

Illuminating the Future: Afterglow Materials for Biomedical Applications



Partners involved

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Objectives

The main goal of our study is to synthesize nanoparticles capable of emitting persistent light, aimed at combating lung infections caused by bacteria.

This implies several requirements: the material must be non-toxic, stable, and colloidal in aqueous solution, with high emission intensity and long-time emission. The wavelength of the emitted light must match the absorption of the endogenous porphyrins of the bacteria, which is around 410 nm.

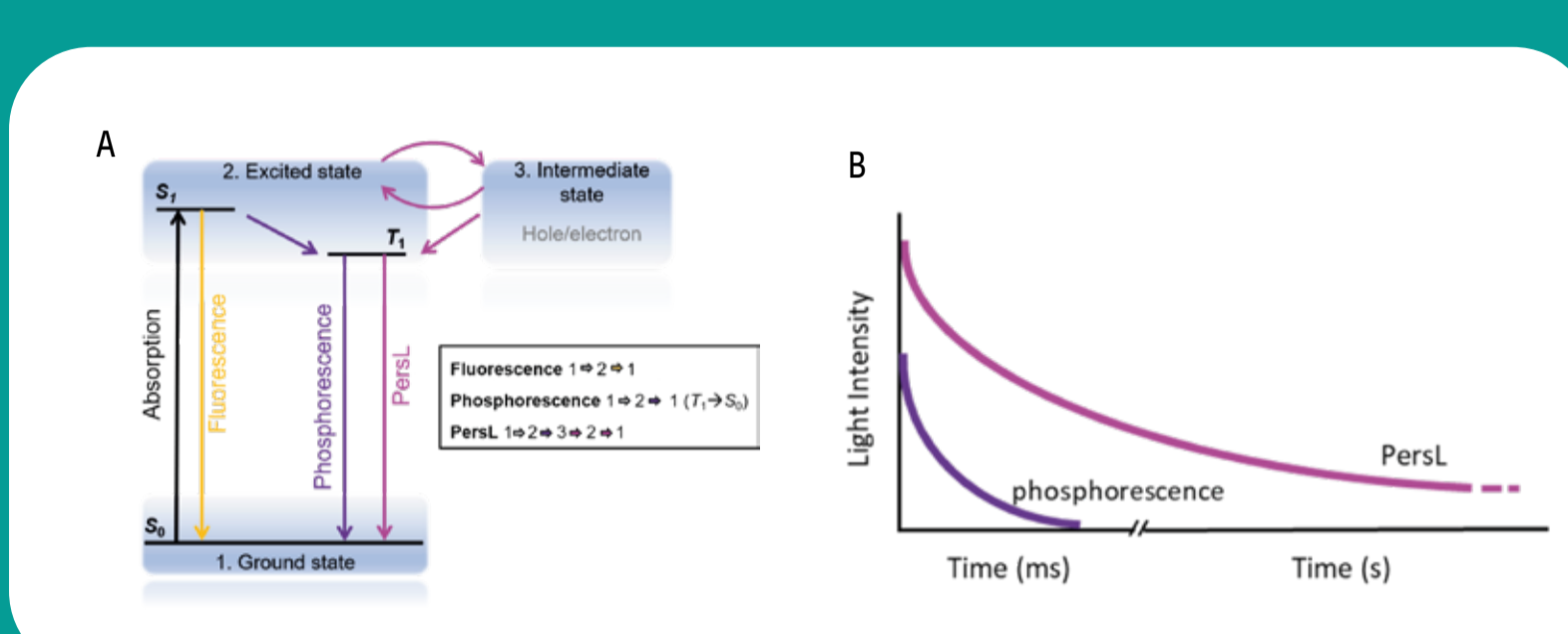


Figure 1
Diagram of the general processes of fluorescence, phosphorescence, and persistent luminescence (PersL) (A) and example of a phosphorescence and PersL decay at different timescales (B).

Methodology

Several materials have been prepared by using two different methods: conventional sol-gel and combustion. The prepared materials are: BaZrO₃:1.5%Mg²⁺, CaAl₂O₄:1%Eu²⁺, 1%Nd³⁺, SrAlO₄:Eu²⁺, Dy³⁺, ZnGa₂O₄:0.5%Bi³⁺, and ZrO₂:Ti⁴⁺, the latest proving the most promising results in this project.

Furthermore, various methods have been explored to disperse the ZrO₂:Ti⁴⁺ nanoparticles in an aqueous solution, including surface functionalization using glutamic acid and polyethylene glycol, coating the particles with SiO₂ prior the calcination step, and the in-situ synthesis on commercial SiO₂ particles.

