

Phase Inversion Temperature Nanoemulsion Synthesis of Brookite Titanium Dioxide Nanoparticles

Diego F. Soto Nieves^a, Anushka M. Castro Vázquez^a, Gabriel Quiñones Vélez^a, Chris Pollock^b, Louise Debeve^b, Vilmalí López-Mejías^a

^aDepartment of Chemistry, University of Puerto Rico, Río Piedras Campus, San Juan, Puerto Rico, 00926.

^bDepartment of Chemistry, Cornell University, Ithaca, NY, 14853.

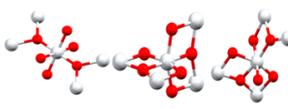
Abstract:

Titania (TiO₂) is an important semiconductor material for solar photovoltaic technology because of its high optical and chemical stability, low toxicity, and low cost. Thin films of TiO₂ used as anodes in dye-sensitized solar cells (DSSCs) present several limitations regarding their high transparency and negligible light scattering due to the particle size. This results in poor light harvesting and low electrical conductivity, which is also affected by TiO₂ polymorphic phases. Enhancement of the photovoltaic conversion efficiency can be improved by modifications in the particle size and polymorphic control. The first aim of this research is to nano-confine the crystallization of TiO₂ to decrease particle size by *in situ* biotemplation with hydroxyethyl cellulose (HEC) using a phase inversion temperature (PIT)-nanoemulsion method. The second aim is to control the polymorphic phase of the resulting TiO₂ nanoparticles by controlling its calcination temperature to obtain the brookite phase. Biotemplated syntheses for TiO₂ nanoparticles using the PIT method were performed in both acidic and alkaline media. The resulting nanomaterial was characterized before and after calcination. To calcinate, the temperature set point used was 500 °C, moreover, the calcination protocol lasted a period of 24 hr. The pre-calcinated nanoparticles were analyzed by thermogravimetric and dynamic light scattering analysis. Thermographs of the pre-calcinated nanoparticles presented the degradation of HEC at ~280 °C indicating that the polymer was entrapping the amorphous TiO₂. The particle size distribution of the amorphous product range between 180-420 d.nm according to dynamic light scattering analysis. After calcination, powder X-ray diffraction analysis confirmed the presence of crystalline TiO₂ composed of a mixture of anatase and brookite phases. X-ray absorption spectroscopy analysis also confirmed the presence of a mixture of brookite and anatase phases within the samples. This work illustrates that biotemplated TiO₂ nanoparticles can be synthesized via the PIT-nanoemulsion method and calcinated to control its crystal size and phase, respectively. This work could potentially enhance the semiconductor properties of TiO₂ for applications in DSSCs.

Introduction:

Dye-sensitized solar cells (DSSCs) are based on a semiconductor formed between a photosensitized anode and an electrolyte.¹ Thin films of TiO₂ are used as anodes in DSSCs because

of their high optical and chemical stability, low toxicity, and low cost.^{2,3} However, these thin films present a limitation regarding their polymorphic phase and particle size.⁴ Titanium dioxide (TiO₂) possesses three polymorphic phases: rutile, anatase, and brookite. A great difference of structural stability and photoelectron-chemistry property has been shown in these phases. (**Table 1**)⁵



	Rutile	Anatase	Brookite
Electrical conductivity	Red	Yellow	Green
Band gap (eV)	2.98	3.05	3.26
Conduction band (V)	-0.37	-0.45	-0.46
Surface energy (J/m²)	1.1	0.5	0.7

Table 1. Summary of the structural stabilities and photoelectron-chemistry properties presented for each of the TiO₂ phases.⁵

Recent studies have demonstrated a difference in electrical conductivity, band gap energy, conduction band, and surface energy among the three phases. The brookite phase represents the phase that contains the best attributes regarding these parameters among all other phases of Titania. (**Table 1**)

