

Near-infrared upconversion composite for photocatalytic applications

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Master Program in *Nanoscience, materials and processes: chemical technology at the frontier*,
2014-2015

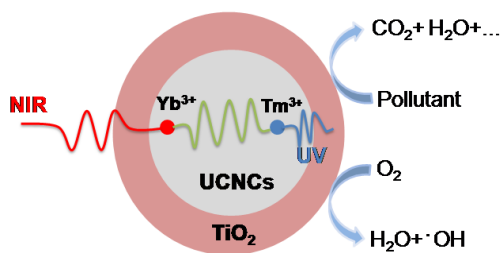
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Abstract. Innovative near-infrared photocatalyst composed by upconversion nanocrystals and TiO_2 anatase nanocrystals was synthesized and characterized during the course of this study. Upconversion nanocrystal/ TiO_2 nanocrystal composites were prepared via core-shell methodology. The surface modification of upconversion nanocrystals and the TiO_2 nanocrystals was done with thioglycolic acid and mercaptoethanol. By environmental scanning electron microscopy images, we showed that TiO_2 nanocrystals are uniformly dispersed on the surface of the upconversion nanocrystals. Upconversion

process was studied via photoluminescence spectra under 980nm excitation.



Keywords: TiO_2 , synthesis, upconversion, optical characterization, nanocrystals.

1. Introduction

During the last decades, titanium dioxide (TiO_2) has been reported to be an effective photocatalyst for environmental remediation such as water and air purification [1, 2], self-cleaning surface [3, 4] or antibacterial agent [5, 6]. The first time that TiO_2 was investigated as a photo-sensitizer for bleaching dyes in the presence of oxygen was in the late 1930 [7]. That work reported the UV enhancement of the production of reactive oxygen species on the surface of TiO_2 leading to organic matter degradation. The properties that make TiO_2 a model for photocatalytic applications are due to the chemical and thermal stability, low toxicity and cost, high photocatalytic activity leading to long operational life time [8].

The activity of this photocatalyst derives from the fact that TiO_2 has a large band gap (3.2 eV) corresponding to the spectral absorption mainly in the ultraviolet (UV) region. When UV photons reach the TiO_2 surface, an electron is promoted from the valence band (vb) to the conduction band (cb) leaving a positive hole in the vb. This hole will react with water/humidity on the surface of TiO_2 leading to the formation of highly oxidative hydroxyl radicals. Moreover Ohtani *et al.*, reported that charge recombination on TiO_2 can happen due to

the presence of defects or being amorphous [9].

One of the drawbacks to use TiO_2 is the requirement of high energy photons to guarantee a photocatalytic response. It has been shown that TiO_2 shows limited activity under solar light [10] comprising just 5% of UV. In order to extend the use of solar energy and to use cheaper light sources, many strategies were adopted: coupling with metal/metal oxides (Pt, Ag, Cu) [11, 12], sensitizing with dyes (thionine) [13] or doping with upconversion (UC) luminescence agents [14].

The most used approach to take profit of the near infrared (NIR) light of the sun is the combination of a photocatalyst with an UC phosphor. Phosphors are inorganic solids doped with some optically active ions that can absorb and convert certain types of energy into luminescent radiations. UC is a non linear optical process where two or more photons with low energy are absorbed and emit a higher energy photon. This is a useful method to generate visible or UV light from NIR light sources. The kind of light generated depends of the used doping agents. For example, when UV light is required, the ions most used are thulium (Tm^{3+}) and ytterbium (Yb^{3+}) that will produce UV and blue light. Using holmium (Ho^{3+}) or

erbium (Er^{3+}) and Yb^{3+} as doping agents will produce visible light in the green wavelength range via UC [15]. The use of NIR light for photocatalysis was demonstrated for the first time by Qin *et al.*, in 2010 [16]. In this work, they combined TiO_2 with UC nanocrystals for photocatalysis by a core/shell structure. The photocatalytic activity of the core/shell $(\text{Tm,Yb})\text{:YF}_3/\text{TiO}_2$ material was tested by methylene blue degradation under 980nm excitation and NIR radiation of the sunlight. Later, Tang *et al.*, [17] reported a new core/shell composite material, $(\text{Tm,Yb})\text{:NaYF}_4/\text{TiO}_2$ for NIR photocatalytic process. More recently Wang *et al.*, reported for the first time double-shell-structured $(\text{Er,Tm})\text{:NaYF}_4@\text{SiO}_2@\text{TiO}_2$, which shows high efficiency for Rhodamine B degradation under NIR excitation [18].