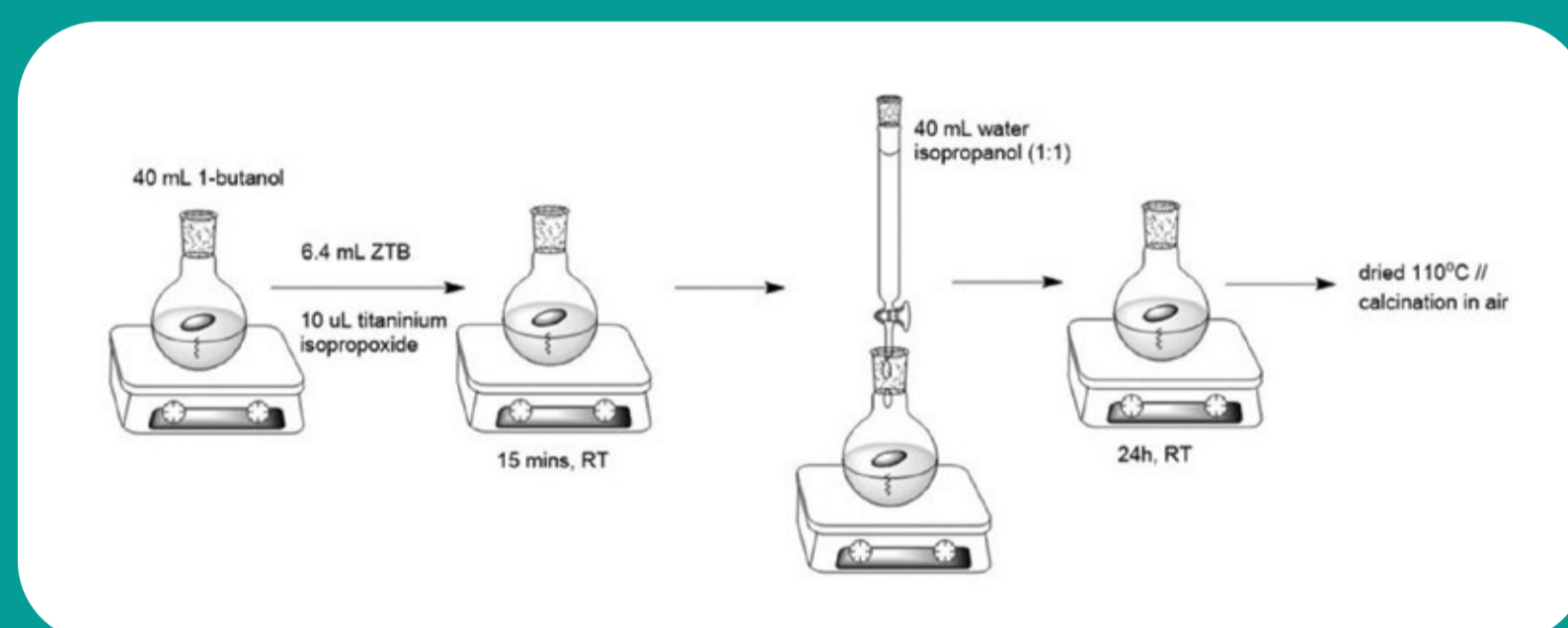


Figure 2
Synthesis by conventional sol-gel method of the titanium doped zirconium oxide nanoparticles (ZrO₂:Ti⁴⁺).

