



**PHYSICAL CHEMISTRY 2021**

15<sup>th</sup> International Conference  
on Fundamental and Applied Aspects of  
Physical Chemistry

Proceedings  
Volume II

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*The Conference is dedicated to the*

*30<sup>th</sup> Anniversary of the founding of the Society of Physical  
Chemists of Serbia*

*and*

*100<sup>th</sup> Anniversary of Bray-Liebhafsky reaction*

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**September 20-24, 2021  
Belgrade, Serbia**

**Title:** Physical Chemistry 2021 (Proceedings) **ISBN** 978-86-82475-40-8

**Volume II: ISBN** 978-86-82475-39-2

**Editors:** Željko Čupić and Slobodan Anić

**Published by:** Society of Physical Chemists of Serbia, Studentski Trg 12-16, 11158, Belgrade, Serbia

**Publisher:** Society of Physical Chemists of Serbia

**For Publisher:** S. Anić, President of Society of Physical Chemists of Serbia

**Printed by:** "Jovan", <Printing and Publishing Company, 200 Copies

**Number of pages:** 6+388, Format A4, printing finished in December 2021

Text and Layout: "Jovan"

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## SYNTHESIS OF CORE-SHELL NaYF<sub>4</sub>:Yb,Tm@TiO<sub>2</sub>-Acac MICRO- AND NANO-SIZED PARTICLES FOR EFFICIENT PHOTOCATALYSIS

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### ABSTRACT

Micro- and nano-sized core-shell particles for efficient photocatalysis were successfully synthesized by a two step wet-chemical route. The core composed of up-converting (UC) NaYF<sub>4</sub>:Yb,Tm phase was prepared through EDTA assisted hydrothermal process, while the shell of anatase TiO<sub>2</sub> – Acetylacetonate (TiO<sub>2</sub>-Acac) charge-transfer complex was formed *via* a sol-gel method. During coating, the effect of polyvinylpyrrolidone (PVP) addition on the core and shell coupling was investigated. Two forms of core structures were obtained: hexagonal microprisms of β-NaYF<sub>4</sub>:Yb,Tm and α-NaYF<sub>4</sub>:Yb,Tm nanospheres, both coated with TiO<sub>2</sub>-Acac nanocrystals.

### INTRODUCTION

In the past decades, several methods have been tested for achieving efficient TiO<sub>2</sub>-based photocatalysis. The formation of hetero-junction, dye sensitization and metal/non-metal doping were used for extending absorption of TiO<sub>2</sub> toward the visible light range of solar spectrum. However, boosting photocatalytic efficiency is restricted due to the increase of electrons/holes recombination. To extend the light harvesting to the near-infrared (NIR) range of solar spectrum, we combined two extraordinary materials in a unique core-shell structure. NaYF<sub>4</sub>:Yb,Tm, used as a core, converts NIR to UV/VIS light, whereas TiO<sub>2</sub>-Acac charge-transfer complex, as a shell, absorbs the converted light, increasing in such way light harvesting. Up-conversion is the non-linear optical process which is most efficient in trivalent rare earth (RE<sup>3+</sup>)-doped NaYF<sub>4</sub> hexagonal phase. A suitable choice of sensitizer and activator ions, such as Yb<sup>3+</sup> and Tm<sup>3+</sup>, respectively, tunes UC emission toward blue and red part of spectra, *i.e.* toward wavelengths in which TiO<sub>2</sub>-Acac efficiently absorbs. We already showed that coupling of Acac on nanosized TiO<sub>2</sub> extends its absorption through visible spectral range due to altered optical band-gap to 1.4eV[1].

