



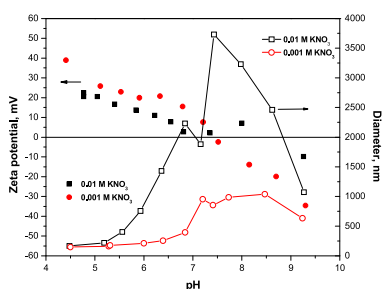
Morphology and the isoelectric point of nanosized aqueous ceria sols

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HIGHLIGHTS

- Ceria sols with cubic phase nanoparticles have been successfully synthesized.
- The isoelectric point of ceria oxide in KNO₃ solutions was $pH_{IEP} = 7.6 \pm 0.2$.
- The specific adsorption of SO₄²⁻ ions causes a shift in IEP to lower pH ($pH_{IEP} = 6.7$).
- The correlation between IEP and the maximum diameter of particles was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

Ceria sols were synthesized by a forced hydrolysis method using cerium sulphate or cerium nitrate as precursors. High-resolution TEM was used to determine the microstructure and particle size of CeO₂. A polycrystalline structure of ceria sols with crystallite sizes of 4.4 and 8.6 nm was obtained. The particles had a well-defined polyhedral shape. Direct bandgaps for ceria nanoparticles were 2.80 and 3.31 eV, respectively. The isoelectric point, pH_{IEP} , of ceria sols in KNO₃ solutions was investigated. The isoelectric point of ceria was found to be $pH_{IEP} = 7.6 \pm 0.2$. The obtained results indicate that the isoelectric point in the presence of SO₄²⁻ ions shifts to lower pH value. The particle size of ceria increases with pH, reaching the maximum value at pH_{IEP} as the result of agglomeration.

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1. Introduction

Ceria has many applications: in solid oxide fuel cells (used as electrolyte) [1–3], gas sensors [4,5], in catalysis [6,7], for chemical–mechanical planarization (as abrasives) [8,9], hybrid solar cells [10], for H₂S removal (as sorbents) [11], and dielectric resonators [12].

The surface charging of the metal oxide–electrolyte solution interface has been extensively studied in the recent decades. Due to its unique properties, ceria is one of the intensively investigated oxides. The charging of particles in aqueous solutions is a factor that

governs many physical phenomena, such as colloidal stability and ion adsorption. Zeta potential is the most prominent parameter used to describe the surface–force interaction and the stability of particles in suspension. Since pH-dependent surface charging is a very important subject of research, measurements of isoelectric point are significant and have been used to define the state of the surface of a dispersed solid phase at a solid–electrolyte solution interface.

The point of zero charge (pH_{pzc}) and isoelectric point (pH_{IEP}) values for various cerium oxides, as well as related materials, reported in literature, vary widely (from pH = 6 to pH = 11.2). These values are collected in Parks [13] and Kosmulski [14–16].

The aim of this study was to synthesize ceria sols by a forced hydrolysis method using cerium sulphate or cerium nitrate as precursors. The geometries and the crystallographic structures of ceria

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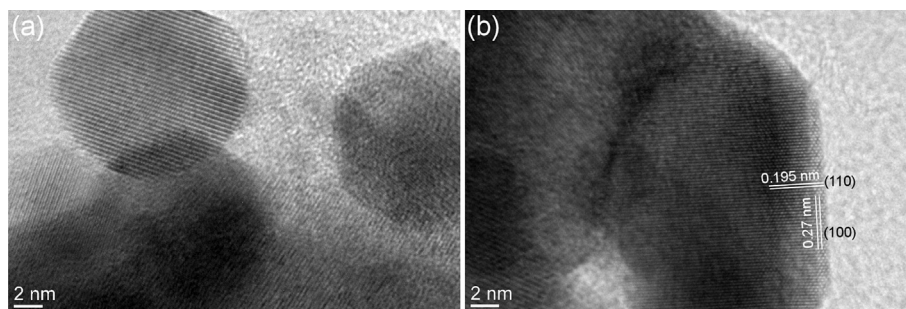


Fig. 1. (a) HRTEM image of CeO₂ nanoparticles obtained by forced hydrolysis of cerium (IV) sulphate (Sol No.1) and (b) HRTEM image of ceria nanocrystallite with the (200) facet corresponding to the cubic CeO₂.

nanoparticles were examined by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and X-ray powder diffraction (XRD) analyses. The direct bandgaps for ceria nanoparticles were also determined from the absorption spectra of ceria sols on a UV–vis spectrometer. The effects of pH and concentrations of KNO₃ and K₂SO₄ solutions on zeta potentials and the mean particle size of cerium oxide were measured by dynamic light scattering (DLS) method.