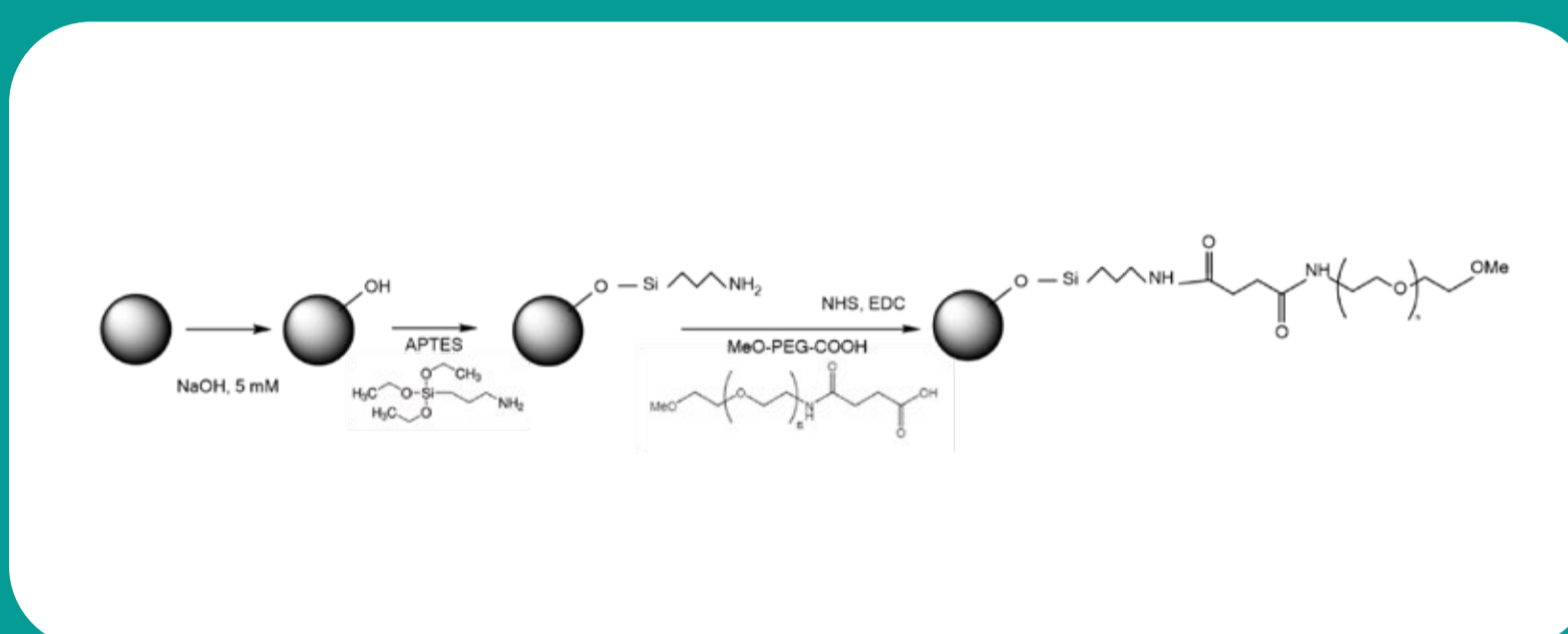


Figure 3
Surface coating process to obtain ZrO₂:Ti⁴⁺@PEG nanoparticles.

