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PREDICTION OF THE ANTIOXIDANT CHARACTER BY USING PHOTOCATALYTIC ACTIVITY OF DIFFERENTLY SHAPED CERIUM-OXIDE NANOPARTICLES

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ABSTRACT. Injury is an everyday risk in our lives, but some of us could have several wound healing problems, originating from additional pathologies (diabetes, cancer, and vitamin defects). As a solution, some metal-based nanomaterials, such as cerium-oxide (CeO_2) could be applied, which could help the regeneration. The CeO_2 nanomaterials need to have antioxidant character in order to be used in wound healing. Besides the wide use of CeO_2 particles in the biological field, it could be also utilized as a catalyst. This study compares these two applications, analyzing the photocatalytic activity of differently shaped CeO_2 nanoparticles and their possible antioxidant character.

Keywords: *photocatalytic activity, morphology, cerium-oxide, nanomaterial, predicted antioxidant character*

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INTRODUCTION

Cerium(IV)-oxide (CeO_2) is receiving a lot of attention in research today. But the question is why does it attract attention? What makes it special from many other metal-based nanomaterials? First, cerium is a metal from lanthanide serial and can switch its oxidation state depending on the environment (Ce^{3+} to Ce^{4+}) [1]. Second, it has two different oxides: (i) cubic–type structure of CeO_2 and (ii) hexagonal A–type structure of Ce_2O_3 [2]. CeO_2 is a much more stable form, which can be involved in catalytic [3], sensor [4], and biological applications [5]. The nanoparticles of CeO_2 (NP-CeO_2) have several unrivalled properties, such as antibacterial, antioxidant, antifungal, anti-inflammatory, angiogenic, anti-apoptotic, and oxygen storage capacity [5,6]. Even though the above-mentioned properties cannot be ignored for some areas of application, it is important to note that the applications in which CeO_2 is used, are greatly influenced by its shape, size, and surface defects that appear on its surface. Thus, the research attention turned to optimizing a synthesis method of NP-CeO_2. NP-CeO_2 could be synthesized with various synthesis methods, such as hydrothermal, precipitation, microwave-assisted, green synthesis, microemulsion, oxidation, and sonochemical [1]. The application of NP-CeO_2 in biological fields (such as cardiovascular, anti-diabetic, photoreceptor protection, wound healing, and biosensor [7]) is not surprising regarding the mentioned characters.

Wound healing has four different stages: hemostasis, inflammation, proliferation, and remodelling [8]. Several studies showed that in the last three stages of wound healing CeO_2 was involved, but only a few articles focused on hemostatic application [5]. To be used in the stage of hemostasis it needs to have several important characters. First, it needs to be stable, which being a metal oxide is not questionable. Second, it needs to have an antioxidant character and third, it needs to be an angiogenic character.

CeO_2 was used as a catalyst in several articles and industries [3], and therefore, the assumption that the NP-CeO_2 has a photocatalytic character is not surprising at all. Since the most widespread use of CeO_2 is as a photocatalyst, why not use this property to predict a preliminary antioxidant property? Thus, we can reduce several experiments. Starting from the fact that while model pollutant degradation needs to have charge carriers and the (photo)catalytic degradation takes place through redox reactions, an antioxidant will capture these radicals. Thus, according to our assumptions, substances proved to be photocatalytically active will not be antioxidants, while a nanoparticle with an antioxidant character will show non-photocatalytic properties. In this way, materials thought to be useless as catalysts may have new uses. Therefore, this article focuses on the synthesis of

differently shaped NP-CeO_2 and using them for paracetamol and methyl orange degradation, for prescreening of the antioxidant character, and for the possible future application in the hemostasis stage of wound healing.

