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## Photoactivity properties of ZnO doped with cerium ions: An EPR study

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Abstract

In the present study, we investigated the effect of cerium doping in zinc oxide matrix, used as photoactive material. Cerium ions into the matrix of ZnO can act like a “trap” for the electrons, lowering the e<sup>-</sup>/h<sup>+</sup> recombination rate and so increasing the photocatalytic efficiency of the ZnO.

We synthesized doped samples using a simple precipitation route. The amount of dopant used was, 1 and 10% molar. The samples have been studied via X Ray Diffraction measurements for the structural characterization; UV visible diffuse reflectance was used for the optical analysis; Branauer-Emmett-Teller (BET) model for the measurement of the surface area. Finally, the samples have been analysed via electron paramagnetic resonance (EPR) spectroscopy for the electronic characterization and for testing their photoactivity. The spin trapping technique was also use to measure the amount of stable radical adducts formed via reaction of OH• radicals with molecules of the DMPO (5,5-dimethyl-1-pyrroline-N-oxide) spin probe.

## 1. Introduction

Nanostructured transition metal oxides have attracted considerable interest in many areas of chemistry, physics, and materials science. Compared to other metal oxide nanomaterials, zinc oxide (ZnO) displays novel nanostructures. ZnO could be considered as an alternative to TiO<sub>2</sub> in photo-catalysis[1], optics and solar cells due to its abundance[2, 3], high physical and chemical stability, low cost, non-toxicity, high electron mobility, low crystallization temperature and simple synthesis. It has a wide band gap (3.37 eV) and a large exciton binding energy (60 meV). [4]

ZnO exhibits the hexagonal (wurtzite) crystal structure with  $a = 3.25 \text{ \AA}$  and  $c = 5.12 \text{ \AA}$ . The Zn atoms are tetrahedrally coordinated to four O atoms, where the Zn d-electrons hybridize with the O p-electrons. Layers occupied by zinc atoms alternate with layers occupied by oxygen atoms.

The optical properties of ZnO studied using photoluminescence, photoconductivity, and absorption spectroscopies, reflect the intrinsic direct bandgap, a strongly-bound exciton state, and gap states due to point defects. The intrinsic defect levels that lead to n-type doping in pristine ZnO lay approximately 0.01–0.05 eV below the conduction band and have been attributed to interstitial Zinc atoms (Zn<sub>i</sub>), oxygen vacancies (VO), or trapped atomic hydrogen introduced during growth. [5] As mentioned before zinc oxide is playing an important role in heterogeneous photocatalysis. This oxide in fact has suitable electrochemical potentials in particular for oxidation. Its main limitation is the propensity for photocorrosion that is higher than that of titanium dioxide. Nanoscale ZnO materials showed higher photocatalytic activity than the bulk materials due to their larger surface area and larger number of active sites. Several authors report that metal ion doping can modify the surface properties of ZnO, hinder the recombination of photo-generated electron-hole pairs and increases the amount of the active sites. In particular the photocatalytic activity of ZnO can be significantly enhanced by doping with lanthanide ions having 4f<sup>x</sup> configuration.[6] Lanthanides are known for their ability in trapping the electrons. This phenomenon can effectively reduce the recombination of photo-generated electron-hole pairs resulting in an improved photo-oxidation ability of the system (driven by reactive holes). Various research groups reported that lanthanides doped ZnO exhibit higher photocatalytic activity than pure ZnO for methyl orange degradation under UV light due to the efficient separation of the photo-generated carriers [7, 8]. S. Anandan et al. found that the photocatalytic activity of La-doped ZnO is much higher than pure ZnO and TiO<sub>2</sub>. Moreover, La-doped ZnO photo-catalysts require shorter irradiation time for complete mineralization than pure ZnO and TiO<sub>2</sub> [13,14]. The enhancement of the photocatalytic activity of the doped samples should therefore be due to the electron transfer at the interfaces between different crystalline structures [9, 10, 12]. In particular the (Ce<sup>3+</sup>/Ce<sup>4+</sup>) redox pair could act as an electron scavenger that traps the bulk electrons in semiconductor modifying the band gap [15].