In this research, we aim to decrease the size of the TiO₂ particles into the nano-range and obtain brookite with the use of the phase inversion temperature (PIT)-nanoemulsion synthesis method. The PIT method consists of an emulsion transitioning from a micro-emulsion in an oil in water system to a nanoemulsion in a water in oil system.⁶ During the synthesis, following the PIT method, the addition of the titanium precursor occurs, and an amorphous TiO₂ product is obtained. Characterization of the given samples consisted of Dynamic Light Scattering (DLS) to determine the particle size distribution of the resulting product.^{7,8} Since a biotemplation is being applied to the synthesis with the use of a polymer, thermogravimetric analysis (TGA) is necessary to confirm the degradation of the polymer. Powder X-ray diffraction (PXRD) along with X-ray absorption spectroscopy (XAS) was performed to determine the polymorphic phase of the given sample. Given studies have proven a difference in XAS spectra because of their structure. Both rutile and anatase have a tetragonal structure while brookite has an orthorhombic structure. These structural differences are transferred to significant differences in the spectra of these forms as shown in **Figure 1.**^{9,10}

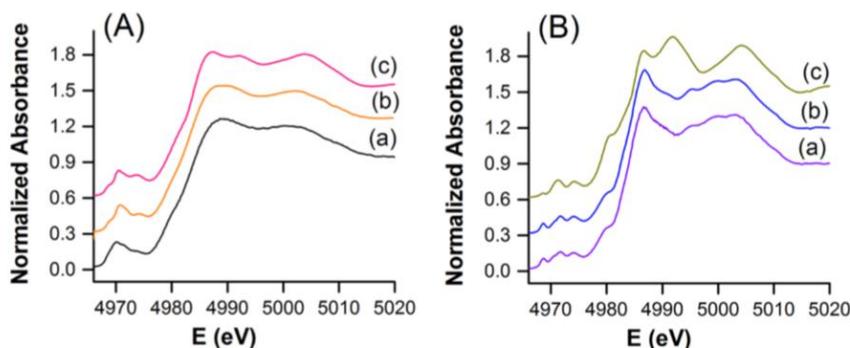


Figure 1. XANES spectra of the Ti K-edge of brookite (panel A, trace c) and anatase (panel B, trace b), rutile (panel B, trace c). Other samples (panel A, trace a,b and panel B, trace a) are irrelevant to this discussion.^{9,10}

Experimental session:

PIT-nanoemulsion Synthesis. To obtain the TiO₂ nanoparticles a nanoemulsion was prepared consisting of an aqueous phase, an oil phase, and a surfactant. Each sample was prepared in different nanoemulsion conditions by only applying a variation in the aqueous phase of the emulsion, while the oil phase and the surfactant remained the same. The oil phase employed was heptane while the surfactant employed in this study was Brij. For a biotemplation in our resulting product, the biopolymer, hydroxyethylcellulose (HEC), was utilized. Two different samples were prepared, one in acidic conditions and the other in alkaline conditions. The sample prepared in alkaline conditions with biotemplation required a nanoemulsion of H₂O:NaOH:HEC/Heptane/Brij. The sample prepared in acidic conditions with a biotemplation required a nanoemulsion of H₂O:HNO₃:HEC/Heptane/Brij to proceed to the following of the synthesis. Even though the conditions may vary, the same procedure was applied to both samples.

Once the nanoemulsion is prepared, it is homogenized and put in a reactor at 7 °C for 30 min under continuous stirring. Then the sample is transferred to a second reactor at 45 °C for 30 min. Once the 30 min were completed, 1 mL of the titanium(IV) isopropoxide precursor is added to the solution and continued for 70 min at 70 °C. Once this process is completed, the vial with the emulsion was taken out of the Crystalline instrument and a small sample of the emulsion was dispersed onto a microscope slide for it to be calcinated at 500 °C in an Isotemp Muffler Furnace. Finally, the vial with the emulsion was left undisturbed for 24 hrs. before analyzing the supernatant from the aqueous phase by dynamic light scattering (DLS). Size measurements were performed after 2 min of sample equilibration inside the instrument at room temperature (25°C). The refractive index used for the sample was 1.372, which corresponds to TiO₂ in water.