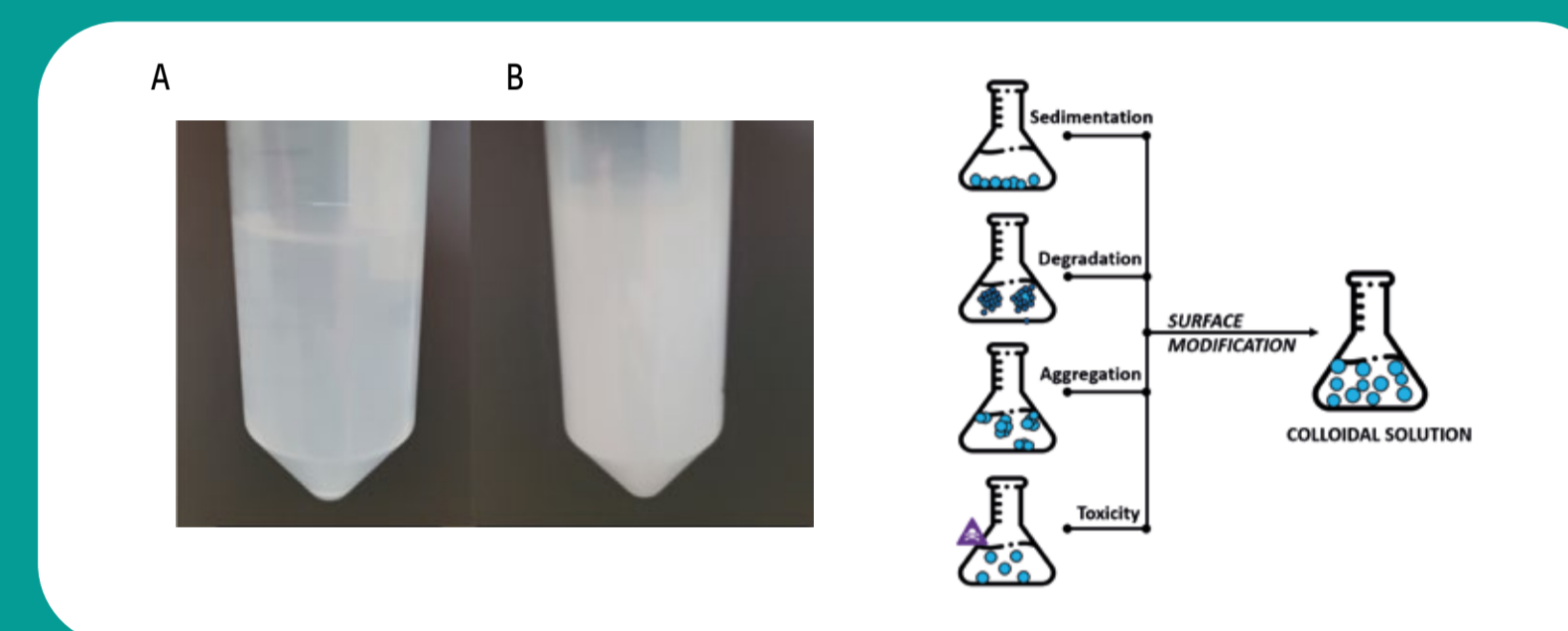


Figure 4
ZrO₂:Ti⁴⁺ (A) and ZrO₂:Ti⁴⁺@PEG (B) nanoparticles in aqueous solution after 6 hours of sonication. On the right, a scheme of the surface modification advantages to obtain a colloidal solution.

Results

ZrO₂:Ti⁴⁺ nanoparticles were successfully synthesized and characterized by using different techniques. Following the sol-gel synthesis, the particles exhibited uniform nano-scale sizing and excellent dispersion in aqueous solution. However, upon undergoing the calcination step, aggregation occurred, resulting in decreased size uniformity among the particles (see TEM images).

The X-ray diffraction (XRD) analysis revealed an amorphous phase in the particles in their as-cast state. As the calcination temperature increased, there was a notable enhancement in the crystallinity of the material. Additionally, the ZrO₂:0.2%Ti⁴⁺ composition transitioned from a mixture of tetragonal and monoclinic phases to predominantly monoclinic phase, which is known for its superior luminescence properties.

Photoluminescence emission spectra were recorded at various calcination temperatures, with the highest intensity observed at the highest temperature tested. These spectra were obtained under excitation at 280 nm. Persistent luminescence was evaluated using a Xenon lamp for a duration of 5 minutes. Subsequently, after stopping the excitation source, the luminescence was monitored over a period of time. The percentage of doping cation (Ti⁴⁺) in the zirconium oxide was also optimized, ranging from 0 to 1%, to explore its impact on the luminescence properties (Fig. 8).