In the recent past an additional role of cerium doping has been put into evidence by our group, namely the capability to sensitize a wide band oxide to the visible light. This has been observed in the case of Ce doped zirconium dioxide a system that, in spite of the ZrO<sub>2</sub> band gap of about 5 eV becomes visible light sensitive with the introduction of Ce ions [16]. Even if, at variance with the system here described, in the case of Ce/ZrO<sub>2</sub> the doping Ce<sup>4+</sup> ions are diluted into the oxide matrix, it is worth of exploring if some activity of cerium in promoting visible light sensitisation is obtained also in the case of ZnO. This problem has been already considered in the past, and several authors reported experimental results related to ZnO doped with cerium or more generally rare earth ions. In structural terms, due to both the remarkable difference in size of the Zn<sup>2+</sup> (0.074 nm) and Ce<sup>4+</sup> (0.101 nm) ions and especially

the different crystal structure of the two oxides, the insertion of cerium ions in the lattice of ZnO is highly improbable [9-11]. Moreover data reported are very heterogeneous, some authors indicating that cerium ions enter in the ZnO phase influencing the lattice parameters of the oxide [17] some others pointing to the segregation of a cerium oxide phase influencing the particle size and particle growth of the ZnO matrix [7]; in general the CeO<sub>2</sub>-ZnO system remains poorly understood as well as its photoactivity properties.

On the basis of the above concerns, this work reports on the features of Ce doped ZnO nanoparticles (CZ) with two different cerium loading (1 and 10% molar) prepared by a simple chemical precipitation route without any organic solvent or surfactant. The prepared ZnO-based materials were characterized by different techniques and their photo-activity in the visible range was tested monitoring the formation of OH reactive radicals under polychromatic irradiation with  $\lambda > 420\text{nm}$ . To measure the amount of photo formed radicals the spin trapping technique was used based on the detection, by Electron Paramagnetic Resonance (EPR), of stable radical adducts formed via reaction of OH• radicals with molecules of the DMPO spin probe.

## 2. Experimental

### 2.1 Samples preparation

Bare ZnO and Cerium doped ZnO were prepared via a precipitation method, that allowed to obtain a larger surface area than that reported for classical synthesis of ZnO [18]. The undoped ZnO was prepared dissolving 2.2g of Zn(CH<sub>3</sub>COO)<sub>2</sub>•2H<sub>2</sub>O (Sigma Aldrich 90.0%) into 160 ml of bi-distilled water and 80 ml of ethanol: the solution was maintained under magnetic stirring for 1 hour at room temperature. Then, 160 ml of a NaOH aqueous solution 1M was added drop by drop, allowing the precipitation. Finally, the solution was kept stationary for 48 hours. After that, the precipitate was separated via filtration, washed and dried at 70°C for 12 hours. The final product was obtained after calcination at 300°C for 30 hours in air.

Two kinds of doped materials with different Ce loading (1% and 10% molar percentage respectively) were prepared dissolving 0.038 g and 0.38 g of CeCl<sub>3</sub>•7H<sub>2</sub>O (Sigma Aldrich 99.99%) respectively in the mother solution.

The three materials obtained as described before were labelled ZnO, CZ1 and CZ10, respectively.

### 2.2 Samples characterization

The prepared samples were investigated via X-ray diffraction (XRD), N<sub>2</sub> adsorption to evaluate BET surface area, diffuse reflectance UV-Vis spectroscopy and electron paramagnetic resonance (EPR) spectroscopy.