EXPERIMENTAL

Synthesis of the nanocubes and polyhedral of CeO_2

The hydrothermal synthesis method of the nanocubes and polyhedral nanoparticles only differs from the used amount of NaOH (sodium-hydroxide, pellets, 99%, VWR Chemicals) and it is based on the synthesis methods of Mai and co-workers [9]. As cerium precursor $Ce(NO_3)_3 \cdot 6H_2O$ (cerium (III)-nitrate hexahydrate, 99%, Sigma-Aldrich) was used in both syntheses of nanocubes and polyhedral. Two different solution was made with mentioned precursors: (1) 0,868 g of $Ce(NO_3)_3 \cdot 6H_2O$ was added into 5 mL of ultrapure water and (2) 8,4 g of NaOH (amount used for the synthesis of nanocube) // 14 mg of NaOH (amount used for the synthesis of polyhedral) was added into 35 mL of ultrapure water (in ice bath). Both solutions were introduced into a Teflon autoclave and were stirred at room temperature for 30 minutes, afterward, it was transferred into an oven and kept at 180°C for 24 hours. The solution was cleaned for the unreacted components with a centrifugation cleaning process for 10 min and 6,000 RPR with 2 × 50 mL of ultrapure H_2O and 2 × 25 mL EtOH (absolute ethyl alcohol; Chimreactiv SRL). The abbreviation of the samples will be the following: nanocubes and polyhedral.

Synthesis of the nanosphere of CeO_2

The synthesis method of nanosphere was produced using Wang and co-workers [10] hydrothermal synthesis method. The cerium precursor was the same used for the synthesis of nanocubes and polyhedral particles. Polyvinylpyrrolidone (PVP, average mol wt. 40,000; Sigma-Aldrich) was used as a shaped-tailoring agent. In a solution of 30 mL of EtOH and 10 mL ultrapure water 1.63 g $Ce(NO_3)_3 \cdot 6H_2O$ and 1.11 g PVP were added. The mixture was stirred for 30 minutes and transferred to an oven, where it was kept at 160°C for 1 hour. The obtained solution was centrifuged at 15,000 RPR for 5 minutes in 2 mL of Eppendorf and cleaned several times with water. Only the white part of the solution was dried and used for analysis. The obtained nanoparticles will be abbreviated as nanosphere.

Characterization, adsorption, and photocatalytic test

The obtained nanoparticles were **characterized** by:

- Shimadzu 6000 X-ray diffractometer (XRD), with the following parameters: 40 kV (30 mA), radiation with $\lambda_{CuK\alpha}$ = 1.54 Å), scanning between 5 and 80° (2θ range), and with scan speed 2° · min^{-1}.
- FEI Technai G2 F20 high-resolution transmission electron microscopy (TEM) with 200 kV and 300 mesh Cu grid.
- Confocal multi-laser Renishaw inVia Reflex spectrometer equipped with a Rencam CCD detector with the following laser parameters: 633 nm, and 17 mW.
- Jasco-V650 diffuse reflectance spectroscopy (DRS) equipped with an ILV-724 integrative sphere, the spectrum was taken between 190-800 nm. Kubelka Munk equation [11] was used to estimate the bandgap energy values of samples.

The **adsorption test** was used to understand the adsorption properties of the sample. 30 mg of nanomaterial was added in 30 mL of methyl orange (Chempur, 97%; C=50 µM)/ paracetamol (Helcor, pill of 500 mg; C=0.1 mM). A 50 mL Berzelius beaker was used, and it was surrounded with aluminium foil, to avoid all the sunlight. The sampling was in 20, 40, 60, 90, 120 minutes. The obtained sample was centrifugated (3 minute, 15,000 RPR), filtered and the concentration changes were analyzed using JASCO-V650 tip spectrophotometry.

A double-walled photoreactor, with a suspension concentration of 1 mg · mL^{-1} was used for analyzing the **photocatalytic activity** of the samples. Two different model pollutants were used: (i) methyl orange (C=50 µM) and (ii) paracetamol (C=0.1 mM) and two different lamp sources were used: (i) 6 × 6 W UV lamps and (ii) 6 × 15 W visible lamps (only in the case of MO). The test was taken for 2 hours, with a sampling from ten to ten minutes in the first hour and then from 20 to 20 minutes in the second hour. Before the test, the suspensions were ultrasonicated for 15 minutes and they were kept in the dark for 10 minutes to reach the adsorption-desorption equilibrium. The concentration changes of the model pollutant were determined for the MO the same as in the case of the adsorption test. Merck-Hitachi L-7100 high-performance liquid chromatography (within a low-pressured gradient pump; Merck-Hitachi L-4250 UV-Vis detector, and Lichrospher Rp 18 column) was used to define the concentration change for paracetamol measurements. The used parameters were the following: eluent - Acetonitrile: H_2O=20:80, adjusted to a 2.30 pH using 85% phosphoric acid, flow rate: 0.500 mL · min^{-1}, and detection wavelength at 243 nm.