In order to improve the efficiency of the UC process a new host matrix is selected to enhance the photocatalytic activity of TiO_2 . Furthermore there is an increasing demand of UC phosphor without halide elements [19]. In the literature, it has been found that NaYF_4 matrix is more effective under NIR excitation than YF_3 [19] and also rare earth oxysulfides ($\text{Re}_2\text{O}_2\text{S}$) are 6.5 times brighter than rare-earth oxides [20]. Other properties that also make suitable the use of oxysulfides as UC phosphors are the low toxicity, high chemical and thermal stability and their low production cost [21]. In addition, in order to improve the photocatalytic efficiency of TiO_2 , the coverage of the UC phosphor is needed to optimize with core-shell structure via surface functionalization.

In this study we describe new NIR photocatalysts composed by UC nanocrystals (UCNCs) based on oxysulfide compounds and TiO_2 . The synthesis of TiO_2 nanocrystals (NCs) and UCNCs where optimized during the course of this study. The doping agents are Tm and Yb ions with a concentration of 1 at. % and 8 at. % respectively. The doping concentrations are the optima to enhance the UV conversion via UC according to Han *et al.*, and Pengde *et al.*, [22, 23].

Their crystallographic and morphological characterization and optical properties were investigated in detail. The innovative prepared composite material can be of potential use in solar photocatalytic reactors, self-cleaning surfaces in clean rooms or as a painting for environmental remediation (NO_x or CO_2 degradation).

2. Experimental section

2.1 Chemicals

Titanium (IV) oxide (TiO_2 , 99.8%), ethylene glycol anhydrous (EG, 99.8%) and iron (III) oxide (Fe_2O_3 , 99%) were purchased from Sigma-Aldrich. Anhydrous Citric acid ($\text{C}_6\text{H}_8\text{O}_7$, 99.5%) was bought from Fluka. Nitric acid (HNO_3 , 65%) was acquired from Merck. Yttrium (III) nitrate hexahydrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.8%), Ytterbium (III) nitrate pentahydrate ($\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99.9%), Thulium (III) nitrate pentahydrate ($\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99.9%), Thioacetamide (CH_3CSNH_2 , 99%) were bought from Sigma-Aldrich. Ethanol (pure, $\text{C}_2\text{H}_6\text{O}$) was purchased from Merck and washed Sulphur (S, 99%) was acquired from Rectapur. Thioglycolic acid (HSCH_2COOH , 98%) and 2-Mercaptoethanol ($\text{HSCH}_2\text{CH}_2\text{OH}$, 99%) were bought from Sigma-Aldrich.

2.2 Synthesis of TiO_2 and (Tm, Yb) doped TiO_2 NCs.

TiO_2 and (Tm,Yb) doped TiO_2 NCs were prepared by the Pechini method [24]. The dispersed metal oxides were dissolved in nitric acid and evaporated around 356K in order to obtain the corresponding nitrate powders. The mixture of nitrates was dissolved in citric acid with a molar ratio $C_M=2$ ($C_M=\text{mol CA/mol Metal}$, CA=Citric acid) under stirring for 2h to form metal-citrate complexes. Ethylene glycol (EG) is added with a molar ratio $C_E=0.5$ ($C_E=\text{mol CA/mol EG}$) to produce a polymeric network. The used molar ratios were obtained from the literature [25]. After drying the solution overnight in a sandbath, the complex gel is pre-calcined in a muffle under air. Subsequently the precursor is calcined to produce TiO_2 NCs in air at calcination temperature, $T_c > 800\text{K}$ during some hours, t_c . Table 1 summarizes the experiments performed.

Table 1. Experimental parameters of the synthesis of the TiO_2 NCs.

SAMPLE	T_c [K]	t_c [h]	DOPING
1	806	1,75	-
2	863	1,67	-
3	973	1,17	-
1N	973	1,5	0,5 at. % Tm^{3+} , 4 at. % Yb^{3+}
2N	973	1,5	1 at. % Tm^{3+} , 8 at. % Yb^{3+}

2.3 Synthesis of UCNCs

2.3.1 EASC method

Ethanol assisted combustion synthesis (EACS) method is used to obtain the doped-yttrium oxysulfide nanocrystals [26, 27]. The raw materials, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and CH_3CSNH_2 , were dissolved with distilled water and ethanol (0.0025M) in a zirconia crucible at 353K for 1h. The molar ratios between the sulfur and the yttrium used were $\text{S/Y}=1$ or 4. Then, the mixture was heated in a tubular furnace at the synthesis temperature, T_E for some time, t_E under the selected atmosphere. Some obtained samples were post-treated by annealing at different temperatures. The post-treatment was done under hydrogen atmosphere (5vol. % H_2 and 95vol. % Ar) where all the samples are named by "number of sample. number of post-treatment". Table 2 summarizes the experiments performed.