Powder X-rays diffraction (XRD) patterns of the synthesized samples were recorded with a PANalytical PW3040/60 X'Pert PRO MPD using a copper K $\alpha$  radiation source (0.154056 nm). The signals were scanned continuously in the 2 $\theta$  ranges between 20° and 80°. In order to identify the phases presented in the samples, the X'Pert High-Score software was employed. The Scherrer equation has been used to evaluate the crystallite size of the existing phases.

$$D = 0.9\lambda / \Delta \cos\theta$$

Where D is the average crystallites size (in nm),  $\lambda$  the wavelength of the radiation,  $\Delta$  is the full width of half maxima and  $\theta$  is the half diffraction angle.

The specific surface area measurements were carried out on a Micromeritics ASAP 2020 using the Brunauer-Emmett-Teller (BET) model on the N<sub>2</sub> adsorption measurement. Prior to the adsorption run, all the samples were outgassed at 573 K for two hours.

The UV-Vis absorption spectra were recorded using a Varian Cary 5 spectrometer, equipped with an integration sphere for diffuse reflectance studies, using a Carywin-UV/scan software. A sample of Teflon with 100% reflectance was used as reference.

The sample optical band gap energies were calculated taking into account that the energy dependence of the absorption coefficient ( $\alpha$ ) for semiconductors in the region near the absorption edge is given by:

$$\alpha \propto (h\nu - E_{bg})^{\eta} / h\nu \quad (\alpha h\nu)^{1/\eta} \propto (h\nu - E_{bg})$$

Where  $h\nu$  is the energy of the incident photon and  $E_{bg}$  is the optical absorption energy.  $\eta$  depends on the type of optical transition, in crystalline semiconductors is 1/2 (direct-allowed), 3/2 (direct-forbidden), 2 (indirect-allowed), and 3 (indirect-forbidden). As far as ZnO is concerned, this oxide shows a direct-allowed optical transition, with a value of 1/2 for  $\eta$ . Finally, since the scattering coefficient weakly depends on energy and  $F(R_{\infty})$  can be assumed proportional to the absorption coefficient within the narrow range of energy containing the absorption edge feature.

$$F(R_{\infty}) \propto (h\nu - E_{bg})^{\eta} / h\nu \quad [F(R_{\infty}) h\nu]^{1/\eta} \propto (h\nu - E_{bg})$$

The plot  $(F(R_{\infty}) * h\nu)^{1/\eta}$  vs  $h\nu$  can be thus used to determine the absorption edge energies and the energy gaps.

X-band continuous wave (CW) EPR spectra of the solids in various conditions have been recorded on a Bruker EMX spectrometer equipped with a cylindrical cavity and operating at a 100 kHz field modulation. The measurements were carried out at the liquid nitrogen temperature (77 K) in quartz cells that can be connected to a conventional high-vacuum apparatus (residual pressure  $<10^{-4}$  mbar). In order to investigate the redox behaviour of the materials a batch of the samples was thermally annealed at 570 K for one hour under vacuum condition and then analysed via EPR spectroscopy. The analysis of the photo-activity of the system was performed irradiating a suspension of the samples with a 1000 W Xenon lamp (Oriol instruments) equipped with a IR water filter. The formation of OH radical species upon irradiation was monitored by the EPR spin trapping technique using a Miniscope 100 spectrometer from Magnetech and using DMPO (5,5-dimethyl-1-pyrroline-N-oxide, Alexis Biochemicals, San Diego, CA) as spin trapping agent.

### 3. Results and discussion

#### 3.1. Materials characterization

Figure 1 shows the X-ray diffraction patterns of the three samples prepared in this work. All the samples show the peaks typical of the hexagonal wurtzite phase of ZnO (00-036-1451 ICDD pattern). Ce doping leads to the formation of additional peaks corresponding to cubic ceria. In particular, the peak at  $2\theta = 28.6^\circ$  corresponds to the (111) planes (00-034-0394 ICDD pattern) [19]. The ZnO wurtzite phase is not influenced by the introduction of Ce, but a new phase corresponding to CeO<sub>2</sub> is observed. In the case of higher doping level, for the sample CZ10 the presence of CeO<sub>2</sub> is clearly evident but even in the sample with 1% of dopant (CZ1) it can be evaluated. Nevertheless, the presence of few Ce ions trapped into the lattice structure cannot be completely excluded. Table 1 reports the average crystallite values obtained using the Scherrer equation and the specific surface areas measured by the BET method. The ZnO crystallites are quite small, but the CeO<sub>2</sub> crystallites are significantly smaller (about 4 nm). In agreement with the lower crystallite size, the doped materials also show a higher surface area than the bare one.