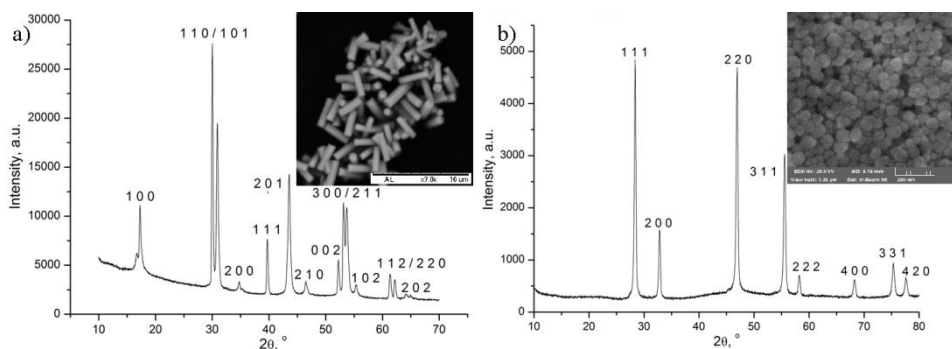
### METHODS

NaYF<sub>4</sub>:Yb,Tm particles with a nominal composition NaY<sub>0.78</sub>Yb<sub>0.2</sub>Tm<sub>0.02</sub> were hydrothermally synthesized from common rare earth nitrate precursor (0.01M) using the RE:F ratio of 14 and 7, respectively. Synthesis procedure is given in details elsewhere [2]. The as-obtained micro- and nano-sized UC particles were coated with TiO<sub>2</sub>-Acac using two methods. In both, the quantity of titanium tetraisopropoxide (TTIP) was calculated to be sufficient for formation of 50 and 10 nm thick shell on micro- and nano-sized particles, respectively, in accordance to sol-gel procedure described in [3]. In the first approach, 20 mg of UC particles were well dispersed in ethanol, using ultrasonic bath. Then acetilacetone (Acac:ethanol=1:10) and TTIP (TTIP:acac=1:2) were dropwise added under sonication. To accomplish the hydrolysis reaction, few drops of HNO<sub>3</sub> 0.307 M aqueous solution was added. Then the as-prepared sol was heated at 60 °C until complete solvent evaporation and the obtained

powder was thermally treated at 300 °C for 2h. In the second method, to explore the PVP use as coupling agent, the coating procedure was modified as followed: UC particles were firstly dispersed in 40ml of ethanol using ultrasonic bath. Then 0.5 g of PVP was added and the mixture was sonicated for 20 min. In a separate glass, 2 ml of TTIP was slowly added to 1.4 mL Acac/7 mL ethanol mixture under vigorous stirring. The obtained yellow solution was subsequently dropped into UC/PVP mixture and left overnight. The coated particles were collected through centrifugation at 7000 rpm and then, washed several times with ethanol and water. After drying, powder was subjected to a heat treatment at 300 °C for 2h. UC powders crystal structure were analyzed through X-ray powder diffraction (XRPD), using Bruker D8 Advance and Philips PW-1050 diffractometer. The morphology and surface properties of the particles, before and after coating, were investigated by field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS), using Mira Tescan 3X and Hitachi TM3000 SEM with Swift ED3000 detector, respectively.