2.3.2 Sulfuration of (Tm, Yb): Y_2O_3

An alternative method to produce yttrium oxysulfide nanocrystals is the procedure to introduce S into a lanthanide doped sesquioxide, Re_2O_3 , via a sulfuration process [28]. The lanthanide doped sesquioxide can be prepared via Pechini method [29] or in this work, we have used the product obtained when the oxysulfide synthesis failed. Then, the sulfuration of the obtained (Tm, Yb): Y_2O_3 NCs was done by different methods. The first method is called double crucible method [30]. An amount of sulphur, carbon and oxide is placed in a small crucible that is inside another crucible. The big crucible contains an excess of sulphur and is covered with a lid. The second method is the sulfide fusion method or flux method [28], where the flux is composed by sulphur and Na_2CO_3 under and oxygen-free atmosphere during the heating. The used molar ratio between the elements are $\text{Y:C:S}=1:1.5:4$ in both cases [31]. Also, in table 2 summarizes the experiments performed.

Table 2. Experimental parameters of the synthesis of the UCNCs.

SAMPLE	S/Y	EACS			REDUCTION			SULFURATION		
		Atmosphere	T_E [K]	t_E [min]	Atmosphere	T_R [K]	t_R [min]	Atmosphere	T_S [K]	t_S [min]
1	4	Air	547	0						
2	1	N_2	573	0						
2.1	1	Calcination	673	60						
2.2	1				H_2/Ar	1173	60			
3	1	N_2	565	0						
3.1	1				H_2/Ar	1073	10			
3.2	1				H_2/Ar	1073	20			
3.3	1				H_2/Ar	1073	30			
3.4	1				H_2/Ar	1073	40			
3.5	1				H_2/Ar	1073	50			
3.6	1				H_2/Ar	673	60			
3.7	1				H_2/Ar	673	5			
3.8	1				H_2/Ar	623	5			
3.9	1				H_2/Ar	673	30			
3.1	1				H_2/Ar	623	120			
3.11	1				H_2/Ar	623	240			
4	1	N_2	673	20						
5	4	N_2	489	0						
6	1	N_2	1173	240						
7	1							N_2	673	20
8	1							N_2	1073	240
9	1	Ar	673	20						
9.1	1				H_2/Ar	623	240			
10	1							Ar	1073	240
11	4							Ar	1173	120
12*	4							Ar	1173	120

*Flux method (sulfuration)

2.4 Preparation of the TiO₂/UCNCs composite

2.4.1 Coverage via functionalization of the TiO₂ and the UCNCs

The composite formed by the UCNCs and the TiO₂ semiconductor was done through an esterification reaction. The surface of the UCNCs was functionalized with mercaptoethanol (as a source of the functional alcohol group) and the TiO₂ NCs surface was functionalized with thioglycolic acid (as a source of the carboxylic functional group). It is known from the literature that the SH groups have a strong interaction with the lanthanide ions leaving OH groups on the surface of the UCNCs. SH groups have been used for TiO₂ NCs self-stabilization and COOH groups for its surface functionalization [32]. The used molar ratios were calculated taken into account the S contained in both compounds, and used as a ligand to the Ti and Y of the NCs. For the thioglycolic acid used, the molar ratio was S/Ti=1 and for the mercaptoethanol was S/Y=10. Both solutions were stirred for 3h and washed with deionized water. In order to produce the esterification, the precursors were heated at 433K for 3h. Afterwards, the expected composite was centrifuged and washed several times with deionized water.

2.4.2. Pechini method for the preparation of the TiO₂/UCNCs composite

The composite TiO₂/UCNCs was also prepared via Pechini method. The already described Pechini procedure was reproduced, and the only difference was that the UCNCs were added with the ethylene glycol. The calcination time and temperature used were the same than for sample 3, table 1.