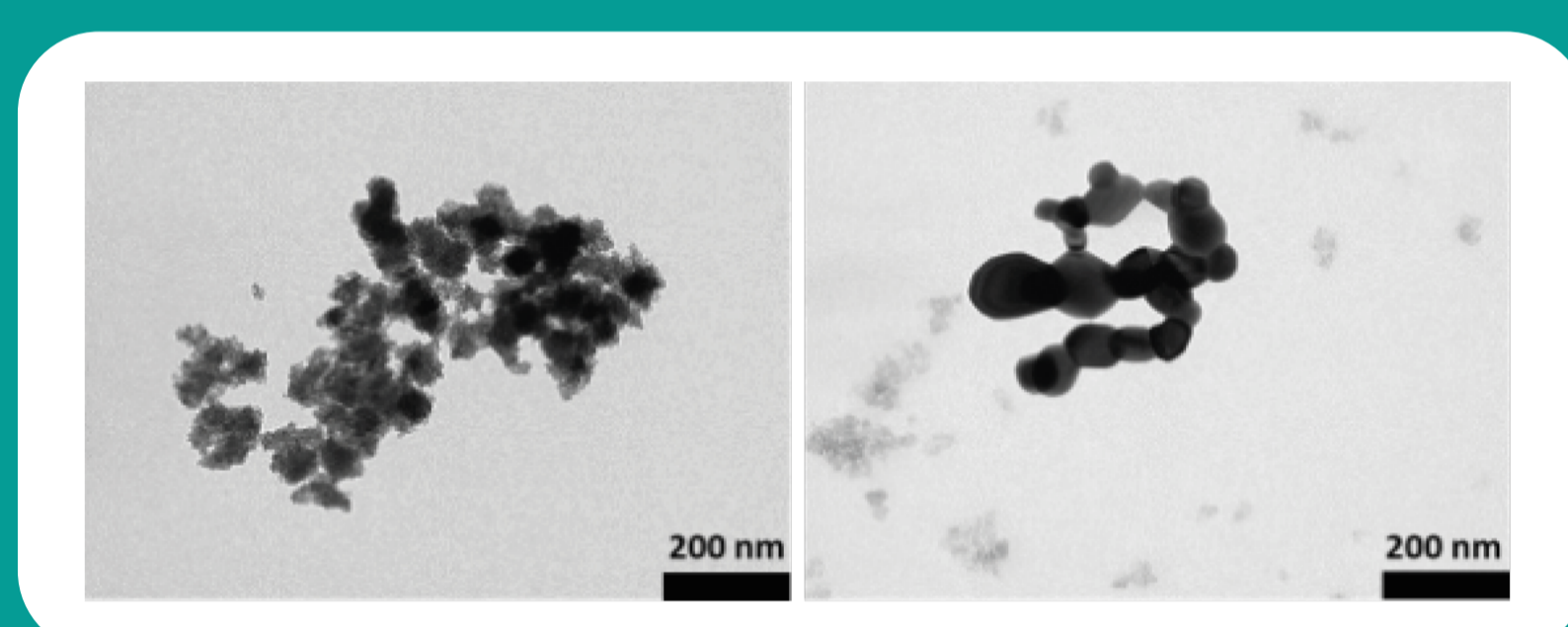


Figure 5
TEM images of ZrO₂:0.2%Ti⁴⁺ nanoparticles before (left) and after (right) the calcination step.

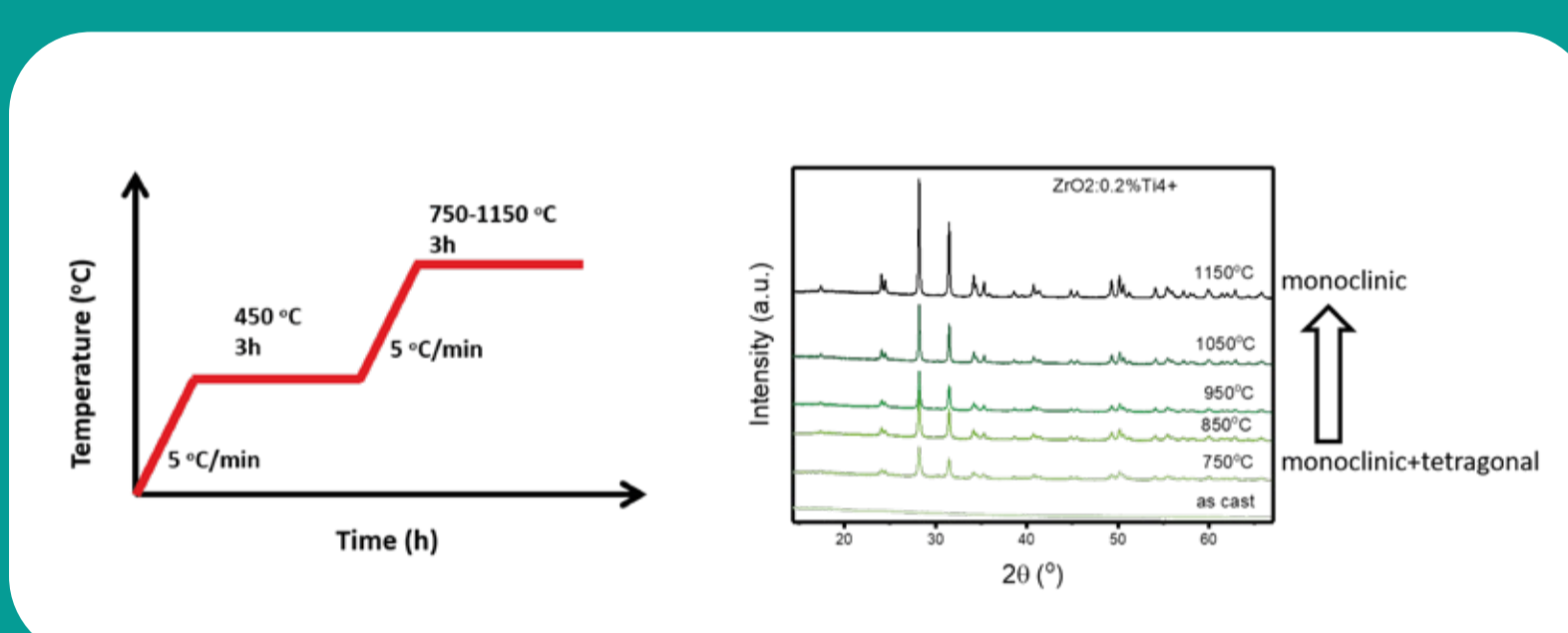


Figure 6
Program used for the calcination step (left) and the XRD analysis from the as-cast to 1150°C.