The paracetamol (Helcor; 500 mg) was cleaned before being used. We used 3 different pills to determine the purity of the active substance. We made a solution, which was filtered with traditional filter paper thus cleaning the paracetamol from possible additives (such as starch).

RESULTS AND DISCUSSION

Two different synthesis methods were used to obtain differently shaped CeO_2 nanoparticles. First, the synthesis methods of nanocubes and polyhedral-shaped nanomaterials are similar, only the amount of NaOH is changed. Similarly with Mai and co-worker [9], we have found that the crystallinity is shape-dependent, and moreover, the pH of the reaction solution influences the obtained shape. The most crystalline nanostructures were obtained in the case of nanocubes.

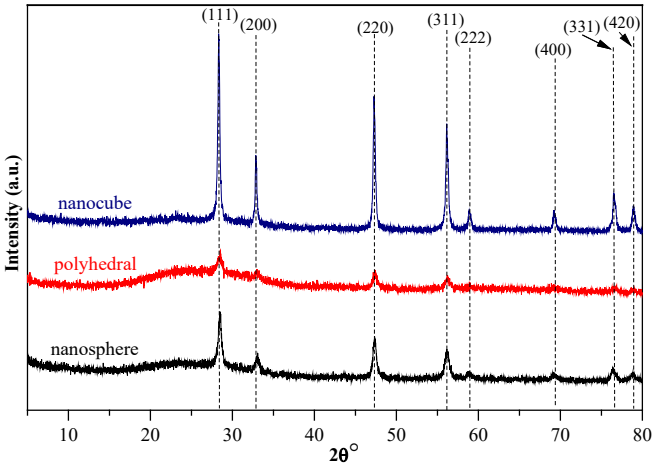

Fig. 1: The XRD patterns of differently shaped CeO_2 nanomaterials: nanocube (blue line), polyhedral (red line), and nanosphere (black line)

In addition, using only additives (in our case PVP; Fig. 1) for the synthesis of nanosphere, higher crystallinity compared with the polyhedral-shaped nanostructures, but lower crystallinity compared to the nanocubes, was observed. All typical reflections of NP-CeO_2 were observed (Fig. 1) in the XRD patterns at 28.55°, 32.81°, 47.26°, 56.20°, 58.95°, 69.27°, 76.61°, and 78.90° indexed with the following Miller indexes (111), (200), (220), (311), (400), (331), (420) using the COD nr. 00-434-3161 card to verify. Indifferent from the obtained shaped, all the reflections were observed in all patterns. No additional reflection was detected in the XRD patterns.

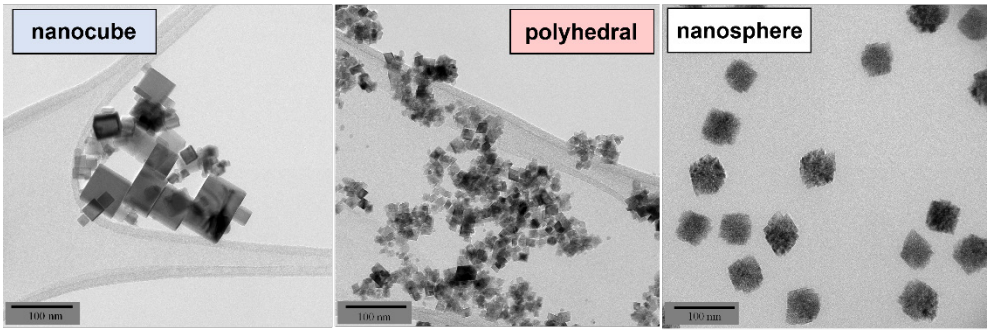

Fig. 2: Transmission electron micrographs of differently shaped CeO_2 nanomaterials: nanocube (đ~25 nm), polyhedral shaped (đ~15 nm), and nanosphere (đ~60 nm).

The next step of this research was to analyze the morphology of the samples for which TEM measurements were used. As can be seen in Fig. 2 all the desired morphologies were synthesized. Unfortunately, the nanocubes have the lowest monodispersity. The highest monodispersity was achieved in the case of the nanospheres. This synthesis method differs from the one used for nanocubes and polyhedral-shaped particles. All the particle sizes of nanomaterials are in the accepted range to be used in biomedical applications, such as wound healing, which are the further plans of this study.

