

Titania-Ceria surfactant assisted sol-gel synthesis and characterization

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Érkezett: 2016. 11. 19. • Received: 19. 11. 2016. • <http://dx.doi.org/10.14382/epitoanyag-jsbcm.2017.2>

Abstract

The nanoparticles of titanium dioxide are important in a wide range of applications such as catalysis, environmental remediation and solar energy conversion. While cerium oxide is rare-earth oxide material used in the fields of photoluminescence, photosensitive material to UV radiation. Furthermore, research on the synthesis of nanoparticles of titanium dioxide has given rise to different methods such as sol-gel, in solid states, hydrothermal processes, among others. The process of solid state synthesis is most often used for the technical production of ceramic materials, while the sol-gel has gained much popularity in recent decades. Between these methods, microemulsion of reverse micelles technique, is one of the most versatile allowing control of particle properties such as size distribution, morphology and surface area. In this work, titania-ceria nanoparticles in anatase phase were synthesized by sol-gel method assisted by microemulsion reverse micelle using titanium butoxide and cerium nitrate hexahydrate as the precursors. The sample was thermally treated at 600 °C at a rate of 3 °C min⁻¹. The residence time of the sample at this temperature was 2 hrs. TEM and XRD analysis were used to characterize the samples obtained. According to the results, the obtained nanoparticles present spherical morphology and have a size distribution of 5 nm for CeO₂, 9.5 for TiO₂ and 14, 17 and 20 nm for the doped TiO₂ with 5, 10 and 15% CeO₂, respectively. The results indicate that the CeO₂ was incorporated into the network of titania.

Keywords: nanoparticles, titania, ceria, microemulsion, sol-gel.

1. Introduction

Nanomaterials based on metal oxides exhibit remarkable physical and chemical properties that enable the development of novel nanodevices that can be used in different physical, biological, biomedical and pharmaceutical applications [1-7]. The surface of these nanostructures is crucial for these applications. These nanostructures excel in catalytic applications because of the presence of surface defects that act as active sites for adsorption of reactive molecules [6]. These defects present in the nanoparticles, especially cerium dioxide and titanium, increase the active surface area that favors the union of a large variety of ligands on its surface [8]. Although so far the use of nanoparticles of titania and ceria in the biomedical and therapeutic area has been carried out separately and not mixed [3-7], it is possible to harness the power possessed by lanthanide ions with electronic configuration 4f, as cerium, which when entering the network of the titania acts as an electronic trap [9-10], which could increase the number of molecules captured on its surface, which will be extremely useful for increasing the binding of drugs in nanoparticles of titania and improve its efficiency as a nanocarrier.

Furthermore, research on the synthesis of these nanomaterials has given rise to different methods such as sol-gel, solid, chemical vapor deposition, hydrothermal processes, among others. The process of solid state synthesis is most often used for the production of technical ceramic materials, while the sol-gel has gained much popularity in recent decades [3]. These methods microemulsion technique reverse micelles is one of the most versatile allowing control of particle properties such as size distribution, morphology and surface area [5]. The

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reverse micelles are used as a micro-heterogeneous medium for generating nanoparticles, where microcavities surfactant provide a similar effect to a cage which influences the particle nucleation, growth and agglomeration. The scale of these nanoreactors size is in the range 2 to 10 nm. This is a dynamic system on a micellar level. Micelles collide with each other and quickly share their content, which is essential for carrying out chemical reactions [11].

In this work a combined method for synthesis of TiO₂ nanoparticles doped CeO₂, for use as drug delivery systems described. Using Tween-20 as surfactant, as cosurfactant methanol, toluene as continuous phase and titanium butoxide and cerium nitrate as precursors.

2. Materials and methods

All reagents used in this study were of analytical grade, Ti(OC₄H₉)₄ (98%, Aldrich), Ce(NO₃)₃·6H₂O (99.8%, Merck), C₇H₈ (99.5%, Merck), CH₃OH (99.8%, Merck), C₅₈H₁₁₄O₂₆ (Merck) and deionized water (Merck).