3. Characterization

The synthesized particles were characterized by X-ray power diffraction (XRPD) with Cu K α radiation ($\lambda=1.5418\text{\AA}$) performed by Bruker D8 Discover diffractometer. The thermal analysis was evaluated by thermogravimetric analysis (TG) and differential thermal analysis (DTA) that was performed by Labsys/Setaram TG DTA/DSC. The crystalline habit of the particles was analysed by environmental scanning electron microscopy (ESEM) and transmission electron microscopy (TEM) that was carried out by Quanta 600 and JEOL model 1011 respectively. Raman spectroscopy was carried out by Raman FTIR Renishaw to identify the characteristic vibrational levels. The UC luminescence was measured under 980nm laser excitation and the spectra were recorded by Yokogawa

AQ6373 spectrum analyser with a cut off filter at 750nm. The optical band gaps of the TiO₂ NCs were calculated using diffuse reflectance spectra (DRS) measured by Cary 5000 spectrometer with internal DRA 2500 accessory.

4. Results and discussion

4.1 Structural and morphological characterization of TiO₂ NCs synthesized.

In order to optimize the calcination temperatures and its effects on the thermal stability of the prepared TiO₂ NCs, the pre-calcined powder is thermally analysed.

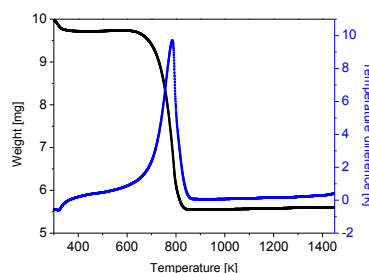


Figure 1. DTA-TGA trace recorded for the pre-calcined powder of TiO₂ under air conditions.

The DTA-TGA analysis shows a weak endothermic peak in the temperature range below 373K that is attributed to the evaporation of water. From 673K to 873K an exothermic peak is observed corresponding to the oxidation of the organic molecules that remains in the sample as the combustion is not complete and also the exothermic crystallization of amorphous TiO₂ into anatase crystallites. This analysis confirms that the calcination temperature of 787K is sufficient to crystallize the amorphous precursors into crystalline TiO₂. The powders were then calcined in air at temperature higher than 787K.

The XRPD patterns of the as-prepared TiO₂ NCs and the data of TiO₂ anatase (JCPDS No. 21-1272) and rutile (JCPDS No. 21-1276) are shown in figure 2. All samples present the diffraction peaks corresponding to the TiO₂ anatase. The average crystal sizes are calculated from the Scherrer formula: $D_{hkl} = K\lambda / \beta \cos\theta$. Where D_{hkl} is the crystal size along the (hkl) direction, K is a constant (0.9), θ is the diffraction angle and β is the full-width at half-maximum (FWHM) [24]. We take two main peaks at $2\theta=25.28^\circ(101)$ and $48.05^\circ(200)$ to calculate the average crystal size of the samples. The crystalline size of sample 1 is 43.5nm, for sample 2 is 44.2nm, for sample 3 is 44.6nm, for sample 1N is 43.7nm and for sample 2N is 44.5nm.

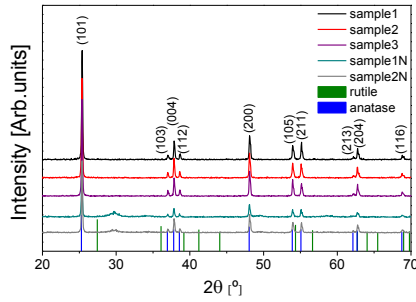


Figure 2. XRPD patterns of the synthesized TiO_2 NCs. JCPDS 21-1276 card of the rutile tetragonal $P4_2/mnm$ and JCPDS 21-1272 card of the anatase tetragonal $I4_1/amd$ are presented in the lower part as references.

Sample 1N and 2N corresponds to the doped (Tm,Yb): TiO_2 . It can be observed that in these samples, an extra peak at about $2\theta=30^\circ$ corresponds to the cubic crystalline phase of the Re_2O_3 sesquioxide. This may be due to the fact that not all doping agents (Tm, Yb) are inside the crystalline structure or that the preparation conditions lead to the formation of ytterbium or thulium oxide.

The morphology and structure of the synthesized TiO_2 NCs are investigated by TEM as shown in figure 3. Figure 3 shows that the synthesized NCs are polyhedral and non aggregated, showing a slight tendency to form spherical shapes. The optimal calcination temperature and time is therefore 973K and during 1.17h where the particle size is the smallest as it can be readily seen in figure 3c).

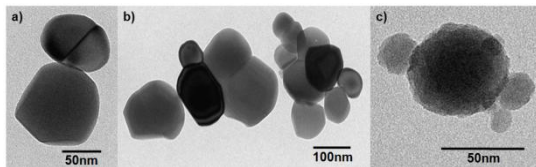


Figure 3. TEM images of synthesized TiO_2 NCs a) sample 1, b) sample 2 and c) sample 3.

