



# Rare earth ions doped ZnO: Synthesis, characterization and preliminary photoactivity assessment



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## ABSTRACT

This work reports the effect of doping zinc oxide with lanthanide ions on structural, EPR and UV visible properties. Bare and doped samples were synthesized using the simple and green hydrothermal process. Different rare earth ions (RE = La, Ce, Pr, Er and Yb) with 1% molar ratio RE/Zn were used. The samples have been studied using X Ray Diffraction, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and UV visible diffuse reflectance spectroscopy. Finally, electron paramagnetic resonance (EPR) spectroscopy, was used to assess the materials photoactivity under UV irradiation, both in solid state, to see the charge carriers' generation and in solution, evaluating the OH• radical formation using the DMPO (5,5-Dimethyl-1-Pyrroline-N-Oxide) spin trapping technique. The results suggest that the synthesized materials could be interesting systems for the photocatalytic abatement of emerging organic persistent pollutants in wastewater treatment plants.

## 1. Introduction

Recently, implementation of water remediation and re-use is gaining attention rapidly world-wide due to the water scarcity occurred as a result of climate change and poor water resource management (i.e. limited access to clean water resources and water demands exceed the available resources). Access to clean water is becoming an increasing problem in an expanding global economy and population countries [1]. Persistent organic pollutants and the new emerging pollutants are considered dangerous for living organisms due to their acute toxicity and bio-recalcitrant nature, in fact they are resistant to environment degradation and have been continuously released into the environment [2,3]. In particular, the biological process is usually ineffective because of a self-inhibitory effect on the microorganisms in the presence of these compounds [4]. For this reason, photocatalytic treatment represents an advanced oxidation technology able to remove organic pollutants thanks to the efficient degradation rate and high mineralization efficiency that leads to CO<sub>2</sub>, H<sub>2</sub>O, and other minerals as final products. Among various semiconductor materials, ZnO has received considerable scientific interest as an alternative to TiO<sub>2</sub> [5,6]. It was also reported by some of us that ZnO was more efficient than TiO<sub>2</sub> in photocatalytic degradation of some emerging pollutants in aqueous solution [7].

ZnO is considered as a benchmark catalyst due to its non-toxic nature, physical and chemical stability coupled with its low cost [8]. One major

drawback of existing technology is the low quantum efficiency of ZnO, which is due to very fast recombination of photogenerated electron-hole pairs. In order to improve the photocatalytic activity of ZnO, several modification methods have been developed. It has been reported that photocatalytic performance of semiconductors can be improved by doping with certain cations, which can act as electron trapping agent to decrease the electron-hole recombination rate [9–11]. The photocatalytic activity of ZnO can be significantly enhanced by doping with the lanthanide ions having 4f configuration, among them, cerium-doped ZnO nanomaterials exhibited versatile properties and much attention has been focused to explore them for possible applications in various technologies [12,13]. Doping RE ions into ZnO produces a significant improvement in the charge separation between photogenerated electrons and holes [14–16]. The efficiency of cerium-doped ZnO towards degradation of water pollutants and emerging contaminants is already well known: phenol, iodinated X ray contrast agents, namely iopamidol, iopromide and diatrizoate, emerging contaminants known to be scarcely abated in the wastewater treatment plants, and acesulfame K, an artificial sweetener, were efficiently abated [7,17]. The role in the photoactivity of the f orbitals, which in the case of cerium and lanthanum are empty and for the others lanthanides are partly filled, is still under debate. Moreover, the presence of lanthanide ions into the ZnO structure has never been demonstrated, thus the understanding of the role of the dopants in the host oxide is crucial.

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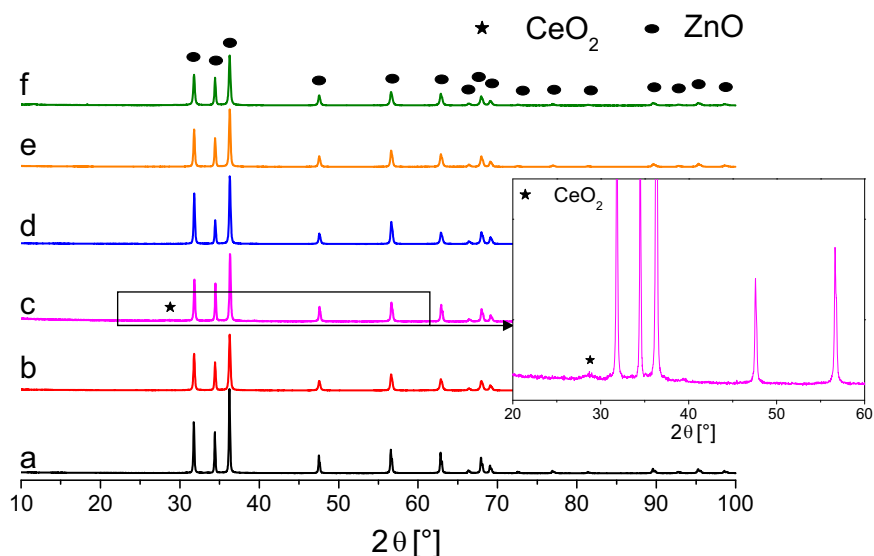


Fig. 1. XRD patterns of a) ZnO, b) ZnO-La, c) ZnO-Ce, d) ZnO-Pr, e) ZnO-Er, f) ZnO-Yb. Inset: enlargement of the ZnO-Ce pattern.