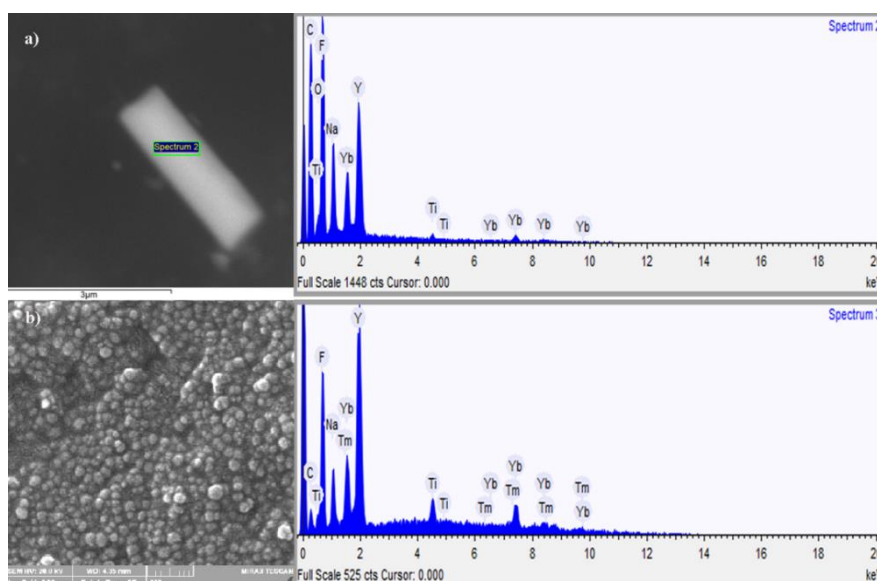
## RESULTS AND DISCUSSION

The XRPD patterns of the  $\text{NaY}_{0.78}\text{Yb}_{0.2}\text{Tm}_{0.02}$  samples obtained using different  $\text{RE}^{3+}:\text{F}^-$  ratio (14 and 7) are presented in **Figure 1**. Higher content of fluoride anions lead to the direct crystallization of the thermodynamically stable hexagonal  $\beta$  phase (space group  $\text{P6}_3/\text{m}$ ; JCPDS file No. 16-0334), **Figure 1(a)**. With a decrease of the fluoride ions-content, the crystallization of the kinetically stable cubic  $\alpha$  phase (group  $\text{Fm-3m}$ , JCPDS file No. 77-2042) occurred, **Figure 1(b)**. The change in the crystal structure arrangement is followed by the change of the particles morphology. The  $\beta$ -phase appears as well-defined hexagonal prisms with the elongated c-axes, sized up to 3  $\mu\text{m}$ , while spherical particles of  $\alpha$  phase, smaller than 50 nm, are readily prepared from a precursor which comprises lower concentration of fluoride ions (insets in **Figure 1**).



**Figure 1.** XRPD patterns and SEM images of  $\text{NaYF}_4:\text{Yb,Tm}$  phases: a) hexagonal,  $\beta$ -phase and b) cubic,  $\alpha$ -phase.

**Figure 2** strongly suggests that core-shell  $\text{NaYF}_4:\text{Yb,Tm}@\text{TiO}_2\text{-Acac}$  structures were obtained through the PVP free procedure, preserving initial particle morphology of both  $\text{NaYF}_4:\text{Yb,Tm}$  phases. The presence of titanium ions at the particle surface is confirmed through EDS analysis of a single particle (in the case of micro-sized particles, Figure 2a) and on a group of nanoparticles (Figure 2b). The presence of the  $\text{TiO}_2\text{-acac}$  shell is additionally revealed by FTIR analysis of core-shell particles (not included here) which shown a characteristic band of  $\nu\text{C}=\text{C}(\text{Ti-Acac})$  group in the enolic form at  $1580\text{ cm}^{-1}$ . The addition of PVP prevents the shell formation over UC nanoparticles and entirely suppresses it when micro-sized UC particles are used as a core.



**Figure 2.** NaYF<sub>4</sub>:Yb,Tm@TiO<sub>2</sub>-Acac core-shell structures

## CONCLUSION

Micro- and nano-sized NaYF<sub>4</sub>:Yb,Tm@TiO<sub>2</sub>-Acac core-shell particles were successfully obtained through the combination of hydrothermal and sol-gel synthesis methods. The presence of UC core should improve the overall sensitivity of TiO<sub>2</sub>-Acac to the solar spectrum, intensifying its photocatalytic properties.

## Acknowledgement

This research was supported by the Science Fund of the Republic of Serbia, program DIJASPORA, #6421090, COSH-PHOTO and Ministry of Education, Science and Technological Development of Republic of Serbia (Contract No. 451-03-9/2021-14/200175). B.A.M. is grateful to CNPq for Research Productivity Grant. T.M. is grateful to CAPES for a post-doctoral scholarship (PNPD-88882.315335/2019-01).

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