2. Material and methods

In this study, two different types of ceria sols were used. One was obtained from a Ce(SO₄)₂·4H₂O salt precursor, Sol No.1 (pH = 1.21, d_{av} = 198 nm, CeO₂ = 1.6 mass.%), and the other from an 1 N Ce(NO₃)₄ aqueous solution, Sol No.2 (pH = 0.66, d_{av} = 71 nm, CeO₂ = 0.5 mass.%). Both ceria sols were synthesized by forced hydrolysis according to the procedure described in previous paper [17]. In order to obtain stable ceria dispersions, partial removal of sulphate or nitrate ions from the prepared sols was performed by ultrafiltration. The ultrafiltration was carried out in a stirred Amicon cell with polyethersulfone biomax PB and PM series type membranes, until a negative reaction of sulphate or nitrate ions in permeate was obtained. For both so prepared sols, the final pH was ~4.

Transmission electron microscopy (TEM) using a JEOL JEM-2100 was used for the determination of the morphological characteristics of CeO₂ nanoparticles. The phase compositions and the crystallite size of CeO₂ nanoparticles were evaluated from the X-ray powder diffraction (XRD) patterns by a D4 Endeavour, Bruker AXS

X-ray diffractometer (radiation wavelength Cu K α = 1.5406⁰ Å). The crystallite size was calculated from X-ray broadening using the Debye–Scherrer equation [18]: $D = 0.9\lambda/\beta \cos\theta$, where D is the crystallite size in nm, λ is the X-ray wavelength, β is full-width at half-maximum of the X-ray diffraction peak in radians, and θ is the corresponding diffraction angle.

The structural and morphological characteristics of the as-formed CeO₂ nanoparticles were determined by high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED). For the TEM analyses, the colloidal dispersions were allowed to evaporate on lacey carbon films covering 300-mesh copper grids.

The absorption spectra of ceria sols were recorded on a Uvicon 810/820 (Kontron Instruments, Austria) UV–vis spectrometer. The absorbance of ceria sols was measured in the range from 190 to 500 nm at room temperature.

A Zetasizer Nano with 633 nm He–Ne laser equipped with an MPT Autotitrator manufactured by Malvern (Malvern, UK) was used to determine the particle size and isoelectric point of ceria sols by a potentiometric titration. This instrument measures particle sizes from 0.6 nm to 6 μ m. The 5 ml of ceria sols were diluted in 5 ml of (0.001–0.1 mol dm⁻³) KNO₃. Then, the samples were placed in a sample container and potentiometric titrations were performed at pH \approx 4 to 9. Zeta, ζ , potentials were calculated by the installed Zetasizer software (Smoluchowski equation). In addition, the influence of SO₄²⁻ ions on the isoelectric point was determined. For these measurements, 5 ml ceria sols were diluted in 5 ml aqueous (5 \times 10⁻⁶–10⁻⁴ M) K₂SO₄ solution. Aggregated particle diameters were measured simultaneously with the electrokinetic potential of ceria sols.

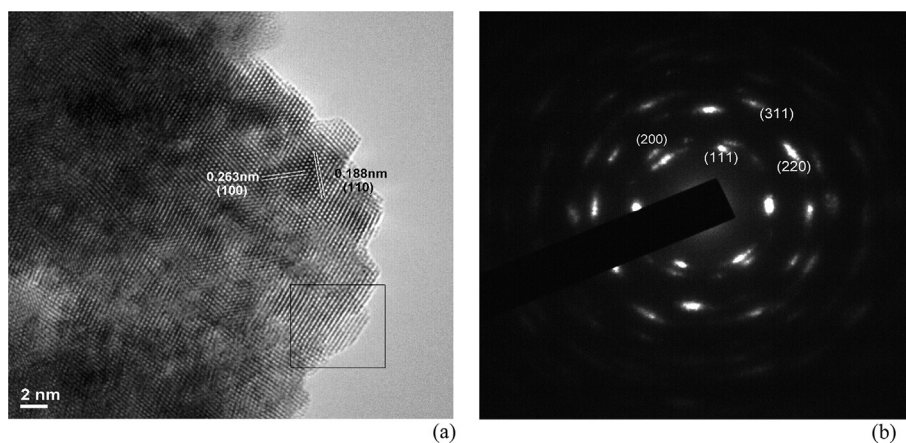


Fig. 2. Typical high-resolution lattice fringe images of CeO₂ grains obtained using cerium (IV) nitrate as a precursor, Sol No. 2, (a) and electron diffraction patterns (b).

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