2.1 Nanoparticles synthesis

TiO₂, CeO₂ and TiO₂-CeO₂ nanoparticles were synthesized by sol-gel method assisted by a surfactant. The precursor Ce(NO₃)₃·6H₂O was dissolved in 2 mL of deionized water (0, 5, 10 and 15 mol%), then slowly added to an organic phase

Tween-20/methanol/toluene in a v/v ratio of 6/1/10 mL and was at a temperature of 60 °C for 10 min, then added drop by drop the titanium butoxide (in the following proportions: 100, 95, 90 and 85 mol%) while preserving the conditions of temperature and agitation for 40 min. The resulting suspension remained standing at room temperature protected from light for 12 hrs. The synthesis of nanoparticles becomes evident that is possible to observe the separation of the microemulsion into two layers. The upper layer is recovered and subjected to drying at 100 °C in an oven for 24 hrs, the resulting powder sample was heat treated at 600 °C at a rate of 3 °C / min¹. The residence time of the sample at this temperature was 2 hrs.

2.2 Characterization

The structural and chemical characterization of the nanoparticles was made from powder samples obtained in the synthesis. The samples were prepared in the form of dilutions of varied concentration (according to the analysis technique), and powders obtained from the heat treatment. The characterization techniques that were used were: X-ray diffraction, XRD and conventional and high resolution transmission electron microscopy, TEM and HRTEM.

3. Results and discussion

3.1 Nanoparticles synthesis

The synthesis process from the hydrolysis reaction of titanium butoxide and the insertion of cerium nitrate into the micelles formed by Tween-20 and methanol under acidic conditions (pH 5) was manifested by the separation of the microemulsion in two layers upon completion of 40 minutes of reaction. The upper layer consists of the organic phase containing the non-agglomerated nanoparticles and the lower layer is treated with the inorganic phase [12].

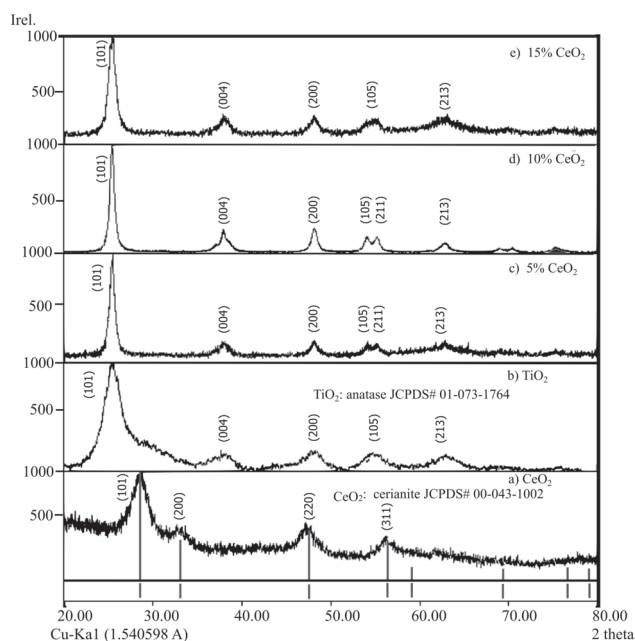


Fig. 1 Diffraction patterns obtained from CeO₂ powders (a), TiO₂ (b) doped 5% (c), 10% (d) and 15% CeO₂ (e).

1. ábra Röntgendiffraktogramok: (a) CeO₂, (b) TiO₂, (c) TiO₂ + 5% CeO₂, (d) TiO₂ + 10% CeO₂, (e) TiO₂ + 15% CeO₂

In Fig. 1, the diffraction patterns of the single TiO₂ (a) and doped with (b) 5%, (c) 10% and (d) 15% CeO₂ powders are shown. In the four diffraction patterns only the reflections corresponding to the anatase phase of titanium dioxide (JCPDS # 01-071-1166) could be identified; while in the three doped titania patterns, the Bragg peaks corresponding to the doping species, CeO₂, were not observed, suggesting the incorporation of CeO₂ in the TiO₂ network. It can also be observed in these three diffraction patterns that, as the CeO₂ percentage increases.