Figure 4 gives the histograms of size distribution of TiO_2 NCs. We can observe that when the time of calcination is decreasing, the particle size is also decreasing. The mean size for sample 1, sample 2 and sample 3 are around 70nm, 90nm and 10nm respectively.

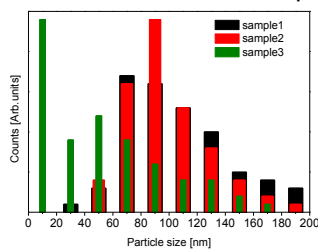


Figure 4. Mean size distribution of the synthesized samples of TiO_2 NCs.

Another analysis to confirm the obtaining of the anatase phase of TiO_2 can be done with the Raman spectroscopy. When the crystal phase desired is anatase, Raman bands can be seen at 114, 197, 399, 515 and 639 cm^{-1} [33]. Figure 5 shows that the doped samples do not change the crystalline phase when the doping agents were added into the crystal structures.

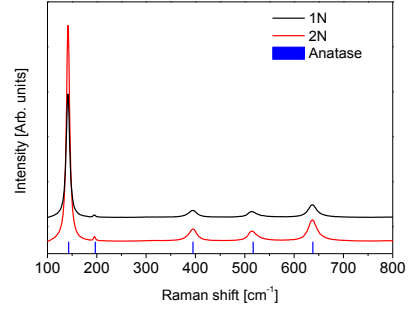


Figure 5. Raman spectroscopy of TiO_2 doped NCs.

4.2 Structural and morphological characterization of synthesized UCNCs.

The synthesized UCNCs are divided in two major groups depending on the crystalline structure obtained, identified by the XRPD analysis shown in the figure 6 and 7. The group corresponding to the cubic sesquioxide Y_2O_3 are called A and the group corresponding to a mixture of $\text{Y}_2\text{O}_2\text{S}$ and $\text{Y}_2\text{O}_2\text{SO}_4$ are called B. As observed, the first group is clearly crystalline, however when the mixture of $\text{Y}_2\text{O}_2\text{S}$ and $\text{Y}_2\text{O}_2\text{SO}_4$ is obtained the samples are poorly crystallized, observed by the broad and few diffraction peaks observed.

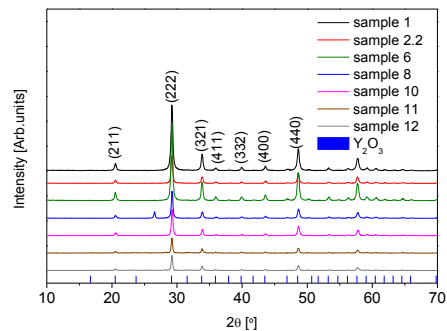


Figure 6. XRPD patterns of the UCNCs synthesized A. JCPDS 88-1040 card of the yttrium oxide cubic $Ia\bar{3}$ is presented in the lower part as reference.

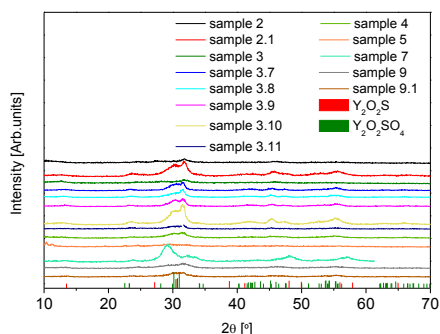


Figure 7. XRPD patterns of the UCNCs synthesized B. JCPDS 24-1424 card of the yttrium oxide sulfide trigonal $P\bar{3}m1$ and JCPDS 53-0168 yttrium oxide sulfate monoclinic $C2/c$ are presented in the lower part as references.

Table 2 summarize all the experiments done to synthesize the UCNCs. The experimental parameters used for the synthesis of the UCNCs were chosen according with the experimental parameters reported in the literature where EACS method was done at 673K [26, 27] and sulfuration was done at 1073K or 1173K [30, 34]. The chosen atmospheres were air, N_2 and Ar. In the literature it was found that it is necessary to control the firing atmosphere and also that when N_2 is used the final products contain amounts of Y_2O_3 . This effect is probably due to the fact that N_2 carries the sulfur out of the crucible [35]. Despite the desired product to be obtained was the Y_2O_2S , a mixture of rather amorphous $Y_2O_2S + Y_2O_2SO_4$ was obtained or the crystalline sesquioxide phase. It is important to highlight that the sesquioxide NCs are also known as interesting upconversion materials [36, 37].

