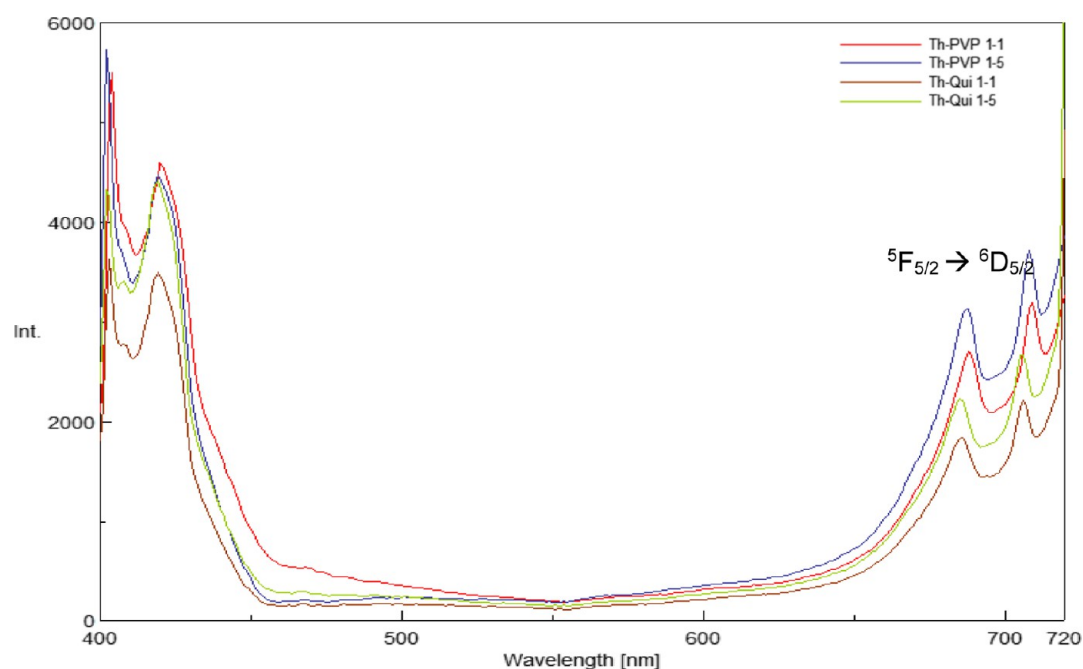
**Photocatalytic Activity.** Although there are scarce reports about the catalytic activity of thoria, no studies about the photocatalytic activity of ThO<sub>2</sub> neither ThO<sub>2</sub>/SiO<sub>2</sub> nor ThO<sub>2</sub>/TiO<sub>2</sub> composites toward contaminant dyes have been

reported. We have performed studies about the use of thoria acting as a photocatalyst for the degradation of methylene blue under solar radiation. As is shown in Figure 11, thoria exhibited an activity of 66 and 67% in 300 min for ThO<sub>2</sub> prepared from the chitosan and PVP precursors, respectively. The absorption decrease in the absorbance at 655 nm of methylene blue versus wavelength at different time intervals for the different studied samples can be observed in Supporting Information S8. The kinetic degradation of methylene blue with ThO<sub>2</sub>/chitosan followed a zero order, while that for ThO<sub>2</sub>/PVP followed a first order. Similar kinetic behavior was observed for the ThO<sub>2</sub>/SiO<sub>2</sub> and ThO<sub>2</sub>/TiO<sub>2</sub> composites, as summarized in Supporting Information S9. On the other hand, the photocatalytic efficiency of the ThO<sub>2</sub>/SiO<sub>2</sub> composite decreased to 25 and 28% for the chitosan and PVP precursors, respectively. As for the case of the ThO<sub>2</sub>/TiO<sub>2</sub> composite, the photocatalytic efficiency decreased to 39.5 and 27% for the chitosan and PVP precursors, respectively. A summary of the kinetic data is shown in Table 1.