Then the calcinated samples were analyzed with PXRD. Powder diffractograms were collected at 300 K over an angular 2θ range between 6 – 60° with a step of 0.01° using the Gandalfi move experiment for powders. TGA analysis were performed for pre-calcinated and calcinated samples. Thermographs of TiO₂, the polymer HEC, and TiO₂-HEC synthesis, were collected using a temperature range of 30 – 700°C at 5 °C/min under a N₂ gas purge (60 mL/min). In all cases, ~1 mg of powder sample was thermally treated. Calcinated samples were also analyzed with X-ray

absorption spectroscopy (XAS) along with PXRD to determine the polymorphic phase of TiO₂. The raw data of this technique was analyzed by using PyMca¹¹ and BlueprintXAS¹² through Matlab.

Results:

DLS analysis was performed in triplicate for each sample. Previous experimental results using the PIT method confirmed a decrease in particle size with samples prepared without the presence of the bio-polymer obtaining a particle size distribution of 9 d.nm with a polydispersity index (PDI) of 0.392. Therefore, we expect an increase in the particle size distribution of biotemplated samples compared with the samples prepared without a biotemplation. Results of the sample performed in acidic conditions demonstrate average particle size distribution values of 148.8, 185.4 and 228.7 d.nm respectively for each measurement performed (**Figure 2**). PDI average values of 0.571, 0.753 and 0.737 were obtained. According to the PDI values, the amorphous TiO₂ nanoparticles measured were highly monodispersive. Results demonstrate that this method increases the particle size of the titania product from 9 d.nm to 187.6 d.nm. in the presence of a biotemplate, HEC. Results of the sample performed in alkaline conditions demonstrate average particle size distribution values of 114.1, 380.3 and 467.7 d.nm respectively for each measurement performed (**Figure 3**). PDI average values of 1.000, 0.594 and 0.615 were obtained. These results demonstrate that this method also increases the particle size of the titania product. The reduction in size of the particles is also caused by the presence of the bio-polymer.

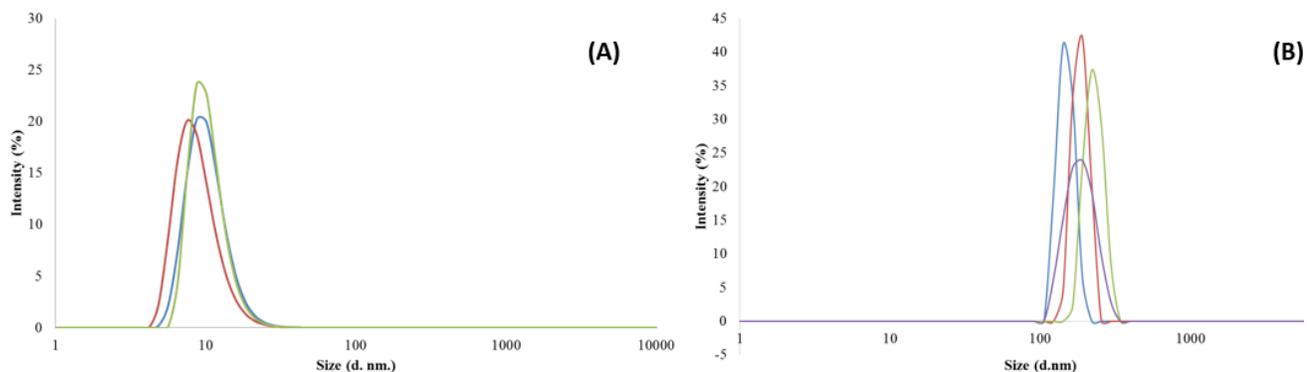


Figure 2. DLS spectra showing particle size distribution (d. nm) for the sample prepared without a biotemplate (A) and for the sample with a biotemplate (B) in acidic conditions.