The average crystallite size (TC) for the four systems studied was determined by the Debye-Scherrer formula, the results of the measurements are shown in Fig. 2. When comparing these results with the simple nanoparticles obtained by this same method, it can be seen that when doping the TiO₂ nanoparticles with CeO₂, the average grain size increases, however as the percentage of dopant increases the size of crystallite decreases, this may be due to the segregation of the dopant cations at the grain boundary may prevent the growth of nanocrystallite in the nanoparticles [2, 13-14]. Another possible cause is that the Ce⁺ ion absorbed in the titania network decreases the free surface energy of the particles, which inhibits the process of aggregation of the nanoparticles [2, 15].

The microstructural effect of spreading in the peaks is the presence of residual stresses in the material due to the inclusion of the cerium atoms in the titania network, causing a deformation of its crystalline planes. In this particular case the effect is presented at the microscopic level, causing a widening of the diffraction profile with respect to the original position of the standard pattern diffraction peaks [9-10]. The evaluation of the microtensions was carried out from the displacement of the crystalline plane (101) of the titania, because they suffer a variation in the interplanar distances caused by the internal residual forces, the results of the estimations are shown in the Fig. 2.

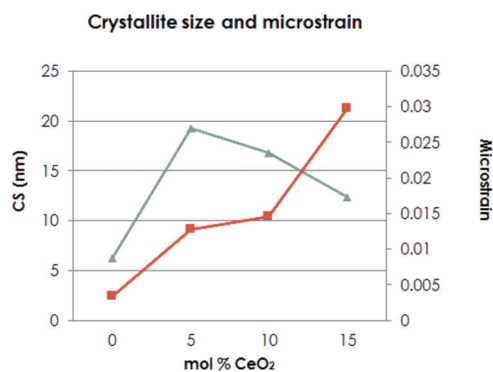


Fig. 2 Crystallite size measurements and microtension diffraction patterns simple and TiO₂ doped 5%, 10% and 15% CeO₂.

2. ábra Krisztallit méret és mikrodeformáció: CeO₂ TiO₂ + 5% CeO₂, TiO₂ + 10% CeO₂, TiO₂ + 15% CeO₂

From the measurements of the crystallite size and microtension in the diffraction patterns of the powders of simple titania and ceria doped, represented in Fig. 2, it is possible to affirm that for the case of simple TiO₂ the increase in the maximum width a half peak (FWHM), is only provoked by the decrease in crystallite size; whereas for the powders of doped titania, it is mainly due to the microdeformations caused in their crystalline planes when the ceria atoms are incorporated and the decrease

of the crystallite size is possibly the result of an increase in the percentage of dopant incorporated in their network. This effect is more noticeable in the system doped with 15% of ceria because when using higher percentages of CeO₂, the greater the tension provoked in the network that of the titania.

The crystallographic data of the phase identified in the pattern of Fig. 1a (TiO₂: JCPDS # 01-073-1764) were used as crystalline model from the obtained diffraction patterns. In Fig. 3, it is seen that as the dopant percentage increases, CeO₂, the Ti factor occupying factor in the unit cell decreases, this suggests that the cerium atoms are incorporated in the titania network by displacing these Atoms.

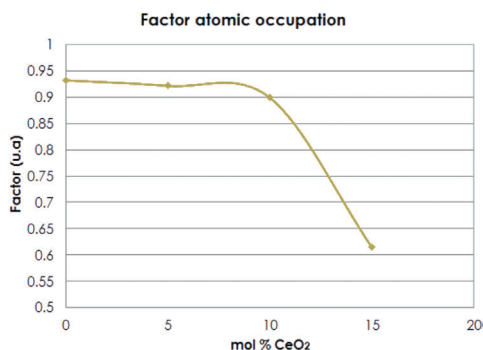


Fig. 3 Factor atomic occupation of simple and TiO₂ doped 5%, 10% and 15% CeO₂.
3. ábra Atom illeszkedési tényező: CeO₂/TiO₂ + 5% CeO₂/TiO₂ + 10% CeO₂/TiO₂ + 15% CeO₂

Fig. 4 shows a high-resolution image, accompanied by its corresponding Fast Fourier Transform (FFT), taken from the TiO₂ sample. The selected nanoparticle has a size which is about 8.5 nm, in which an interplanar distance of about 0.343 nm, corresponding to the plane (101) of the tetragonal cubic structure of TiO₂, could be measured. Likewise, in their respective FFT, the periodic arrangement of the points makes evident the crystalline character of the particle.