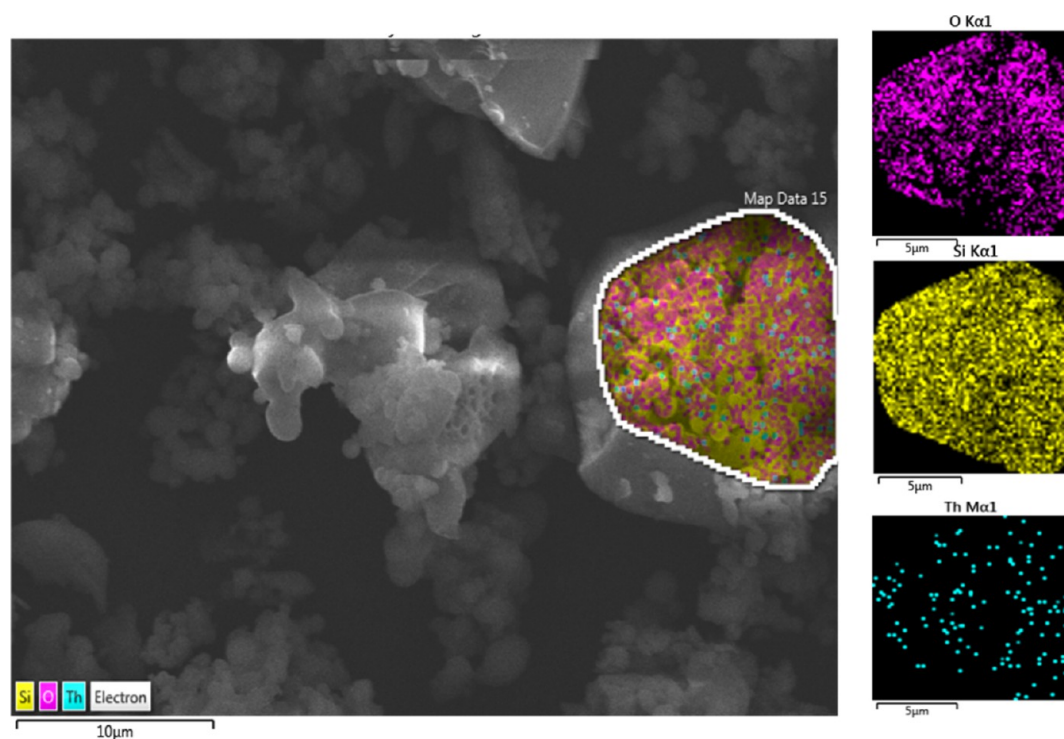
Table 1 shows the obtained values for photodegradation, the speed constant, and the correlation coefficient. In all cases, it is observed that the correlation coefficient ( $r^2$ ) is close to unity, which indicates that the photocatalytic degradation process, mediated by the synthesized thorium oxides, adjusts to the zero-order and first-order kinetics. The estimated rate constant for the degradation of methylene blue in the presence of thorium prepared without the SiO<sub>2</sub> and TiO<sub>2</sub> matrices is greater than that of the pristine compounds, suggesting that the structural modification and synergy of the inorganic component play a fundamental role. This is related with the increase in the photocatalytic efficiency of the semiconductor, due to the greater number of active sites available by the (ThO<sub>2</sub>) *n*-PVP and (ThO<sub>2</sub>) *n*-chitosan precursors. The increase in photocatalytic activity of only ThO<sub>2</sub> with respect to the composites ThO<sub>2</sub>/SiO<sub>2</sub> and ThO<sub>2</sub>/TiO<sub>2</sub> may be due to the greater porosity of thoria alone with respect to the porosity of thoria included in SiO<sub>2</sub> and TiO<sub>2</sub> matrices. This can be observed from the SEM images of only ThO<sub>2</sub>, Figure 1, with respect to the SEM images of ThO<sub>2</sub> included in silica and titania, see Figures 9 and S5 of the Supporting Information. Clearly, the SEM image of ThO<sub>2</sub> is porous, in contrast with the SEM images of ThO<sub>2</sub> including inside SiO<sub>2</sub> and TiO<sub>2</sub> matrices where a dense material is observed.