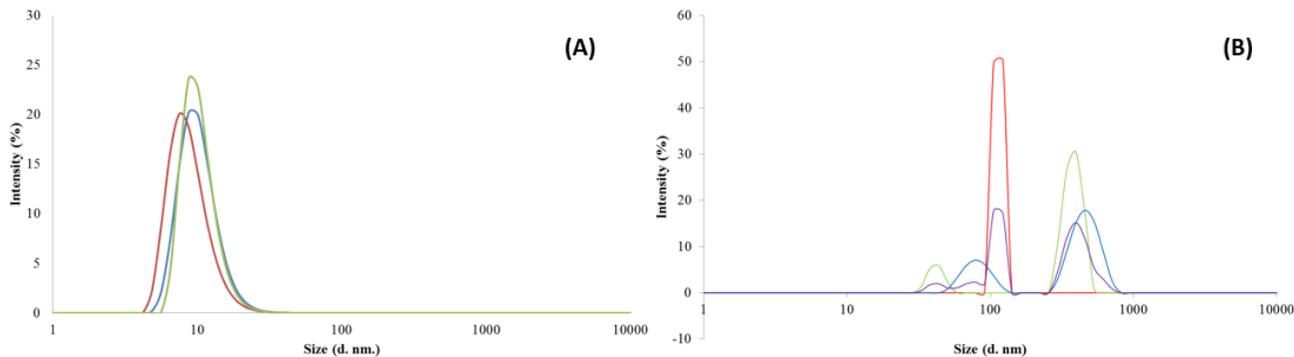


Figure 3. DLS spectra showing particle size distribution (d. nm) for the sample prepared without a biotemplate (A) and for the sample with a biotemplate (B) in alkaline conditions.

Thermogravimetric analysis was employed to compare the thermal degradation of the pre-calcinated samples with the calcinated ones at 500 °C. It was expected to observe three weight losses in the samples before calcination, attributed to the water contained in the material (~100 °C), remains of the surfactant (above 113 °C), and the biotemplate HEC (~280 °C). For the calcinated samples, no degradations were expected, as the metal oxide constitutes the main component of the resulting product (>700 °C). Representative samples were analyzed by TGA (and are shown in **Figures 4** and **5**). Thermographs of the pre-calcinated samples revealed evaporation of the water molecules by presenting a weight loss (~25%) at ~110 °C (**Figures 4A** and **5A**). Following this weight lost, a slight decomposition was observed, which is accounted to the degradation of Brij L4® (~15%) at 115 °C. Following the weight loss produced by the surfactant, the samples revealed the degradation of the bio-polymer HEC presenting a weight loss (~6%) at ~280 °C. No degradation was observed at higher temperatures due to the thermal stability of the metal oxide. Thermographs of the samples in acidic and alkaline conditions were thermally treated at 500 °C and confirmed the presence of TiO₂ as the only component analyzed based on the absence of low temperature thermal events (**Figures 4B** and **5B**).

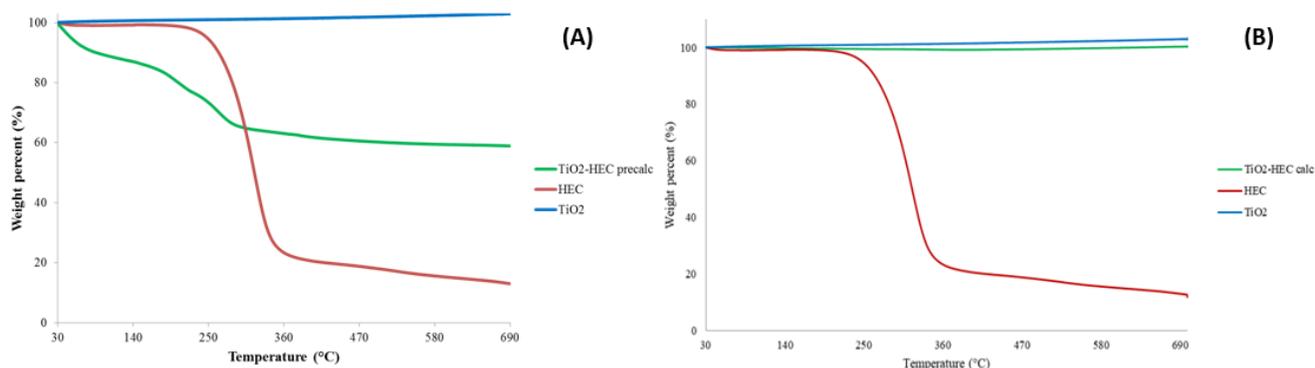


Figure 4. TGA analysis of the pre-calcinated (A) and calcinated (B) TiO_2 -HEC in acidic conditions shows a low temperature (100-250 °C) weight loss 11.69% and 20.69%, which was attributed to the decomposition of water and surfactant, respectively. At a slightly higher temperature (200-350 °C) a weight loss of 5.460% occurred, which was attributed to the degradation of HEC.