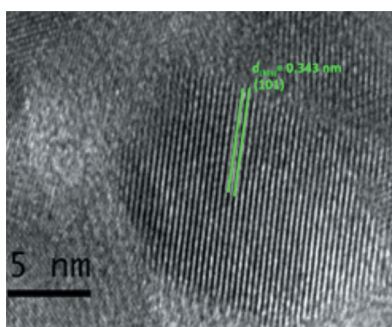


Fig. 4 High resolution micrograph of a nanoparticle showing an interplanar distance of 0.343 nm.

4. ábra Nano-részecske nagy felbontású mikroszkópos felvétele: 0,343 nm síktávolság figyelhető meg

Fig. 5a corresponds to a high resolution image of the doped sample, where spheroidal nanoparticles with a diameter of 20 nm are observed, which is in agreement with the crystallite size estimated from the main intensity in the pattern i.e. the doping at low percentages of CeO₂ increases the size of crystallite and thus the particle diameter; it can be thought that the main reason for this growth is because the radius of the cerium atom is more large than the Ti⁺ and to enter in low percentages causes that the nanoparticles increase their size. While in Fig. 5b, a nanoparticle

with an approximate size of 22 nm is observed, in which an interplanar distance of approximately 2.48 Å, corresponding to the plane (101) of the tetragonal cubic structure of TiO₂. This reinforces the observations in the diffraction patterns, which suggests the incorporation of CeO₂ in the TiO₂ network [16-18].

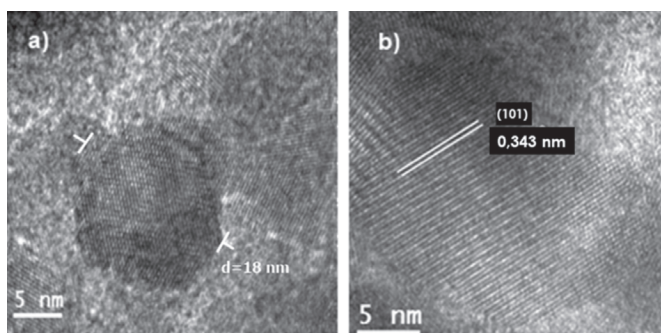


Fig. 5 HRTEM micrographs. One observed nanoparticles of 18 nm (a), a nanoparticle exhibiting an interplanar distance of 0.343 nm (b).
5. ábra Nagy felbontású mikroszkópos felvételek (a) 18 nm méretű nano-részecske, (b) nano-részecske 0,343 nm síktávolsággal.

Fig. 6a and 6b shows clear field micrographs at a magnification of 690,000×, taken in different areas of the doped titania sample with 15% CeO₂, where it is observed that the nanoparticles have average diameters of 14 nm. As can be seen in the micrographs, the particle size decreases with increasing dopant percentage, suggesting that the cerium ion upon incorporation into the titania network slows the growth of the nanoparticles.

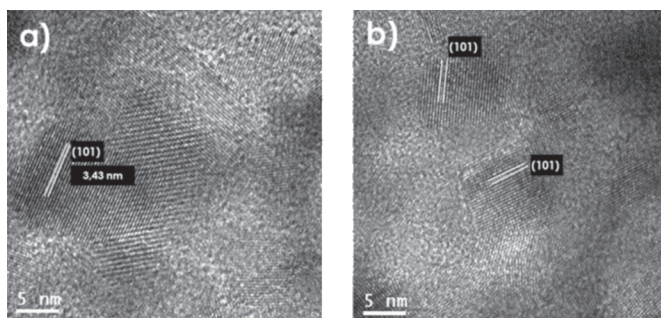


Fig. 6 Brightfield TEM micrographs with a magnification of 690,000×, in which a group of spheroidal TiO₂ nanoparticles doped 15% CeO₂ is observed.
6. ábra Brightfield TEM felvételek 690.000× nagyítással; gömbszerű nano-részecskék figyelhetők meg