**Band Gap Study.** The band gap of metal oxides is an interesting property, which is involved in electronic applications.<sup>30,31</sup> Materials based on thoria are viewed as wide band gap semiconductors. For the case of thoria, there is little information in the literature regarding its band gap. For ThO<sub>2</sub> nanoparticles, Aller et al.<sup>23</sup> reported values in the range 6.22–5.69 eV, while Buono-Core et al.<sup>24</sup> reported values from 4.5 to 4.61 eV for ThO<sub>2</sub> thin films. The study of Aller et al. also reported a wide range of values from 3.84 to 6.9 eV, although some of these values are based on theoretical calculations. Using the solid-state UV–visible absorption and with the Tauc plot for ThO<sub>2</sub>, we estimated a value of 5.66 and 5.76 eV for chitosan and PVP precursors, respectively (see Supporting Information S11). These values are in concordance with those previously reported in the literature.<sup>29</sup> For the ThO<sub>2</sub>/SiO<sub>2</sub> composite, similar values of 5.50 and 5.60 eV were estimated. In this case, there are no literature data for these composites. On the other hand, the band gap values for thoria included in TiO<sub>2</sub> matrices exhibited values of 3.14 and 3.15 eV for the chitosan and PVP precursors, respectively. These values are





**Figure 5.** Luminescence spectra of the  $\text{ThO}_2$  from the precursors Chitosan· $\text{Th}(\text{NO}_3)_4$  and PS-co-4-PVP· $\text{Th}(\text{NO}_3)_4$  in 1:1 and 1:5 molar ratios.

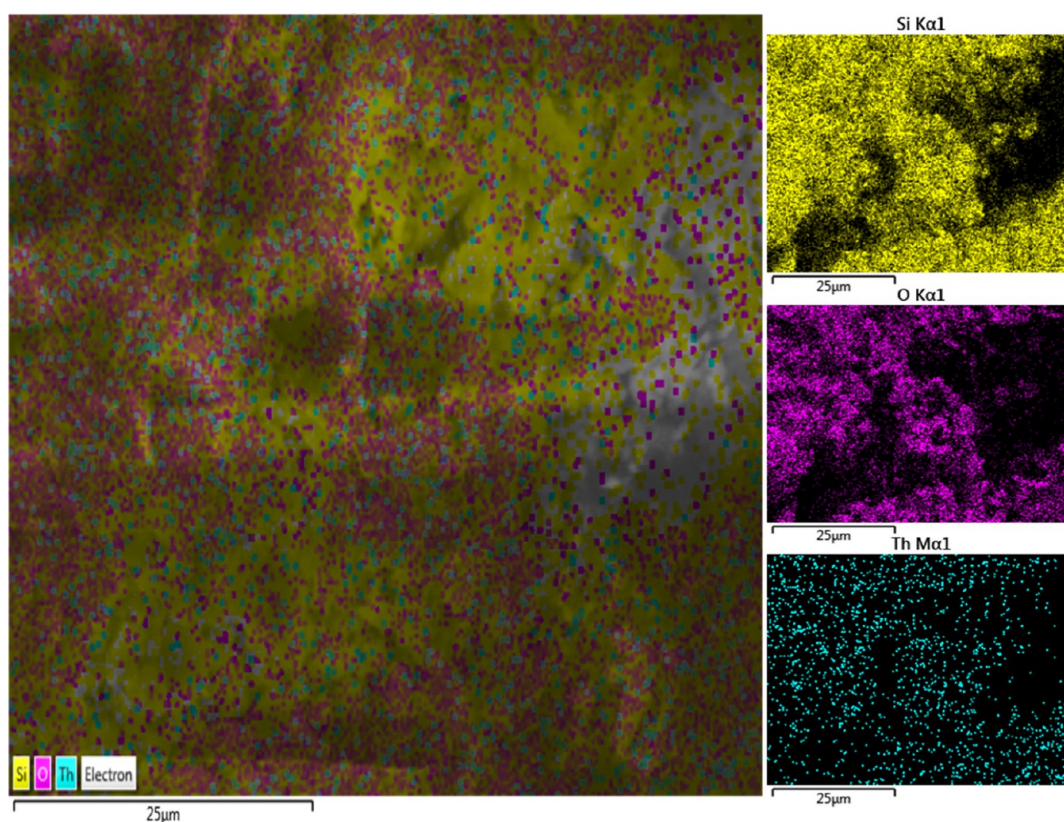


**Figure 6.** SEM–EDS mapping by elements of  $\text{ThO}_2$  inside  $\text{SiO}_2$  from the Chitosan· $\text{Th}(\text{NO}_3)_4$ // $\text{SiO}_2$  precursor.