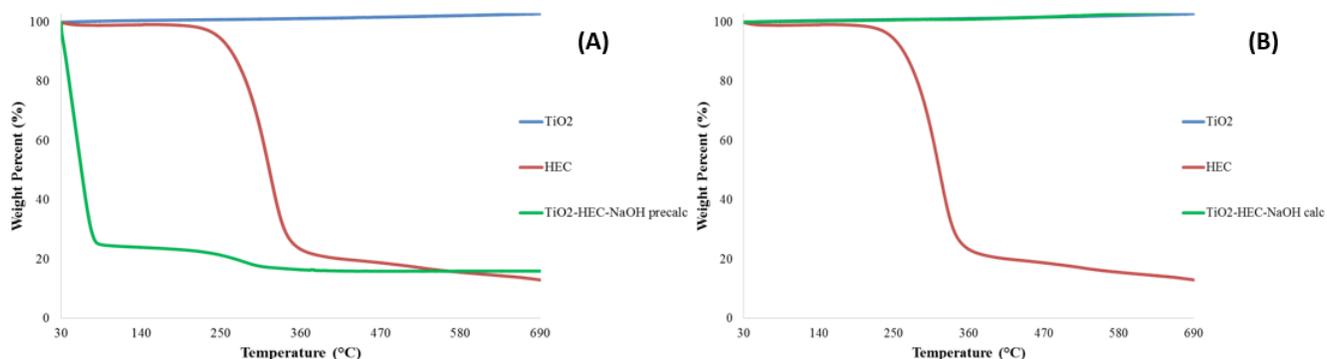


Figure 5. TGA analysis of the pre-calcinated (A) and calcinated (B) TiO_2 -HEC in alkaline conditions shows a low temperature (20-100 °C) weight loss 58.95%, which was attributed to the decomposition of water and surfactant, respectively. At a slightly higher temperature (200-350 °C) a weight loss of 6.817% occurred, which was attributed to the degradation of HEC.

Determination of the thermal conditions in which the brookite phase of TiO_2 can be isolated was monitored by PXRD. Previous measurements of samples without a biotemplate (acidic conditions) demonstrated that a mixture of the brookite and rutile phase was obtained (**Figures 7A and 8A**). Therefore, a variation of acidic and alkaline conditions was applied with the application of a biotemplate in order to isolate the brookite phase. For the biotemplated sample performed in acidic conditions a mixture of the three phases was achieved after calcination at 500 °C (**Figure 7B**). The sample presents prominent experimental reflections (25.5°, 25.7°, 27.7°, 36.0°, 37.8°, 41.3°, 53.9°, 55.2° and 56.8° in 2θ), which can be attributed and are characteristics of a mixture of

the three phases. The peaks of 25.5° , 25.7° , and 55.2° attribute to the brookite phase. The reflections of 37.8° and 53.9° attribute to the anatase phase while the peaks of 27.7° , 36.0° , 41.3° , and 56.8° are attributed to the rutile phase. Therefore, a mixture of the three phases was obtained for the biotemplated sample prepared in acidic conditions.