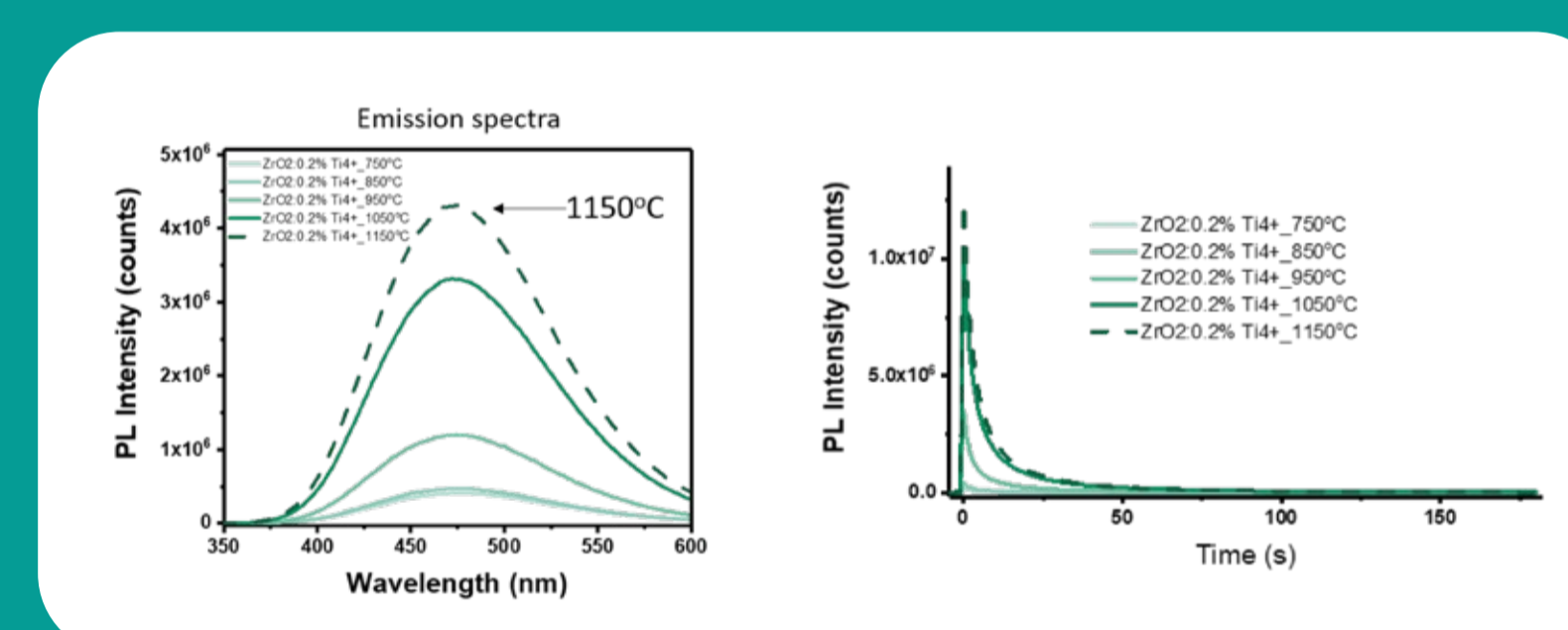


Figure 7
Program used for the calcination step (left) and the XRD analysis from the as-cast to 1150°C.

The material demonstrates outstanding stability, maintaining its emission intensity for over 1 hour under excitation with minimal changes.

