RE-TiO_2 nanocomposites: design, synthesis and characteristics
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1. Objectives

The proposed project is aimed at the better understanding of excitation mechanism of lanthanides-doped TiO_2 and at the development of theoretical model to describe a relationship between electronic and surface properties of RE-TiO_2 with photocatalytic activity. According to Chemical Vision 2020 - Nanomaterials by Design – it is crucial to integrate modeling and simulation methods with experimental results, and to transform of the resulting information into knowledge, which is then applied in processing and manufacturing of structures with nanoscale features (e.g., size, architecture) that deliver unique functionality and utility for target applications. In the proposed project, the theoretical model - connecting band structure, selected surface properties (surface area, porosity, crystal structure, crystallite size, luminescence properties, surface defect, surface composition) of series RE-TiO_2 photocatalysts with photocatalytic activity - will be developed. Based on obtained model, final series of sample will be prepared to verify it (Figure 1). Thus, the proposed approach will allow to proceed in accordance with the principle "build-by-design".

Proposed approach based on following assumptions:

• Lanthanides due to the location of their energy bands have an effect on the photocatalytic activity of TiO_2 under visible and near-infrared (NIR) light irradiation.
• Carbon, which is present on the surface of the TiO_2 photocatalyst is responsible for luminescence quenching processes, which responsible for lower photocatalytic activity of TiO_2.
• Enhancement of luminescence properties of photocatalysts will enhance its photocatalytic activity,
• UV and vis-mediated photocatalytic activity of RE-TiO_2 could be predicted based on selected electronic and surface properties.

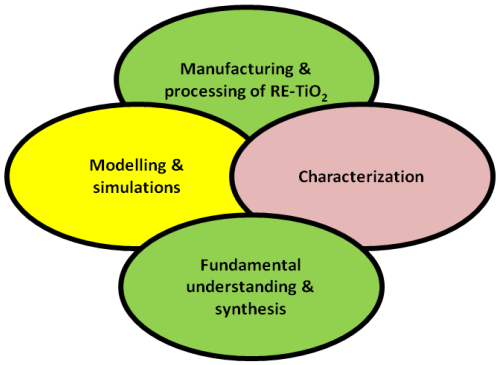

Figure 1. Main components of the proposed project

2. Significance

In recent years, environment friendly contaminant disposal methods and conversion method of organic and inorganic substances are intensively investigated. One of the available method for removing impurities from the aqueous phase and the gas is photocatalytic degradation in the presence of TiO_2 nanoparticles.
At present, the methods of photodegradation in the presence of TiO_2 and solar radiation are used for the purification of water streams, remove pollutants from wastewater and volatile substances from the atmosphere. In this method, in contrast to conventional methods we do not introduce additional chemicals during purification.
The major problem in its practical application is a wide band gap which requires a high energetic UV light for its excitation (e.g. the band gap of anatase form of titania is about 3.2 eV). Therefore, a lot of studies have been performed to develop a photocatalytic system which can be activated under visible light irradiation.
The proposed solution will allow the development of new efficient photocatalysts which allow the use of renewable energy source which is the solar radiation - even in areas where solar radiation has a lower intensity - the removal of volatile impurities from the atmosphere (through photodegradation of pollutants on surfaces coated modified TiO_2 or on the filters modified TiO_2) and to remove impurities from the aqueous phase (contaminated water and sewerage).
Rare metal doping of TiO_2 is a promising method to enhance activity under visible and NIR light due to up-conversion effect. According to available literature, up-conversion luminescence agents could transform the visible and NIR light into the ultraviolet light to satisfy the genuine requirements of TiO_2 photocatalysts. However, the activity of the described in the literature photocatalysts (rare metal doped-TiO_2) was mainly examined in dyes degradation process. The fact that dyes absorb light indicates that a photoreaction might be induced by light photoabsorption (dye sensitization) as well as by photoabsorption of a photocatalyst. Thus, dyes are not good model compounds for mechanism investigation. The simplified mechanism of TiO_2 excitation by up-conversion luminescence agent is presented in Figure 2.

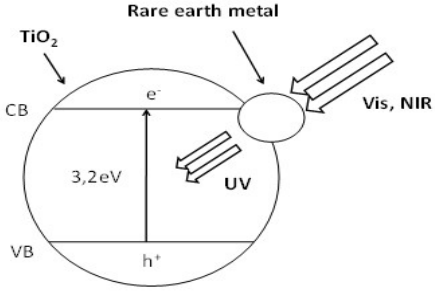

Figure 2. Simplified mechanism of TiO_2 excitation by up-conversion luminescence agent

One of the challenges in the field of heterogeneous photocatalysis is the development of new type of photoactive materials activated by low powered and low cost irradiation sources and to understand the mechanism of photocatalytic reaction in the presence of those materials. It is crucial to integrate modeling and simulation methods with experimental results, and to transform of the resulting information into knowledge, which is then applied in processing and manufacturing of structures with nanoscale features. Better understanding of the dependence of photocatalytic reaction efficiency on the irradiated wavelength will allow to design a

new photocatalytic systems based on the compatible photocatalyst and irradiation source. Future research would deal with visible light-activated TiO_2 functioning in the presence of solar irradiation. One of the most important challenge which faces titania-based catalysis is stable TiO_2 with predictable photoactivity in UV and visible light.

In this regard it is proposed to enhance the effectiveness of photodegradation by developing a new, stable photocatalysts (based on TiO_2) characterized by a high luminescence intensity and activity under the UV, Vis and NIR irradiation. A novel theoretical model - connecting band structure, selected surface of series RE-TiO_2 photocatalysts with photocatalytic activity - will be developed. Based on obtained model, final series of sample will be prepared to verify it.