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Daylight induced antibacterial activity of gadolinium oxide, samarium oxide and erbium oxide nanoparticles and their aquatic toxicity

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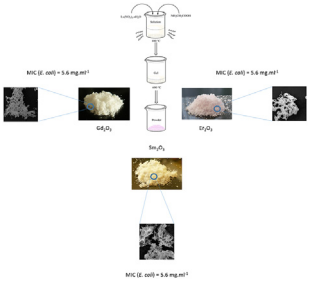
HIGHLIGHTS

- General inexpensive protocol of creation Lx_2O_3 nanoparticles was developed.
- Gd_2O_3 (10 nm), Sm_2O_3 (11 nm) and Er_2O_3 (10 nm) were successfully prepared.
- Antibacterial properties in the dark and in daylight were observed.
- Aquatic toxicity assay displayed that Er_2O_3 the most toxic from tested nanoparticles.

GRAPHICAL ABSTRACT



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ABSTRACT

The present article describes a method of the preparation of three dilanthanide trioxides (Lx_2O_3): gadolinium oxide (Gd_2O_3), samarium oxide (Sm_2O_3) and erbium oxide (Er_2O_3) in a shape of nanoparticles. Thermal decomposition of a transient complex formed *in situ* from $Lx(NO_3)_3 \cdot H_2O$ and glycine was studied using TG/DTA analysis. The resulting 10 (Gd_2O_3, Er_2O_3) to 11 nm (Sm_2O_3) nanoparticles grouped into 8 μm agglomerates were characterized by X-ray powder diffraction analysis, the particle size (PS) and particle size distribution (PSD) analysis. Morphology of the nanoparticles was examined by scanning and transmission electron microscopy. The antibacterial activity against four common human pathogens (*Staphylococcus aureus, Enterococcus faecalis, Escherichia coli, Pseudomonas aeruginosa*) was determined both in dark conditions and on daylight was investigated revealing a phototoxic phenomenon. The lowest determined MICs were as low as 5.6 mg ml^{-1} against *Escherichia coli* and *Pseudomonas aeruginosa*. Moreover, acute aquatic toxicity tests of prepared nanoparticles were driven revealing the moderate toxicities against *Desmodesmus subspicatus* peaking with EC_{50} = 0.47 g dm^{-3} (Er_2O_3 nanoparticles).

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1. Introduction

Material chemistry has witnessed a boom of nanomaterials in the portfolio of commonly used matters of interest in past two decades. The characteristic dimension of 1–100 nm at least in one of their characteristic directions defining the nanomaterials [1] often enriches the matter of typically metal [2–4], metal oxide [5,6], carbon [7], etc. with some unique physical [8–11], chemical [12], medicinal [13,14], gas detecting [15,16] and electromagnetic [17] properties compared to its bulk form. Transition metal oxides, especially in their nanomaterial forms, possess arguably unique photonic [18], (photo)catalytic [19] and antibacterial properties [20–24] which have been extensively studied along with their means of preparation [25,26] and toxicity [27–29]. The success of nano-formed transition metal oxides in various fields also encourages the studies of nanoforms of inner transition metal oxides, especially lanthanide oxides [30]. There are several clues of their potential already. Gadolinium oxide nanoparticles are getting to be applied as new contrast agents during magnetic resonance, unfortunately, with questions on their safety and possible toxicity yet to be replied [31]. Thermally stable samarium oxide nanoparticles are used in solar cells, infrared absorbing glasses, semiconductors and catalysts [32]. Erbium oxide nanomaterials have been studied as effective photoelectrochemical water splitting materials [33] or gas sensors [34].

Nanomaterials based on lanthanide oxides are usually obtained by thermal decomposition [35], spray hydrolysis [36] or sonochemical methods [37]. The most of these methods are time consuming and require an unusual laboratory equipment. Those facts along with the sluggish yields of aforementioned established procedures, compromise the application potential of these materials. Thus, low-cost and effective method of preparation of nano-shaped lanthanide oxides is needed as well.

The great potential, however, might be observed in combustion methods [38,39]. These methods, based on the combustion of suitable fuel and oxidant in presence of source of the inner transition metal, often create as a by-product the ash-like nanostructured product. The most convenient arrangement of these processes appears to be the presence of the oxidant in the inner transition metal precursor such as nitrate [40] or prechlorate anion and an amino acid as a fuel. The simplest system for those processes is the glycine-nitrate combustion which has already been successfully applied on the creation of cerium dioxide nanoparticles [41], gadolinium oxide nanoparticles [42], dysprosium oxide nanoparticles [43] and several other rare earth metal containing (nano)ceramic materials [44–46]. These methods appear to be more convenient in terms of applicability, temperature of the preparation and equipment requirements. Yet, there are a lot of mechanistic and chemical questions and problems still unanswered, which limits their broader application.