From figure 6 and 7 and table 2, we can concluded that at high temperatures ($T < 1000K$) the reaction lead to yttrium oxide independently from the ratio S/Y used. This result is in agreement with Machida *et al.*, were they reported that yttrium oxysulfate decomposes to yttrium oxide at approximately 1223K [38]. Furthermore at low temperatures, ($400K < T < 700K$) a mixture of $Y_2O_2S + Y_2O_2SO_4$ can be obtained with a ratio of S/Y=1. This may be due to the fact that yttrium oxysulfide is rapidly oxidized to yttrium oxysulfate and with further temperature it decomposes to yttrium sesquioxide as reported by Haynes *et al.*, [39].

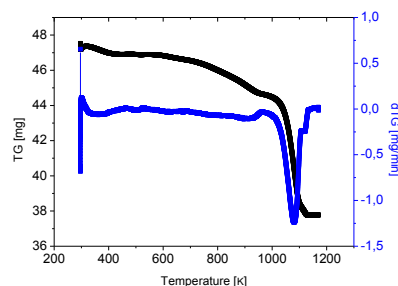


Figure 8. TGA curve and derivative of sample 2 under H_2/Ar atmosphere.

Figure 8 shows the thermal analysis of sample 2 for the post-treatment optimization. The endothermic peak observed at 1073 K for sample 2 has been attributed to the transition to the sesquioxide compound. This hypothesis can be confirmed by the results in sample 2, 3.1, 3.2, 3.3, 3.4 and 3.5, in which the reduction was done at 1073K and it was leading to the formation of pure Y_2O_3 . These results are in agreement with Machida *et al.*, reporting that at high temperature the yttrium oxysulfate decomposes to the yttrium oxide [38]. By decreasing the temperature the samples should stay for longer post-treatment time in order to achieve higher crystal size. It is also readily seen in figure 7 that samples 3.10 and 3.11 should have an optimal time leading to the highest crystallinity (2h) above this time the crystallinity is not favored.

The morphology and structure of the synthesized UCNCs were observed by TEM. Figure 9 shows the UCNCs "A" prepared under air and Ar atmosphere. The nanocrystals show a tendency to be more polyhedral under conditions of Ar atmosphere and high temperature. The crystalline habit resembles the already reported in the Re_2O_3 nanocrystals prepared by Pechini method [37]. The mean size for sample 1 is 35,5nm, for sample 11 is 53,7nm and for sample 12 is 50nm analysed by TEM.

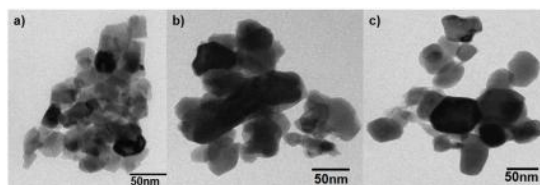


Figure 9. TEM images of a) sample 1, b) sample 11 and c) sample 12.

The TEM images showed in figure 10 illustrate that the UCNCs "B" generally presents an elongated crystalline habit. Figure 10b) shows that the shape is better defined when prepared under Ar atmosphere with an average width of 14nm analysed by TEM.

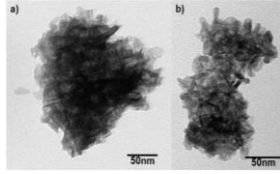


Figure 10. TEM images of a) sample 3.11 and b) sample 9.1.

According to XRPD analysis we selected samples 6, 11 and 12 to represent the group "A". Samples 3.10, 3.11, 9 and 9.1 were chosen to represent group "B". The selected samples will be characterized by further optical studies.

4.3 Structural and morphological characterization of the composite.

Coverage via functionalization is a surface modification of the NCs where an ester is formed between the alcohol and carboxylic groups. It has been widely reported that core-shells prepared by sol-gel method permit the deposition of inorganic oxide layers to solid cores [40]. One drawback of this method is the formation of amorphous materials useless for photocatalytic processes where crystalline phases are needed as reported by Zhang *et al.*[40].

Figure 11 shows the XRPD analysis from the composites UCNCs with sample 3 of TiO₂ NCs. In each sample one can see that both anatase phase and UCNCs coexist.

