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Structural and topographic study of ceria nanoparticles prepared via different techniques

M.A. Ahmed [a,*], Samiha T. Bishay [b], Mai M. El-Masry [c]

[a] Materials Science Lab. (1), Physics Department, Faculty of Science, Cairo University, Giza, Egypt
[b] Phys. Dept., Faculty of Girls for Art, Sc. and Education, Ain Shams Univ., Cairo, Egypt
[c] Basic Science Dept., Higher Engineering Institute, Thebes Academy, Cairo, Egypt

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ABSTRACT

Nano-crystalline ceria was synthesized using four different techniques. The oleic acid was used as a surfactant in the first technique while Polysorbate 80 (Tween 80) was used instead in the third. On the other hand, the other two techniques were carried out in the absence of any surfactant. The first technique produced samples characterized by the smallest crystallite size (2.8 nm (XRD)), and the lowest hydrodynamic diameter (DLS). Also, if the powder of these samples was dispersed in toluene, its nanoparticles would appear in high agglomerated form in (TEM) and (AFM) photographic images. Accordingly, these samples are suitable to be used as a catalytic agent. Moreover, the results revealed that, the samples prepared in the presence of Tween 80 as a surfactant are recommended to be applied in biological fields. These samples are characterized by small crystallite size 6 nm (XRD) and high surface area (BET). They further produced completely free particles without agglomeration when their powder was dispersed in water. The results confirmed also that, the particle size measurements using (UV–Vis) are greater by about 0.34% than the corresponding values calculated from XRD and BET data. This may be attributed to the significant role of the dispersive medium. X-ray photoelectron spectroscopy (XPS) spectrum confirmed the reverse linear proportionality between the percentage ratio of Ce^{3+}/Ce^{4+} and the particle size of the investigated samples.

* Corresponding author. Fax: +20 2 35693738.
E-mail addresses: moala47@hotmail.com, moala1947@yahoo.com (M.A. Ahmed).

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1. Introduction

Cerium is a rare earth element that belongs to the lanthanide group. Several distinguished properties of cerium have been revealed by close examination of its micro structure.

Cerium oxide (ceria) nanoparticles consist of a cerium core surrounded by oxygen [1,2], lattice of cubic fluorite structure with ($Fm\bar{3}m$) and a cell parameter of 0.541 nm at room temperature that giving isolated peaks in X-ray diffraction. Cerium (IV) oxide (CeO_2), or ceria, is a lanthanide oxide. There exists a number of higher oxides of cerium with composition CeO_{2-x}; x = 0–0.5. The practical reduction limit of non-stoichiometric ceria is Ce_2O_3, where all cerium ions are found in a Ce (III) oxidation state. The crystal structure of Ce_2O_3 under normal conditions is the A-type sesquioxide (P3m1).

Ceria is one of the most important rare earth metal oxides due to its wide range of applications especially in hydrogen and oxygen storage [3,4], catalysts [5,6], UV blockers [7], fuel cells [8], and pollutant sorbents [9]. The researches on the controlled preparation of nano-ceria have attracted much attention in recent years [10–14]. Well defined ceria micro/nano-structures with various morphologies, such as nanopolyhedra, nanorods/nanowires [10], nanocubes, nanotubes, nanoplates, and microdisks, have been successfully synthesized [12]. A variety of approaches micro/nanoscale cerium oxides are functions of the preparation techniques.

The physical/chemical properties of cerium oxides are strongly dependent on their microstructures, including size, morphology, and specific surface area [15–17]. Conventional high surface area cerium oxide exhibit excellent poisoning resistance against H_2O_2 and CO_2 in the feed stream where, the cerium oxide ($CeO_{2-\delta}$) materials have been found to possess a significant concentration of Ce^{3+} and oxygen vacancies, even after high temperature (500 °C) calcination. The testing and analysis results of Meia et al. [18] showed that the surface modification might increase the flow ability, decrease the specific surface area and agglomeration of CeO_2 powders.

Kuen-Song and Chowdhury [19] had reported the importance of the morphology of the ceria nanomaterials and its effect on the optical property of absorbance in the UV region to understand the correlation between the band gap energies and the grain size for UV absorbing semiconductor materials. A clear blue-shifting of the absorption threshold edge can be observed for the CeO_2 nanospheres and microrods, contrasting with the bulk powder, due to the decrease of particle sizes and the existence of a large number of defects [20].

Our attention in this work is to highlight the influence of the preparation methodology on the microstructure of nano-ceria. Another important goal is to investigate the proper dispersive media recommended for nano ceria powders.

2. Experimental

2.1. Samples preparation

Four different samples of cerium oxide nano-particles were prepared as illustrated in details in Table 1.

3. Characterization

3.1. X-ray diffraction (XRD)

Proker D_8 advance X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) has been used to assure the preparation of the cerium oxide in single phase. X-ray diffraction pattern was recorded at room temperature in a wide range of Bragg angles 2θ (20° ⩽ 2 θ ⩽ 80°) with 0.02° step size.

3.2. X-ray photoelectron spectroscopy (XPS)

XPS spectra were obtained using X-ray photoelectron spectrometer (model Thermo Scientific K-Alpha) with a monochromatic X-ray source of Al Kα. The acquisition time is 10 min for all samples,