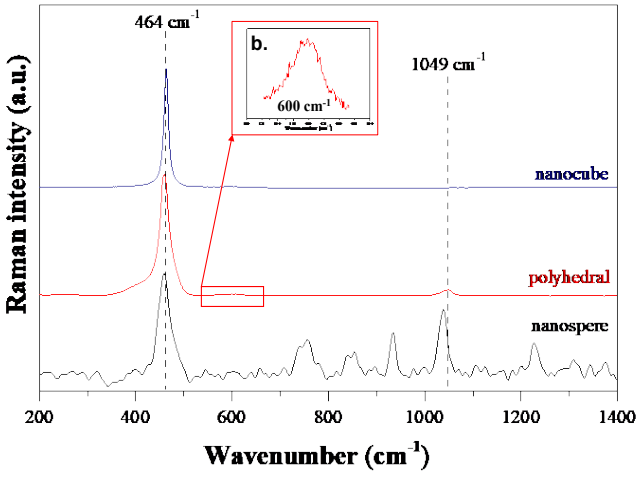

Fig. 3: The Raman spectra for differently shaped CeO_2 nanomaterials: nanocube (blue line), polyhedral (red line), and nanosphere (black line): entire graphs (a) and inserted graph - magnified (b)

According to the XRD measurements (Fig. 1), the samples have different crystallinity amounts regarding the obtained form. Thereby, Raman spectra (Fig. 3) were taken to observe the possible oxygen vacancies in the samples. First, it needs to be mentioned, that the presence of the PVP, which remained from the synthesis, was observed in the Raman spectra of the nanosphere. This PVP could not be washed from the surface of the NP-CeO_2, as tested by the immersion in EtOH and H_2O for 24 hours (this will be not presented here). The PVP adsorption on the surface of the CeO_2 was confirmed by S. Lakhwani *et al.* [12]. The presence of the PVP could be the reason for the low crystallinity, as confirmed by the XRD measurements (Fig. 1). The presence of the PVP does not have a negative effect on the applicability in a biological system [13], thereby the obtained sample is used as synthesized. Three Raman bands were observed in Fig. 3. The most intensive band originates from the cubical structure of the samples and the broadening of the signal (464 cm^{-1}) could be assumed for the obtained morphology [14]. Besides the typical band for CeO_2, two other bands were observed at 610 and 1062 cm^{-1}, which could be attributed to the presence of oxygen vacancies [14]. These bands overlap in the case of nanospheres but are presented in polyhedral. These could be the reason for the low crystallinity since they are not presented in nanocube spectra.

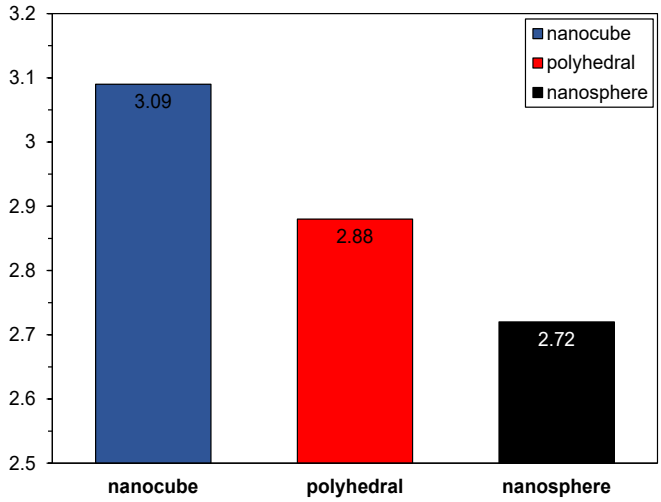

Fig. 4: The estimated bandgap energy values calculated by Kubelka Munk equation for the CeO_2 nanomaterials: nanocube, polyhedral, and nanosphere.

Using a nanomaterial for photocatalytic activity analyzes is necessary to determine their bandgap energy values. The NP-CeO_2 have a bandgap energy value between 3 and 3.40 eV [15]. Similar to TiO_2, it is a UV-active photocatalyst but has

higher oxygen mobility. Surprisingly, the obtained nanomaterials have lower bandgap energy values without any noble metal, or other additional metal-oxide (such as CuO, Ag_3PO_4) capable to reduce the bandgap energy. The obtained values (Fig. 4) show that polyhedral and nanospherical particles could be irradiated by visible light irradiation, while nanocubes can be activated by UV light irradiation. It is important to note that the photocatalytic activity of a nanostructure does not only depend on its bandgap energy but also on its surface properties and the type of model compound chosen. Before starting to discuss the photocatalytic degradation of the chosen model pollutant, it is necessary to understand the relationship between the nanostructure and the model compound, for which we performed adsorption tests (Fig. 5-6).