It has been recently multiply reported the exposure to nanoparticles of lanthanide oxides might have a negative effect on health due to the formation of reactive oxygen species leading to oxidative stress, inflammation, eventually resulting in the stress-induced cell death [47,48]. On the other hand, some other studies showed that cerium oxide nanoparticles bear antioxidant properties, which support cell survival under the conditions of oxidative stress [49]. Thus, cerium oxide nanoparticles can be also used as antioxidant for blocking the enzymatic activity [50]. In our best knowledge, there is still a lack of information about toxicity of lanthanide oxide-based nanomaterials and of studies dealing with an antibacterial activity of these nanomaterials.

The investigation of the mechanism(s) of creation of nanoparticles as well as their interaction with the biological systems has been our focus in a long term basis. Based on assembled facts on the inner transition metals, we have set our goal in the optimization and application of the simple stepwise glycine nitrate process for the inexpensive preparation of gadolinium oxide, samarium oxide and erbium oxide nanoparticles. The characterization of the gained materials includes, apart from the standard evaluation nanoparticles, also the investigations of their antibacterial activity (*Escherichia coli* and *Pseudomonas aeruginosa*) and acute aquatic toxicity to freshwater green algae *Desmodesmus subspicatus* and *Raphidocelis subcapitata*.

2. Experimental

2.1. Materials and methods

For all the solutions, if not determined otherwise, demineralized water from the column Demiwa 10 (Watek) was used. Lanthanide nitrates were purchased from Sigma Aldrich company in reagent grade quality and used as obtained. Glycine was purchased from Lachner in p. a. quality and used as obtained.

As the probe strains of pathogens *Staphylococcus aureus* 3953, *Enterococcus faecalis* 4224, *Escherichia coli* CCM 3954 and *Pseudomonas aeruginosa* 1960 acquired from the Czech Collection of Microorganisms (Czech Republic) were used.

For the acute aquatic toxicity the strains of *Desmodesmus subspicatus* and *Raphidocelis subcapitata* were purchased from Culture Collection of Authotropic Organisms (Institute of Botany of the Academy of Science of the Czech Republic).

Differential thermal analysis and thermogravimetric analysis (TG/DTA) were carried out by the method of simultaneous thermal analyzer STA 504 (TA Instruments). Each sample was gradually posed into corundum crucible and then to the analyzer. The compressed air with the flow rate of 5 $dm^3\ h^{-1}$ was used as a furnace atmosphere. Temperature program was set from ambient temperature to 373.15 K with heating rate 10 K min^{-1}. The rate of heating was decreased between 373.15 and 873.15 K–2 K min^{-1}.

X-ray powder diffraction analysis (XRD) was performed using the X-ray diffractometer Ultima IV Rigaku (Rigaku, Japan), operated at 40 kV and 40 mA with CuKα radiation (reflection mode, Bragg-Brentano arrangement, scintillation counter). The XRD patterns were recorded in the 10–70° 2θ range with a scanning rate of 2° per min. The samples were placed in a ground glass depression in the sample holder and flattened with a glass slide. X-ray beam was demarcated by 2/3° divergence, 10 mm divergent height limiting, 2/3° scattering and 0.6 mm receiving slits. Phase analysis was evaluated by database PDF-2 Release 2011. Graphics processing XRD patterns was made using OriginPro8. Gd_2O_3. Sm_2O_3 and Er_2O_3 reflections of the (222) planes were used to determine crystallite size using the Scherrer formula (1) [51],

$$L_c = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \quad (1)$$

where K is the factor of microstructure (K = 0.94), λ is the wavelength of radiation, β is the full-width at half-maximum (FWHM) and θ is the diffraction angle.

Scanning electron microscope MAIA3 GMU (TESCAN) an ultra-high resolution SEM with Schottky field emission cathode was used. Images were taken by using a combination of InBeam SE + Low-Energy BSE detector at 2.5 kV. Furthermore, the product morphology was also observed by scanning electron microscope Quanta FEG (FEI) and transmission electron microscope JEOL1200EX.

Particle size (PS) and particle size distribution (PSD) analyses were performed using diffraction laser analyzer HORIBA LA-950. For analyses the powder samples were diluted in 10 ml of