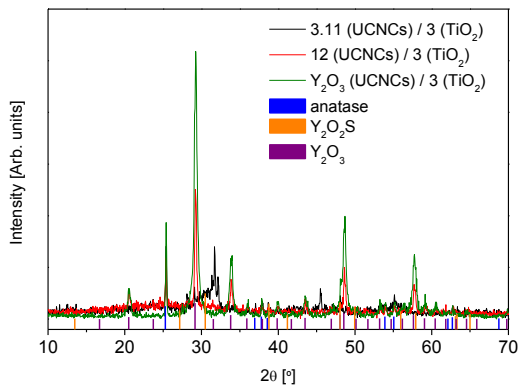


Figure 11. XRPD patterns of the composites UCNCs with sample 3 of TiO₂ NCs. JCPDS 21-1272 card of the anatase, JCPDS 24-1424 card of the yttrium oxide sulfide and JCPDS 88-1040 card of the yttrium oxide are presented in the lower part as reference.

Figure 12a) and 12b) show a rough surface demonstrating the successful coupling of the TiO₂ on the UCNCs. During this study the samples prepared by Pechini method, as described in section 2.4.2 were aggregated as it can be seen in figure 12c). One way to overcome this problem is to add an ultrasonication step to disperse the UCNCs before the precursor resin is formed [41].

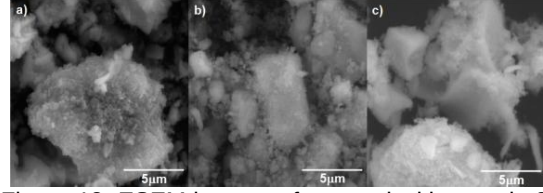


Figure 12. ESEM images of covered with sample 3 of TiO₂: a) sample 3.11, b) sample 12 and c) UPNCs composite prepared via Pechini method.

4.4 Band gap determination of the synthesized TiO₂ NC.

The band gap of the synthesized TiO₂ NCs can be estimated from the diffuse reflectance spectra using Kubelka-Munk function. As the samples have a rough surface, the use of Kubelka-Munk model seems correct [42].

For infinite length, the absorption coefficient (α) can be related to the reflectance (R) by the following relation: $F(R) = (\alpha/s) = (1-R)^2/2R$ where $F(R)$ is the Kubelka-Munk function. R is the reflectance and s is the scattering coefficient. Plotting $[F(R)hv]^2$ front hv and making an extrapolation to the x-axis when $[F(R)hv]^2 = 0$, this intercept will give the value of the sample band gap.

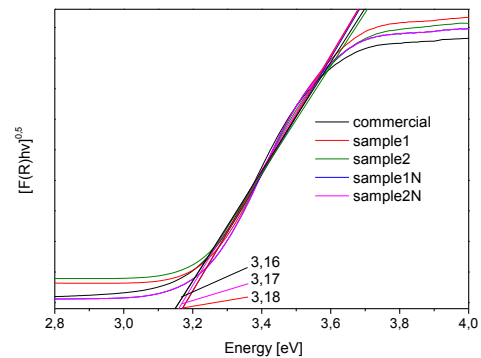


Figure 13. Diffuse reflectance spectra of the synthesised TiO₂ for optical band gap determination.

It has been widely reported that the band gap for commercial TiO₂ with a crystallite size of 39nm is about 3.2eV [43]. As figure 13 shows the band gap of the commercial TiO₂ was about 3.16eV and for the synthesized NCs was about 3.17eV that are in concordance with the literature [43]. For doped TiO₂ (sample 1N and 2N) also the band gap is 3.18eV. It has been shown that slightly blue-shifted band gap can be attributed to the interaction of electrons from the conduction band above the first excited state of the rare earths [44]. In our case all the samples have the band gap as is expected from the literature, around 3.2eV regarding the crystal size.

4.5 Optical absorption in the NIR and UC emission spectra of the synthesized UCNCs.

The optical absorption of the samples was measured at room temperature to confirm the presence of Yb^{3+} and its NIR absorption. To verify that UCNCs and TiO_2 NCs were doped with Yb^{3+} , the expected absorption will be in the range of 900-1000nm. This absorption is attributed to the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ electronic transition of Yb^{3+} ions.

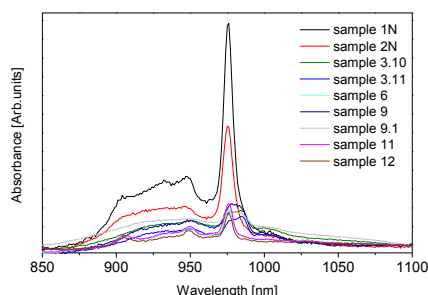


Figure 14. Optical absorption in the NIR for synthesized UCNCs and doped TiO_2 NCs.