Figure 1: XRD patterns of (a) ZnO, (b) CZ1, (c) CZ10.

Table 1: Average crystallite size (d) obtained for the two phases from Scherrer analysis, BET surface area (SSABET) and energy gap (Eg) calculated with the Tauc plot

Sample	d ZnO (nm)	d CeO <sub>2</sub> (nm)	SSABET (m <sup>2</sup> g <sup>-1</sup> )	Eg (eV)
ZnO	39±3	-	20±0.0535	3.278
CZ1	27±8	4.3±2	31±0.0644	3.273
CZ10	26±10	2.6±1	54±1.1090	3.256

We investigated the electronic structure of the materials by means of Diffuse Reflectance Spectroscopy (DRS). Figure 2 shows the Kubelka-Munk transformed diffuse reflectance spectra (which are proportional to the absorbance) obtained for bare and doped samples. The spectra are dominated by the valence band (VB) – conduction band (CB) transition occurring at about 370 nm, typical of the ZnO phase. We calculated the energy gap (Eg) value for all samples using the Tauc plot. Energy gap values have been calculated by linearization of the plot reporting  $(\alpha h\nu)^2$  vs  $h\nu$  typical of direct band gap transitions [20] for ZnO and doped materials. The calculated Eg values for ZnO, CZ1 and CZ10 are 3.278, 3.273, 3.256 respectively and 2.9 eV for CeO<sub>2</sub> (table 1). The energy gap calculated for the three samples are very close one to each other, showing that doping did not cause a significant change in the electronic properties of the main ZnO matrix. The effect related to Ce doping is observed in terms of the onset of an optical absorption in the visible region (roughly between 400 nm and 470 nm) which corresponds to the absorption shown by bare CeO<sub>2</sub> in the same region (Fig. 2d), and which is proportional to the Ce loading.

Figure 2: Absorbance (Kubelka-Munk transformed diffuse reflectance) spectra of (a) ZnO, (b) CZ1, (c) CZ10, (d) CeO<sub>2</sub>

The bare and doped ZnO powders display EPR spectra characterized by a slightly asymmetric line with  $g_{av} = 1.96$  (Fig. 3a). This signal, widely reported in the literature, [21] is always present in native ZnO and has been assigned to shallow donor impurities [22]. No sign of any hyperfine interaction is detectable for this signal that is also present in doped materials but with a lower intensity. In the case of pure ZnO the intensity of this signal is quite high while for the CZ1 sample seems to disappear. The presence of Ce in the structure or at the interface of ZnO crystallites plays a crucial role in trapping electrons that, if free, could reduce the Zn<sup>2+</sup> ions to Zn<sup>+</sup>. This behaviour is more evident in the case of low Ce concentration while when the amount of Cerium is higher we observed clearly the formation of cerium oxide and consequently, a different process is observed and the signal at  $g=1.96$  increases again.

Figure 3. EPR spectra of as prepared samples a) ZnO, b) CZ1, c) CZ10

Furthermore, another non symmetric signal centred at about  $g=2.000$  is also present in all the spectra. It has been assigned to a hole defect generated during the synthesis process. To compare the redox behaviour of the materials a reducing thermal annealing under vacuum at 570K for 1 hour was performed on the samples. When the oxygen partial pressure in the atmosphere over the solid is decreased even at moderate temperature, ZnO loses oxygen from the lattice. This causes the simultaneous formation of oxygen vacancies and excess electrons in the reduced solid according to the following equation:



where the oxygen vacancy is indicated using the Kröger and Vink notation and is usually thought to be empty as excess electrons are stabilized under the form of paramagnetic interstitial  $Zn^{i+}$  ions. [23] The three samples behave differently when submitted to this treatment. The sample CZ1 only seems to be affected by the reduction treatment, in particular the signal centred at  $g = 1.96$  increases its intensity of more than one order of magnitude, on the contrary the same signal decreases in bare ZnO and in CZ10. In this case the presence of Cerium (only at low percentage) in the sample increases dramatically the reducibility of the ZnO matrix, and for this reason the intensity of the signal at  $g=1.96$  is ten times higher in comparison to the same signal in the bare ZnO. Again when the concentration of cerium is higher (10% molar) the behaviour is different, the formation of ceria seems to create a competitive interaction with the bare ZnO. Defects in the region of  $g = 2.00$ , generally assigned to holes, are not affected by the reduction process.

Figure 4. EPR spectra of samples annealed under vacuum a) ZnO, b) CZ1, c) CZ10  
 Contacting reduced samples with molecular oxygen an electron transfer from the solid to the oxygen molecule is observed with the formation of a new paramagnetic species assignable to superoxide radical anions,  $O_2^-$ . The computer simulations of the superoxide signals are also included in Figure 5 and the related spectral parameters are reported in Table 2. The intensity of the spectra related to ZnO and CZ1 is one order of magnitude lower than that of CZ10. For this reason, panel B reports a magnification of the two less intense spectra with the corresponding simulation. The  $g_{zz}$  component (the z direction corresponds to the intermolecular axis) characterizes the superoxide signal. In the case of ZnO the value is  $g_{zz} = 2.051$  (Fig. 5a', a'sim) and as already reported elsewhere is typical of  $O_2^-$  adsorbed on  $Zn^{2+}$  ions. [26] Spectra b and c, related to the sample containing respectively 1% and 10% of cerium, seem to be more complex. The chemistry of superoxide adsorbed on ceria has been thoroughly described in a paper by Conesa and co-workers [25] who specifically adopted this reactivity as a tool to investigate the level of defects of the surface of the oxide. It is well known that bare  $CeO_2$  easily loses and reincorporates oxygen under reductive and oxidative conditions respectively. This redox cycle occurs in the conditions of catalytic processes. The spectrum related to CZ10 (Fig. 5c) shows the well-known [26] typical features of superoxide ions at the surface of  $CeO_2$ . The computer simulations reported in Fig. 5csim have been performed using the following values for the g tensor elements:  $g_{zz} = 2.036$ ,  $g_{yy} = g_{xx} = 2.011$  (Table 2). The value of the high field component is quite anomalous being  $g_{xx} = 2.011$ , instead of having the free spin value ( $g_e = 2.0023$ ) as expected in terms of the ionic model of adsorbed superoxide [24],  $g_{xx}$  is very close to  $g_{yy}$  producing an unresolved perpendicular line. The anomalous value of  $g_{xx}$  shown by superoxide ions on cerium dioxide has already been discussed elsewhere [27] in terms of a model involving some degree of covalence in the interaction of adsorbed oxygen with the 4f cerium orbitals and causing deviations from the purely ionic model. The redox chemistry of the system containing 10% of cerium oxide seems thus dominated by the contribution of the latter. The spectrum in Fig. 5b (CZ1) is more complex and can be interpreted in terms of the superposition of the two spectra in Fig 5a and 5c thus indicating an intermediate behaviour of the low Ce loading material. The two species ( $O_2^-$  on  $Zn^{2+}$  and  $O_2^-$  on  $Ce^{4+}$ ) are present in nearby equivalent amount.

Figure 5. EPR spectra of superoxide species on Panel A: a) ZnO, b) CZ1, c) CZ10. Panel B is a magnification of ZnO and CZ1 spectra with their computer simulation.