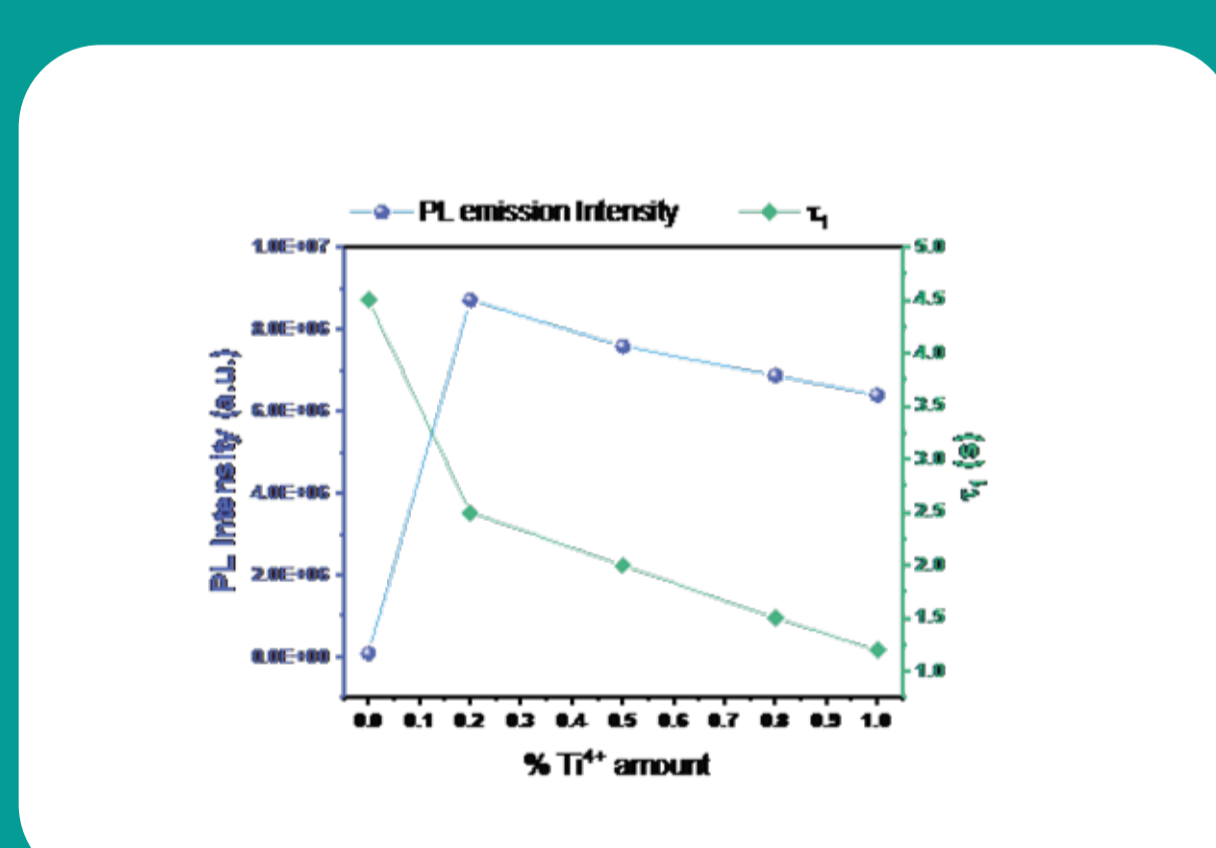


Figure 8
Luminescence properties of ZrO₂ doped with different amounts of Ti⁴⁺.