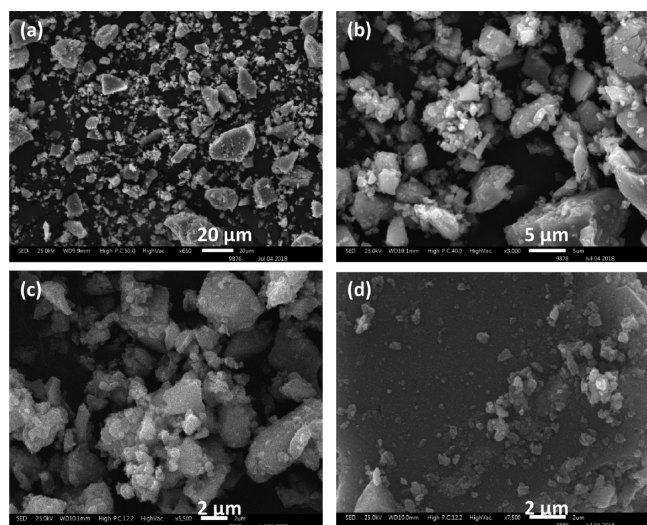
significantly lower than those of  $\text{ThO}_2$  and  $\text{ThO}_2/\text{SiO}_2$ . As pointed by Buono-Core et al.,<sup>24</sup> the optical band gap energy is very sensitive to the preparation method and the experimental parameters applied in the synthesis.<sup>24</sup> In fact, Mahmoud also reported a value of 3.82 eV for  $\text{ThO}_2$  prepared by a spray pyrolysis technique.<sup>25</sup>

**Formation Mechanism Probable.** A proposed formation mechanism is discussed here based on previous studies of solid-state nanostructures using the same synthetic approach.<sup>19,32</sup> According to these studies, the first step on

heating the samples involves the formation of a 3D network to produce a thermally stable matrix. This step is crucial as it offsets the sublimation (see Figure 12). The first heating step could involve a cross linking of the chitosan or PSP-4-PVP polymer, giving a 3D matrix containing the  $\text{Th}(\text{NO}_3)_4$  compound linked to the polymeric chain. The following steps could involve the organic carbonization, producing holes where the nanoparticles begin to nucleate. As confirmed in earlier studies,<sup>32</sup> the  $\text{ThO}_2$  oxide could grow over the layered



**Figure 7.** SEM–EDS mapping by elements of  $\text{ThO}_2$  inside  $\text{SiO}_2$  from the precursor  $\text{PS-co-4-PVP}\cdot\text{Th}(\text{NO}_3)_4//\text{SiO}_2$ .

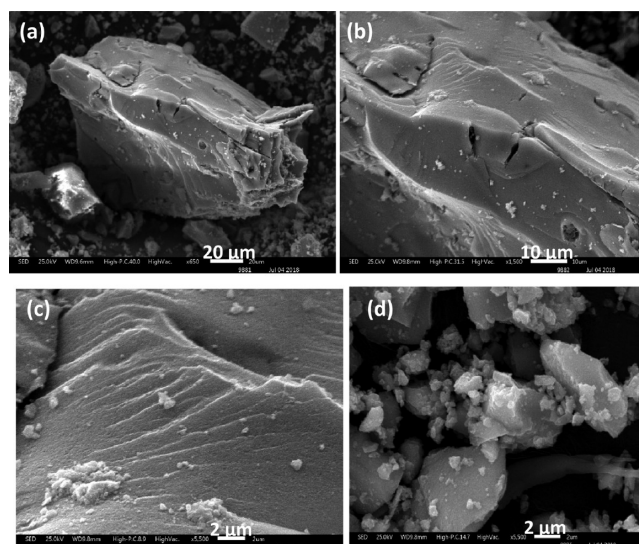


**Figure 8.** SEM image of the  $\text{ThO}_2//\text{TiO}_2$  composites arising from the Chitosan- $\text{Th}(\text{NO}_3)_4//\text{TiO}_2$  precursors: 20 (a), 5 (b), and 2  $\mu\text{m}$  (c,d).

graphitic carbon host which is lost during the final annealing temperature, that is, 800 °C.