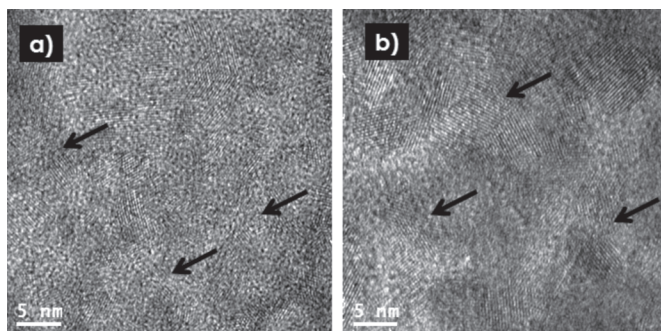


Fig. 7 Light field micrographs with a magnification of 99,000×, obtained by TEM.
7. ábra Light field TEM felvételek 99.000× nagyítással

Fig. 7a and 7b correspond to clear-field micrographs taken from a CeO₂ sample, in which spheroidal nanoparticles with an average size of 5 nm (indicated by arrows) are observed. These

results indicate that using the proposed methodology can be obtained CeO₂ nanoparticle, and suggesting that during the joint process of synthesis and doping both types of nanoparticles, however, because the CeO₂ nuclei are smaller, due to the low concentration of reagent, gives a secondary nucleation, where the nanoparticles of TiO₂ are formed [12, 19].

4. Conclusions

The conditions for the synthesis of nanoparticles of TiO₂ doped with ceria were established by the inverse micelles method, emphasizing the surfactant handling and the formation of suspensions in which the material is synthesized.

By the microemulsion method of reverse micelles, nanoparticles of anatase phase titania and titania doped with ceria of spheroidal shape were obtained with an average diameter of 9.5, 14 and 20 nm, respectively. This suggests that in the interior of the micelles there is a greater availability of water to carry out the hydrolysis and dopant insertion reaction in the TiO₂ nanoparticles, which favors the nucleation stage, so it is probable that Increase the number of nuclei produced thereby forming smaller particles.

5. Acknowledgments

This research was funded by CIC UMSNH (Universidad Michoacana de San Nicolás de Hidalgo, México) and CONACYT (Consejo Nacional de Ciencia y Tecnología, México), A. Torres-Romero, received a doctoral grant from CONACYT.

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Ref.:

Torres-Romero, A. – Cajero-Juárez, M. – Contreras-García, M. E. : *Titania-Ceria surfactant assisted sol-gel synthesis and characterization*
Építőanyag – Journal of Silicate Based and Composite Materials, Vol. 69, No. 1 (2017), 8–11. p.
<http://dx.doi.org/10.14382/epitoanyag-jsbcm.2017.2>

Szol-gél eljárás jellegzetességei titándioxid és cériumdioxid alapanyag szintézisével

Titándioxid nano-részecskék fontos szerepet töltenek be a katalízisben és a napenergia hasznosításban, sok egyéb más területtel együtt. A cériumdioxid egy ritkaföldfém vegyület amelyet elsősorban fotolumineszcens anyagként, fényérzékeny anyagok előállításánál során hasznosítanak. Napjainkban a szol-gél eljárás egy népszerű módszer mezopórusos anyagok előállítására. A cikk bemutatja anatóz fázisú titándioxid-cériumdioxid nanorészecskék előállítását szol-gél eljárással, amelynek során a kiindulási prekursorok titánbutoxid és cérium-nitrát-hexahidrát. A hőkezelés hőmérséklete 600 °C, sebessége 3 °C min⁻¹, a hőtartás időtartama 2 óra volt. TEM és XRD vizsgálatokon keresztül figyelhetjük meg az elkészült termék jellegzetességeit. Azeredmények igazolják, hogy a CeO₂ beépül a TiO₂ szerkezetbe. Kulcsszavak: nanorészecskék, titán, cérium, mikroemulzió, szol-gél