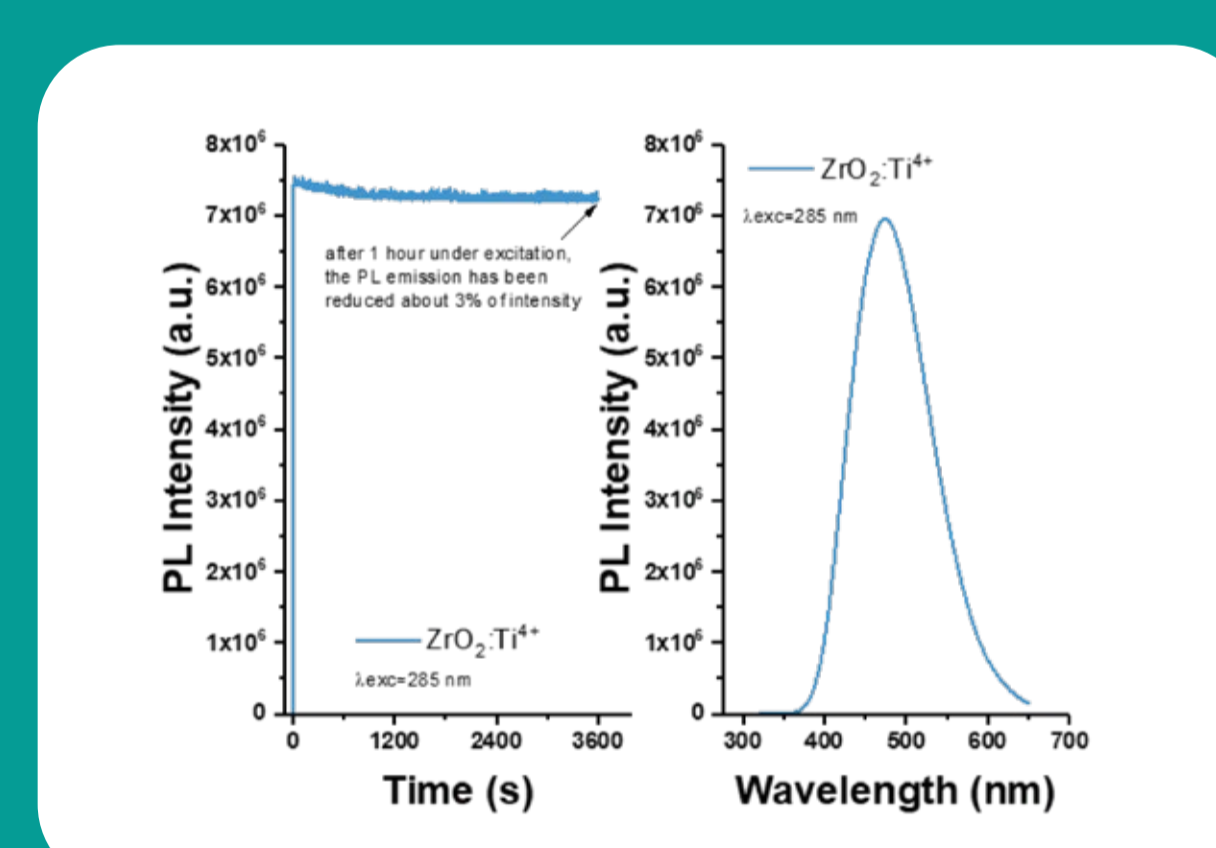


Figure 9
Emission stability of ZrO₂:Ti⁴⁺ nanoparticles over 1h under excitation at 285 nm.

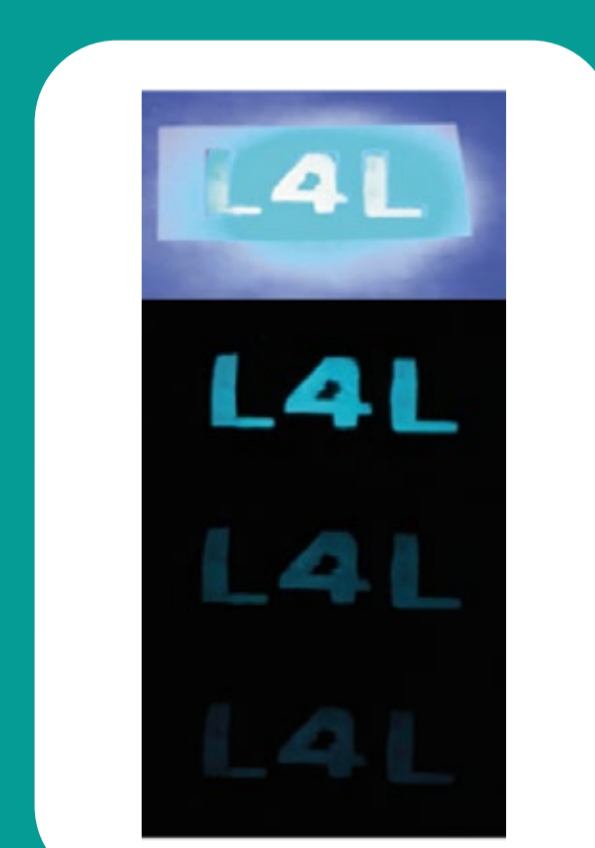
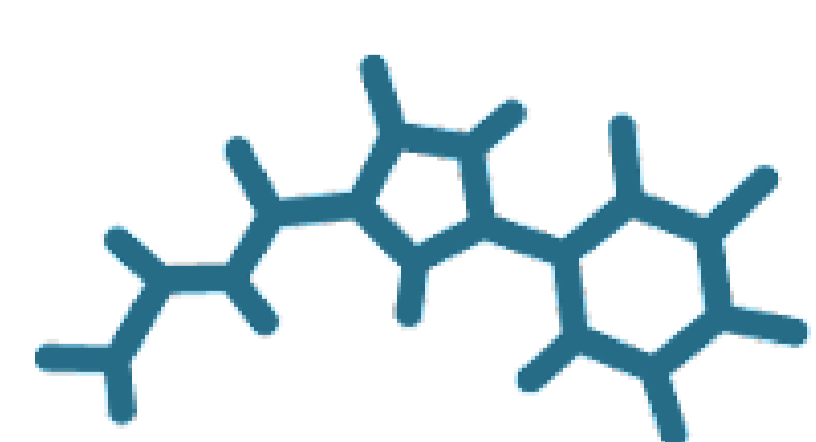


Figure 10
L4L project logo made of ZrO₂:Ti⁴⁺ nanoparticles showing the emission under excitation (first image on the top) and after 5, 10 and 15 seconds after stopping the excitation (persistent luminescence).

Conclusions

Various persistent luminescence materials were synthesized and thoroughly characterized, with the ZrO₂:0.2%Ti⁴⁺ composition emerging as the most suitable candidate for this application. Notably, this material has been shown to possess non-toxic properties, facile functionalization capabilities, and excellent emission properties, exhibiting persistent luminescence in the second-scale range at the desired wavelength.



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