## CONCLUSIONS

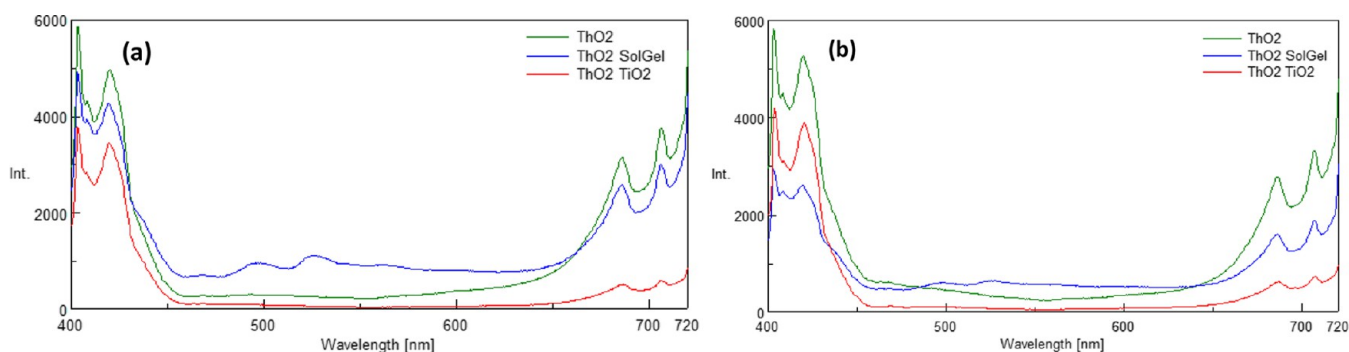
$\text{ThO}_2$  nanoparticles were satisfactorily prepared by solid-state pyrolysis of the Chitosan- $\text{Th}(\text{NO}_3)_4$  and  $\text{PS-co-4-PVP}\cdot\text{Th}(\text{NO}_3)_4$  precursors. The particle sizes were in the range of 40–50 nm depending on the polymer solid-state template. The luminescence of  $\text{ThO}_2$  arising from both polymers exhibits a dependence with the nature of the precursor and with the metal/polymer ratio being the most intense emission for the



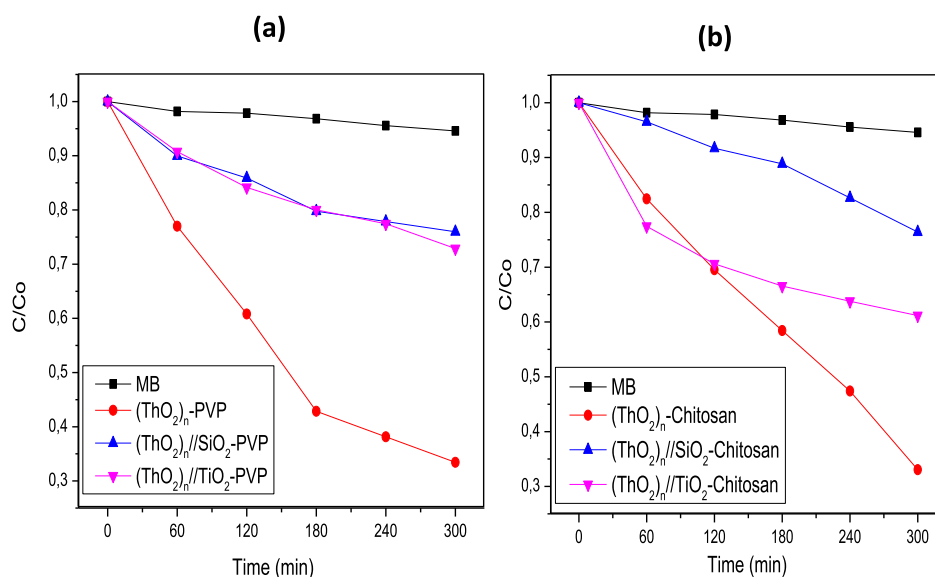
**Figure 9.**  $\text{ThO}_2//\text{TiO}_2$  composites arising from the  $\text{PS-co-4-PVP}\cdot\text{Th}(\text{NO}_3)_4//\text{TiO}_2$  precursors: 20 (a), 10 (b), and 2  $\mu\text{m}$  (c,d).