Table 2: EPR parameters (g values) of superoxide species for all the samples

Sample	Abundance	gzz	gyy	gxx	ref
ZnO	1	2.0506±0.0001	2.0092±0.0001	2.0027±0.0001	This work
CZ1	0.51	2.0531±0.0001	2.0089±0.0001	2.0026±0.0001	This work
	0.48	2.0365±0.0001	2.0116±0.0001	2.0116±0.0001	
CZ10	1	2.0365±0.0001	2.0116±0.0001	2.0112±0.0001	This work
CeO <sub>2</sub>	1	2.030	2.010	2.010	[27]

### 3.2 Photoactivity and photochemical properties

The potential photo-activity of the materials was tested irradiating an aqueous suspension of the various solids with the polychromatic light emitted by a Xe lamp bearing a cut off filter at 420nm and using DMPO (5,5-dimethyl-1-pyrroline-N-oxide) as spin trapping agent to detect the formation of hydroxyl radicals (OH•) in solution. The DMPO molecule (diamagnetic) forms a stable paramagnetic adduct with OH radicals (DMPO/OH•), detectable by the EPR technique [28]. The hydroxyl radicals are responsible for the oxidative degradation of organic molecules in photocatalytic reactions, and they are formed under irradiation according to the following process:



The aqueous suspension of pristine ZnO, as expected, does not form an appreciable amount of OH radicals under visible irradiation while doped samples are active. Figure 6 (panel A) reports the classic four-lines EPR spectra of the DMPO/OH• adduct, as observed after 60 minutes of irradiation. This time roughly corresponding to the maximum intensity reached by the EPR spectra, and consequently to the higher amount of hydroxyl radicals generated. Panel B reports the integrated values of the EPR spectra (which are proportional to the radical concentration present in solution) as a function of the irradiation time. Both doped samples are photoactive under visible light and the production of OH radical reaches its maximum value between 30 min and 60 min. In particular, the activity is proportional to the Ce loading and the CZ10 sample clearly results more active if compared to the CZ1 one.

Figure 6. Panel A: EPR spectra of the DMPO/OH• adduct produced by irradiation of an aqueous suspension of the three samples ZnO, CZ1 and CZ10 with visible/NIR light ( $\lambda > 420\text{nm}$ ) in 60 minutes; Panel B: Integrated intensities of the EPR spectra as a function of irradiation time.

### Conclusions

Zinc oxide and cerium dioxide have no or little propensity to form solid solutions. When prepared by co-precipitation from a solutions containing Zn and Ce ions, a solid with two independent phases of the two oxides is formed as indicated by XRD. The optical properties of the mixed systems (with Zn:Ce molar ratio of 0.01:1 and 0.1:1) are those of ZnO (band gap around 3.2-3.3 eV) with the onset of a broad absorption from 370nm to 450 nm due to the presence of CeO<sub>2</sub> phase. The latter phase decorates the surface of ZnO as indicated by a clear role of cerium in the surface chemistry of the mixed systems (Fig.5). Reductive annealing of the solid and successive contact with oxygen in fact lead to the formation of superoxide anions that are exclusively adsorbed on Ce<sup>4+</sup> surface ions (high Ce loading sample, CZ10) or shared by Ce<sup>4+</sup> and Zn<sup>2+</sup> surface sites (low Ce loading, CZ1). The interaction between the two phases however produces an interesting photochemical effect: the presence of cerium sensitizes the system to visible light. Irradiation, in fact, generates electron-hole pairs and the hole form, reactive OH• radicals detected by spin trapping EPR. The mixed systems have

therefore a potential photocatalytic activity under visible light. The detailed mechanism of photo-activation is, at the moment, under investigation in our laboratory. The presence of cerium brings about absorption of visible photons (Fig. 2) but probably also contributes to the described photochemical effect subtracting part of the photo-generated electrons using  $Ce^{4+}/Ce^{3+}$  pairs, thus limiting the effect of electron-hole recombination that is detrimental to photo-activity.

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