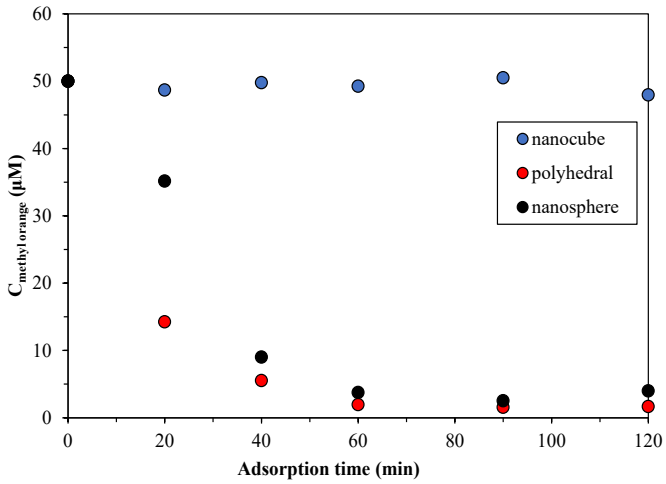

Fig 5: The MO adsorption test of differently shaped CeO_2 nanomaterials: nanocube (blue dots), polyhedral (red dots), and nanosphere (black dots).

The MO adsorption test of CeO_2 nanomaterials shows that the polyhedral-shaped and nanospherical nanoparticles have adsorbed the total amount of MO. Therefore, its photocatalytic activity cannot be determined. Against this, the nanocube does not adsorb any of the MO. The result was compared with the XRD patterns (Fig. 1), where the most crystallized particles were the nanocube-formed particles. In the case of spherical and polyhedral particles, differences can be observed, the magnitude of which is small, but the spherical particles show slower adsorption (Fig. 5). As it was seen in XRD patterns (Fig. 1), the spherical structures exhibited higher crystallinity. According to our assumption, the nanoparticles may have an amorphous structure, so that the MO molecules are adsorbed on their

surface, moreover, the presence of the oxygen vacancies could favor the adsorption of the MO molecules. Thus, our further assumption is that the crystallinity of the nanoparticles is related to their photocatalytic applicability, since the complete adsorption of the model compound, the existence of photocatalytic activity can be completely ruled out.

Although we expected similar results during the adsorption of paracetamol, we were surprised to find that no adsorption was observed in all cases, independently of the synthesized morphology.

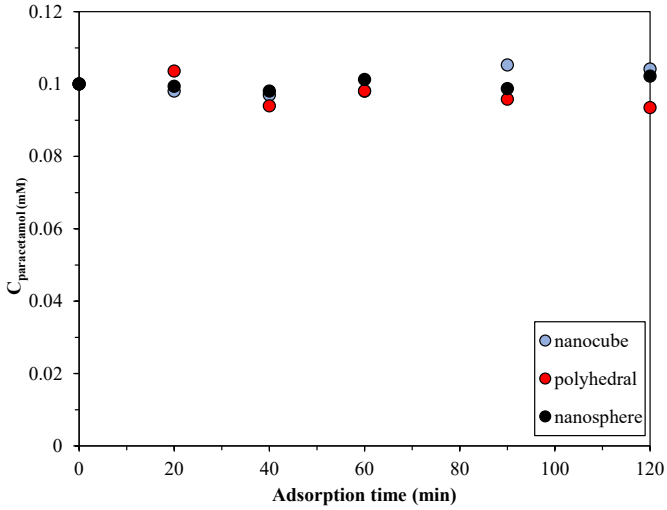

Fig. 6: The paracetamol adsorption of differently shaped CeO_2 nanomaterials: nanocube (blue dots), polyhedral (red dots), and nanosphere (black dots).