$\text{ThO}_2$  arising from  $\text{PS-co-4-PVP}\cdot\text{Th}(\text{NO}_3)_4$  in the molar ratio 1:1. The photocatalytic efficiency of  $\text{ThO}_2$  toward the degradation of methylene blue was around 66% in 300 min for the thoria obtained from both precursors. The inclusion of thoria into the  $\text{SiO}_2$  and  $\text{TiO}_2$  matrices was achieved by solid-state thermolysis of the solid Chitosan- $\text{Th}(\text{NO}_3)_4//\text{MO}_2$  and  $\text{PS-co-4-PVP}\cdot\text{Th}(\text{NO}_3)_4//\text{MO}_2$  precursors, where  $\text{MO}_2 = \text{SiO}_2$  and  $\text{TiO}_2$  to give the  $\text{ThO}_2//\text{SiO}_2$  and  $\text{ThO}_2//\text{TiO}_2$  composites. SEM–EDS mapping analysis showed a regular dispersion of the thoria into the  $\text{SiO}_2$  and  $\text{TiO}_2$  matrices. The particle size of





**Figure 10.** Luminescence spectra of the ThO<sub>2</sub> from the precursors ThO<sub>2</sub>, Chitosan·Th(NO<sub>3</sub>)<sub>4</sub>//SiO<sub>2</sub> (a), and PS-co-4-PVP·Th(NO<sub>3</sub>)<sub>4</sub>//TiO<sub>2</sub> (b)  $\lambda_{\text{exc.}} = 366 \text{ nm}$ .



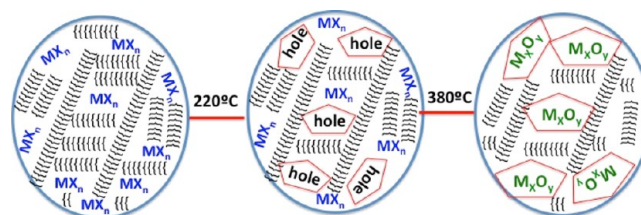
**Figure 11.** Normalized concentration change in MB without the catalyst and in the presence of ThO<sub>2</sub> from the PS-co-4-PVP·Th(NO<sub>3</sub>)<sub>4</sub> (a) and Chitosan·Th(NO<sub>3</sub>)<sub>4</sub> (b) precursors.

**Table 1.** Kinetic Data for the Photodegradation Process of MB with ThO<sub>2</sub> and with the Composites ThO<sub>2</sub>/SiO<sub>2</sub> and ThO<sub>2</sub>/TiO<sub>2</sub>

photocatalyst	apparent photodegradation	discoloration rate (%)	$r^2$ linear fit (%)
ThO <sub>2</sub> -Chitosan	$3.7 \times 10^{-3}$	67	0.992
ThO <sub>2</sub> -PS-4-PVP	$2.2 \times 10^{-3}$	66	0.967
ThO <sub>2</sub> /SiO <sub>2</sub> -Chitosan	$7.7 \times 10^{-4}$	24	0.979
ThO <sub>2</sub> /SiO <sub>2</sub> -PS-4-PVP	$8.5 \times 10^{-4}$	25	0.923
ThO <sub>2</sub> /TiO <sub>2</sub> -CHITOSAN	$1.4 \times 10^{-3}$	39	0.815
ThO <sub>2</sub> /TiO <sub>2</sub> -PS-4-PVP	$8.7 \times 10^{-4}$	27	0.941

ThO<sub>2</sub> increases by about 19 times for the nanoparticles obtained from chitosan as they are included in SiO<sub>2</sub>, while for the ThO<sub>2</sub> obtained from PS-co-4-PVP, an increase of 6 times is observed when the ThO<sub>2</sub>/SiO<sub>2</sub> composite is formed. The effect of the polymer precursors on the particle size is little for the free matrices of ThO<sub>2</sub>, while that when included inside silica is in the particle size order chitosan > PS-co-4-PVP by nearly four times.