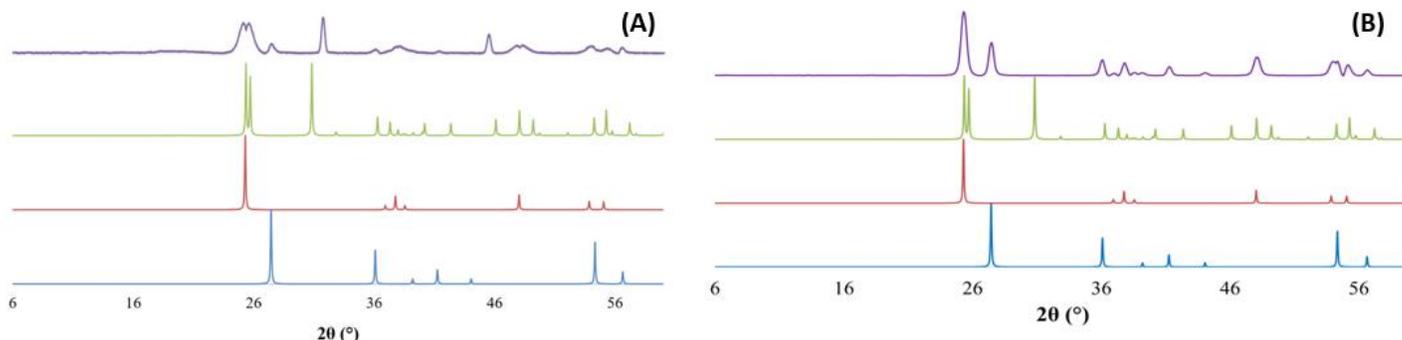


Figure 7. Powder X-ray diffractogram overlay of the three TiO_2 crystal phases rutile (blue), anatase (red), brookite (green) and the experimentally synthesized TiO_2 without the biotemplate (purple, A) and the biotemplated TiO_2 in acidic conditions (purple, B).

In terms of the biotemplated sample prepared in alkaline conditions and calcinated at 500°C (**Figure 8**), the anatase phase was obtained. The experimental biotemplated sample prepared in alkaline conditions obtained characteristic peaks of anatase (25.3° , 36.9° , 37.8° , 38.6° , 48.3° , 53.9° and 55.0° in 2θ). Therefore, it can be stated that only the anatase phase was obtained under these conditions.

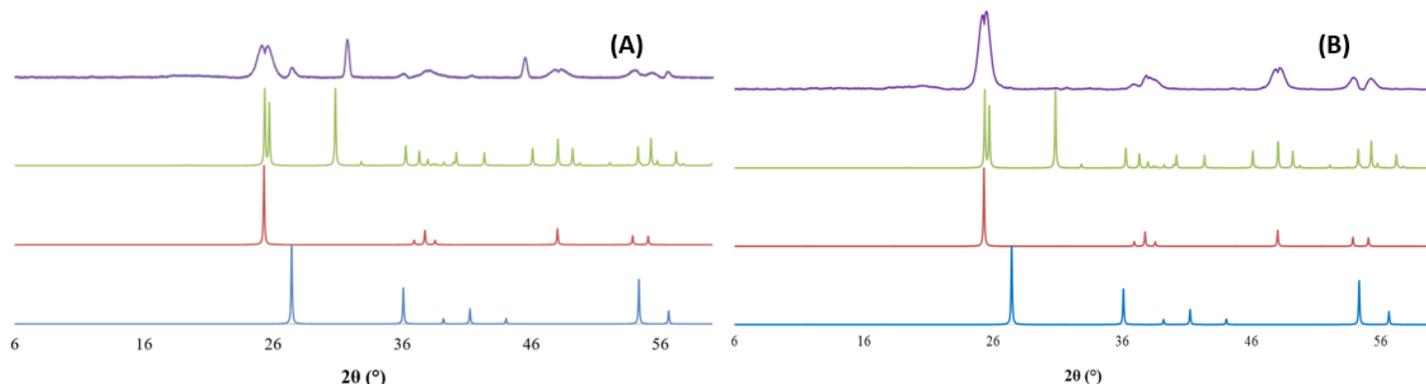


Figure 8. Powder X-ray diffractogram overlay of the three TiO_2 crystal phases rutile (blue), anatase (red), brookite (green) and the experimentally synthesized TiO_2 without the biotemplate (purple, A) and the biotemplated TiO_2 in alkaline conditions (purple, B).

X-ray absorption spectroscopy was applied to determine the polymorphic phase of the resulting product. As mentioned earlier, the brookite phase possesses a different structure (orthorhombic) compared to anatase and rutile (tetragonal) therefore, with XAS analysis should be able to differentiate between these species. Self-absorption is a distortion that occurs for (relatively) concentrated samples measured in fluorescence mode. A sign that may demonstrate that self-absorption has occurred is that as a result the pre-edge intensity is enhanced while the edge tends to become decreased in intensity. This tendency can be seen with the biotemplated sample prepared in alkaline conditions shown in **Figure 9**. Compared with a standard anatase

sample presented in **Figure 9**, the biotemplated sample prepared in alkaline conditions is self-absorbed due to an enhancement in the pre-edge but a decrease of intensity in the edge. Even though this sample may tend to self-absorbed, the energies of the 3 peaks match with the standard anatase sample. **Table 2** demonstrates the match the 3 peaks in the pre-edge area of the XAS spectra. Therefore, according to this data, it can be stated that the polymorphic phase anatase is present in these samples and an enhancement of intensity in the pre-edge area and a decrease in intensity in the edge is caused by self-absorption of the sample.