The next step of our studies was to assess the photocatalytic activity by using MO, as a model pollutant, and visible and UV light, as an irradiation source. Based on the observed adsorption we will discuss only the degradation using nanocubes. First, we used visible light irradiation, where no photocatalytic activity of nanocubes was observed. In this case, the estimated bandgap energy is at 3.09 eV (Fig. 4), therefore it is not surprising that no photoactivity was observed (Fig. 7a). Secondly, the same test was done; only the lamp`s source was changed to UV light, where no degradation was observed either (Fig. 7b). Therefore, it can be concluded that by using MO as a model pollutant no degradation could be seen regardless of the used lamp source (Fig. 7). This could be predicted to have a good antioxidant character.

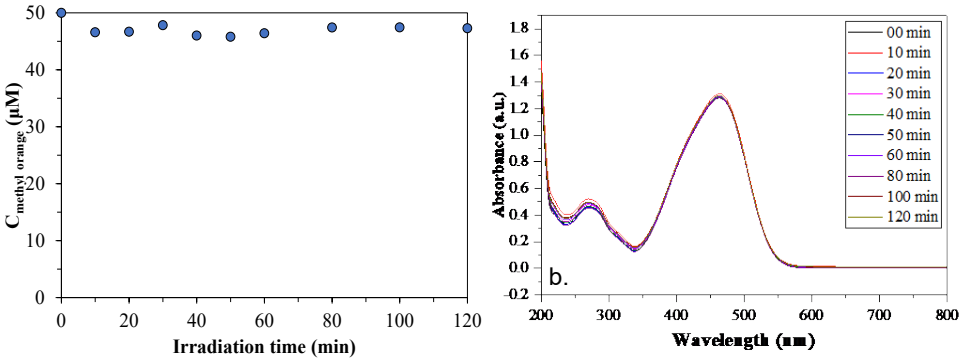

Fig 7: The photocatalytic degradation of MO using nanocube in visible (a) and UV light (b) irradiation.

The paracetamol degradation of CeO_2 nanomaterials was done by using UV light as a light source. No degradation of paracetamol was observed regardless of the differently shaped nanomaterials. Thereby, we assume a good antioxidant character. It needs to be emphasized that the obtained materials have sufficient bandgap energy for producing photocatalytic activity and in the case of polyhedral the presence of oxygen vacancies was also confirmed. The no photocatalytic activity observed in the case of MO (Fig. 7) and paracetamol (Fig. 8) could be a predictor for high antioxidant character.

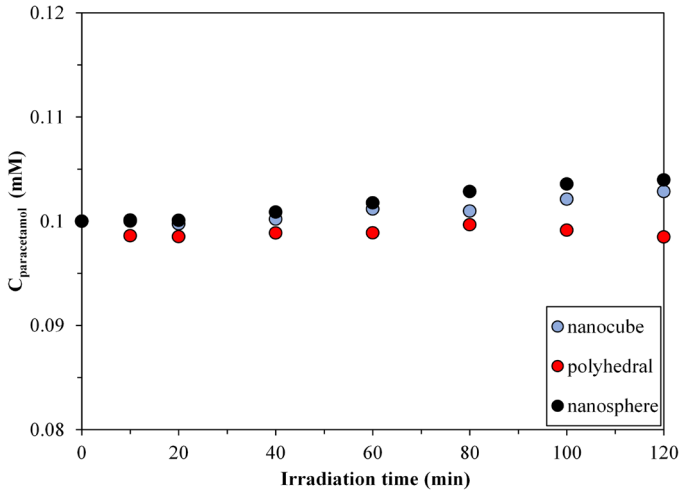

Fig 8: The photocatalytic degradation of paracetamol using nanomaterials: nanocube (blue dots), polyhedral (red dots), and nanosphere (black dots) (due to the small amount of material the 30- and 50-minutes sample was not taken).

The reason for this is that during a photocatalytic activity is mandatory to have charge carriers (e^- and h^+), which could start the degradation of the organic dyes by oxidation of its. Having an antioxidant, as a definition “delays or prevents oxidation of that substrate” [16], therefore the oxidation with the charge carriers is less probable to occur.

CONCLUSIONS

In this work were synthesized two different morphologies of CeO_2 nanoparticles (nanocube, and nanosphere) and a reference material in the form of polyhedral nanoparticles. It has been confirmed that the crystallinity of the samples has a relation with the obtained morphologies. Adsorption of the MO was observed in the case of nanosphere and polyhedral-shaped nanoparticles. No paracetamol and MO degradation was confirmed regardless of the used CeO_2. The non-photocatalytic activity could predict a good antioxidant character and a promising application in wound healing.

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