The intensity of the emission at 420 nm followed the order ThO<sub>2</sub> > ThO<sub>2</sub>/SiO<sub>2</sub> > ThO<sub>2</sub>/TiO<sub>2</sub> which was explained by the surface's defects on the ThO<sub>2</sub> associated with their inclusion into SiO<sub>2</sub> and TiO<sub>2</sub> matrices. The photocatalytic activity



**Figure 12.** Schematic representation of the proposed mechanism of the formation of the metal oxide nanoparticles. MX<sub>n</sub> represents the general formula of the metallic salt coordinated to the chitosan and PSP-4-PVP polymer, Th(NO<sub>3</sub>)<sub>4</sub> and {}{}{}{}{} represent the chitosan and PSP-4-PVP polymer, respectively. The temperatures are referential general values.

toward methylene blue degradation follows the order of ThO<sub>2</sub> > ThO<sub>2</sub>/TiO<sub>2</sub> > ThO<sub>2</sub>/SiO<sub>2</sub> and was attributed to the encapsulation of the ThO<sub>2</sub> into the different matrices. Similar results on the effect of the SiO<sub>2</sub>, TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> on the nanostructured NiO have recently appeared.<sup>33</sup>

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c05811>.



Experimental details of the synthesis of the precursors; XRD diffraction pattern of  $\text{ThO}_2$  from the Chitosan- $\text{Th}(\text{NO}_3)_4$  and PS-co-4-PVP- $\text{Th}(\text{NO}_3)_4$  precursors; SEM-EDS image for  $\text{ThO}_2$  from precursors Chitosan- $\text{Th}(\text{NO}_3)_4$  1:1 and 1:5 and  $\text{ThO}_2$  from the PS-co-4-PVP- $\text{Th}(\text{NO}_3)_4$  precursor, 1:1 and 1:5; diffraction patterns of  $\text{Th}/\text{SiO}_2$  from the Chitosan- $\text{Th}(\text{NO}_3)_4//\text{SiO}_2$  precursor and from PS-co-4-PVP- $\text{Th}(\text{NO}_3)_4//\text{SiO}_2$ ; SEM image from the pyrolytic product of the Chitosan- $\text{Th}(\text{NO}_3)_4//\text{SiO}_2$  precursor at several magnifications; XRD patterns for the  $\text{ThO}_2/\text{TiO}_2$  composite from the Chitosan- $\text{Th}(\text{NO}_3)_4//\text{TiO}_2$  and PS-co-4-PVP- $\text{Th}(\text{NO}_3)_4//\text{TiO}_2$  precursor; SEM-EDS mapping of the composite  $\text{ThO}_2/\text{TiO}_2$  from the Chitosan- $\text{Th}(\text{NO}_3)_4//\text{TiO}_2$  and PS-co-4-PVP- $\text{Th}(\text{NO}_3)_4//\text{TiO}_2$  precursor; decrease absorption of the absorbance at 655 nm of methylene blue versus wavelength at several times for  $\text{ThO}_2$ ,  $\text{ThO}_2/\text{SiO}_2$ , and  $\text{ThO}_2/\text{TiO}_2$  from the two precursors having PS-co-4-PVP and chitosan polymers; kinetic of the degradation for the  $\text{ThO}_2$ ,  $\text{ThO}_2/\text{SiO}_2$ , and  $\text{ThO}_2/\text{TiO}_2$  from the two precursors PS-co-4-PVP and chitosan polymers; and Tauc plots for band gap determinations of  $\text{ThO}_2$ ,  $\text{ThO}_2/\text{SiO}_2$ , and  $\text{ThO}_2/\text{TiO}_2$  (PDF)

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### Notes

The authors declare no competing financial interest.

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