Figure 14 shows in the range between 900 to 1000nm an absorption with the highest peak at 975nm. With these results we can confirm that the UCNCs and TiO_2 NCs are doped at least with Yb^{3+} . In order to show the UC process these samples can be excited with a wavelength of 980nm. UCNCs doped with (Tm,Yb) are typical ions to convert the NIR to the UV range. Under a 980nm laser excitation, UCNCs emits UV and blue light. Figure 15 shows an energy diagram of Tm^{3+} and Yb^{3+} and the UC process after NIR excitation via energy transfer upconversion (ETU). Yb^{3+} ions are excited from $^2\text{F}_{7/2}$ to $^2\text{F}_{5/2}$ when NIR light around 980nm is absorbed. The upconversion emission is generated when the excited Yb^{3+} ions transfer energy to the Tm^{3+} ions and this energy is emitted radiatively to the lower-energy state as light [36].

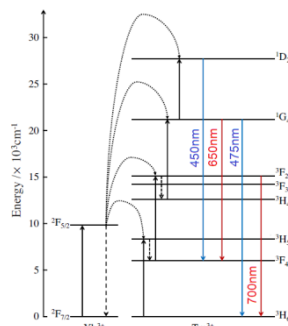


Figure 15. Upconversion process via ETU and energy diagram of Tm^{3+} and Yb^{3+} ions [36].

Photoluminescence spectra measured are shown in figure 16 and 17.

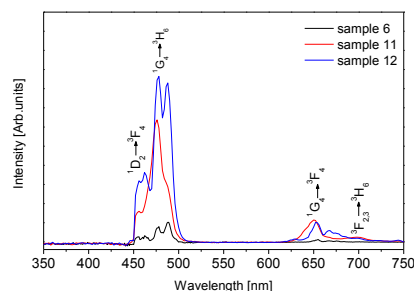


Figure 16. UC luminescence spectra of UCNCs A doped with (Tm, Yb) upon excitation under 980nm.

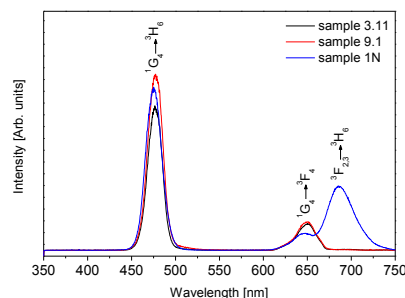


Figure 17. UC luminescence spectra of UCNCs B and TiO_2 NCs doped with (Tm, Yb) upon excitation under 980nm.

Figure 16 and 17 show two peaks at 450 and 475nm are assigned to $^1\text{D}_2 \rightarrow ^3\text{F}_4$ and $^1\text{G}_4 \rightarrow ^3\text{H}_6$ electronic transitions of Tm^{3+} ions corresponding to the blue light. We can also see two more peaks at 650 and 700nm assigned to $^1\text{G}_4 \rightarrow ^3\text{F}_4$ and $^3\text{F}_{2,3} \rightarrow ^3\text{H}_6$ electronic transitions of Tm^{3+} ions corresponding to the red light.

5. Conclusions

Undoped and lanthanide doped TiO_2 NCs were synthesized successfully by the Pechini method. The average size obtained is below the 50 nm for the optimal conditions. In all cases, the crystalline phase obtained belongs to the anatase phase. The optical band gap as expected was around 3.2 eV in all samples. UCNCs were synthesized by EACS and sulfuration method. Cubic crystalline nanocrystals with sizes around 35 nm, of $(\text{Tm},\text{Yb})\text{:Y}_2\text{O}_3$ were obtained, besides a more amorphous nanoparticles with a mixture composition of $\text{Y}_2\text{O}_2\text{S} + \text{Y}_2\text{O}_2\text{SO}_4$ also in the nanometer range. Further optimization of the synthesis method is required to obtain pure $\text{Y}_2\text{O}_2\text{S}$ nanocrystals.

TiO_2 NCs were deposited on the surface of UCNCs via core-shell and via surface functionalization. TEM images confirm the attachment between TiO_2 NCs and UCNCs. UC processes were identified with the optical absorption of Yb in the NIR and with the photoluminescent spectra of Tm in the visible range for all doped synthesized samples.

Aknowledgements

This work was supported by AGAUR through the grant: AAD3. Also the author wants to acknowledge Cinta Pujol for her support and scientific advices and the technical staff of FiCMA and FiCNA group for their support.

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