In this work different materials based on ZnO doped with a low amount of RE elements (RE = La, Ce, Pr, Er and Yb), aimed to develop new photocatalysts, were synthesized. Pure and doped ZnO with low RE loading (1% molar) were prepared via hydrothermal process, a simple and green way to obtain controlled nanostructures at relatively low temperatures. Compared with other techniques this method is fast, cheap and highly efficient. The precursors used are easily available on the market and the amount of rare earth compound employed is very low and does not affect dramatically the final price of the catalyst. The morphological and textural features, the crystal structure and optical properties of the synthesized materials were investigated and their photoactivity was assessed by EPR spectroscopy. The use of a spin probe molecule like DMPO (5,5-Dimethyl-1-Pyrroline-N-Oxide) allowed the evaluation of oxidant species present in solution.

## 2. Experimental

### 2.1. Sample preparation

All reactants employed in this work were purchased from Sigma-Aldrich (Milan Italy) and used without any further purification treatment. All the samples have been synthesized following hydrothermal synthesis. Bare ZnO sample was synthesized starting from a 1 M water solution of zinc nitrate. Then a 4 M NaOH solution was added dropwise until the pH was 11. Finally, the solution was transferred into a PTFE-lined stainless steel 100 mL autoclave (filling 70%), and treated at 175 °C for 15 h. The product was centrifuged, washed three times and dried at 70 °C overnight. The doped samples (RE=Ce, La, Er, Yb, Pr, molar concentration 1%) were prepared adding to the starting solution the RE precursor salts in stoichiometric amount ( $\text{RE}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ,  $x = 5$  or 6 depending on the RE). Hereafter the doped samples will be labelled as ZnO-RE.

### 2.2. Characterization techniques

X-rays powder diffraction (XRPD) patterns were recorded using a PANalytical PW3040/60 X'Pert PRO MPD, Lissone (MI) Italy (45 kV, 40 mA) with a copper K $\alpha$  radiation source (0.15418 nm). Samples were scanned continuously in the  $2\theta$  range between 10° and 100°. The X'Pert High-Score software was used to identify the mineral phases present in the samples. A Rietveld refinement was performed on the acquired patterns using the MAUD 2.2 software [18].

The morphology of the materials was studied by scanning electron

microscopy (SEM) using a JEOL microscope (JSM-6510-LV, JEOL, Tokyo, Japan) and by a transmission electron microscopy (TEM) using a Jeol JEM 3010 (300 kV) microscope.

The UV-Vis absorption spectra were recorded using a Varian Cary 5000 spectrophotometer, coupled with an integration sphere for diffuse reflectance studies (DRS), using a Carywin-UV/scan software. A sample of PTFE with 100% reflectance was used as reference.

Electron Paramagnetic Resonance Spectroscopy (EPR) was employed, using an X-band CW-EPR Bruker EMX spectrometer equipped with a cylindrical cavity operating at 100 kHz field modulation. The effect of UV light on EPR spectra was investigated using a 1600 W Xenon lamp (Oriol Instruments) equipped with an IR water filter. The samples were treated before the measurement as follows: first, the sample was heated under vacuum at 300 °C for 30 min, then heated under oxygen pressure (50 mbar) at 500 °C for 1 h. The formation of OH $\cdot$  radical species upon irradiation (500 W, Xenon lamp, Oriol Instruments) was monitored by EPR spin trapping technique using a Miniscope 100 spectrometer from Magnettech and using DMPO (5,5-dimethyl-1-pyrroline-N-oxide) as spin trapping agent.

## 3. Results and discussion

### 3.1. Structural, morphological and spectroscopic characterization

XRPD patterns of the samples investigated in this work are shown in Fig. 1. The pattern of bare ZnO shows peaks corresponding to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2) and (2 0 1) planes of the wurtzite hexagonal phase of ZnO [19].

The introduction of dopants does not bring relevant modifications in the diffraction patterns of ZnO with the exception of the sample ZnO-Ce in which we observed the formation of a tiny amount of the CeO $_2$  crystalline phase (see Fig. 1, inset). On the XRD patterns we performed a Rietveld refinement using the MAUD software [18]. Table 1 lists the obtained average crystallite size and the lattice parameters for all the detected phases. Moreover, the difference in the lattice parameters ( $a$  and  $c$ ) due to the addition of lanthanides ions inside the ZnO structure is also evidenced ( $\Delta a/c = a/c(\text{ZnO-RE}) - a/c(\text{ZnO})$ ). The lattice parameters of the ZnO phase are slightly influenced by the introduction of lanthanides, bringing to a limited contraction of the unit cell for all the doped samples respect to that of pure ZnO. The average crystallite size of bare zinc oxide is quite large ( $d = 256$  nm), the insertion of RE ions in the structure causes in general a decrease in the average crystallite size, the sample ZnO-Yb being the

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