	NaOH HEC Spectrum (47 fits)	HNO ₃ HEC Spectrum 2 (23 fits)	Anatase standard (37 fits)
Overall Area	136 ± 11	137 ± 9	75 ± 2
Overall IWAE	4971.44 ± 0.14 eV	4971.36 ± 0.15 eV	4971.69 ± 0.08 eV
Peak 1	21 ± 3	21 ± 3	9.8 ± 0.1
Peak 1 IWAE	4968.11 ± 0.02 eV	4968.18 ± 0.02 eV	4968.09 ± 0.01 eV
Peak 2	57 ± 4	64 ± 9	28 ± 1
Peak 2 IWAE	4970.62 ± 0.06 eV	4970.65 ± 0.12 eV	4970.57 ± 0.1 eV
Peak 3	58 ± 9	52 ± 9	37 ± 3
Peak 3 IWAE	4973.48 ± 0.04 eV	4973.51 ± 0.07 eV	4973.49 ± 0.01 eV
P1:P2	0.37 ± 0.05	0.34 ± 0.09	0.35 ± 0.01
P1:P3	0.37 ± 0.06	0.41 ± 0.09	0.27 ± 0.02
P2:P3	1.02 ± 0.19	1.26 ± 0.33	0.75 ± 0.06

Table 2. Numerical values of the experimental XAS data of the biotemplated samples prepared in acidic and alkaline conditions and the standard anatase sample.

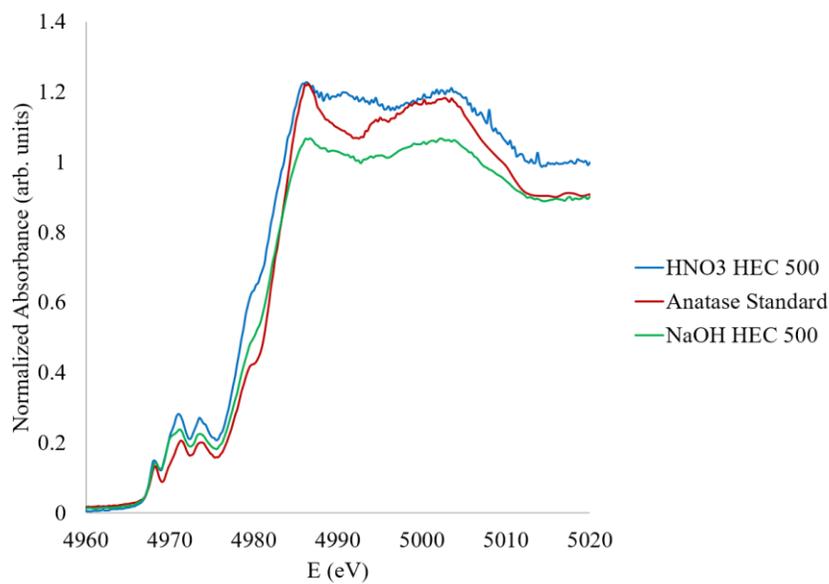


Figure 9. XAS experimental data of the biotemplated sample prepared in acidic conditions (blue), in alkaline conditions (green) and a standard sample of pure anatase (red).

Conclusions:

In conclusion, the use of the PIT-nanoemulsion synthesis in the presence of a biotemplate proved to increase the size of the TiO₂ particles compared to the samples prepared without a biotemplation. According with the PXRD and XAS analysis a mixture of the three phases was obtained for the biotemplated sample prepared in acidic conditions. Further PXRD and XAS analysis confirmed the anatase phase was obtained in the biotemplated sample prepared in alkaline conditions. Furthermore, according to TGA results, the biotemplate HEC was removed from the TiO₂ sample once calcinated at 500 °C in both conditions, acidic and alkaline. Future synthesis will involve variations in pressure and/or biotemplate in order to isolate the brookite phase.

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