

Composite cerium dioxide with silver

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Abstract. The radiation-chemical method is used to synthesize the mesoporous nanocomposite "cerium-silver dioxide." An aqueous solution of silver nitrate was used as a precursor. Precipitation of Ag nanoparticles was carried out on solid nanoparticles CeO₂ previously tested using the pulsed electron beam evaporation method in vacuum. The synthesis product after XRD and elemental analysis (XPS method) was free of related impurities. The composite consisted of two crystalline phases-CeO₂ and metal nanoparticles Ag and had a form of 3D spatial nanostructures in the form of "clouds" made by agglomerates of NPles CeO₂ less than 10 nm, which were coated with placers of individual and chain nanoparticles Ag, spherical in size from 10 to 200 nm, without obvious signs of the formation of Ce-O-Ag chemical bonds. The specific surface area of the composite (126.5 m²/g) decreased relative to the specific surface area of pure CeO₂ (190 m²/g). XPS showed the presence of metallic nanoparticles Ag (1.29 wt.%) in the composite. The presence of metal nanoparticles Ag and semiconductor CeO₂ makes it possible to count on the appearance of plasmon resonance in such heterophasic structures.

Keywords: CeO₂-Ag nanocomposite, radiation-chemical synthesis.

1. Introduction

Silver-doped cerium dioxide has great potential for use as a photocatalyst, antibacterial agent [1, 2] and in many other applications. In this work, the CeO₂-Ag nanocomposite was produced by depositing Ag nanoparticles (NPles) using the radiation-chemical method [3] in an aqueous solution of silver nitrate on the surface of cerium dioxide NPles, previously produced by pulsed electron beam evaporation in vacuum at the NANOBIM-2 installation [4].

2. Experimental

2.1. Synthesis method

The synthesis of the nanocomposite CeO₂-Ag was carried out using the radiation-chemical method. CeO₂ NPles was previously prepared using the PEBE method according to the procedure described in [5]. Deposition of Ag NPles on cerium dioxide was carried out continuously using pulsed electron beam (electron energy ~500 keV) on a repetitive accelerator URT-0.5M in a liquid medium mixture of an aqueous solution of AgNO₃ nitrate with an aqueous suspension of solid, water insoluble NPles CeO₂. Ratio of phases in the mixture: H₂O (liq.) – 100 ml, AgNO₃ (s) – 0.6 g and CeO₂ (s) – 0.55 g.

2.2. Samples characterization

X-ray diffraction (XRD) analysis was conducted using a D8 DISCOVER diffractometer (Cu K α _{1,2} λ = 1.542 Å) with a graphite monochromator on a diffracted beam, employing the TOPAS 3 program. Brunauer-Emmett-Teller (BET) surface area analysis and Barrett-Joyner-Halenda (BJH) pore size and volume analysis were performed using a Micromerics TriStar 3000 V6.03 Analyzer, a preliminary degassing of the sample for 1 hour at a temperature of 100 °C. The scanning electron microscopy (SEM) morphology studies and chemical analyses were taken with an analytical scanning electron microscope Zeiss Merlin working at 10–20 kV and equipped with an energy dispersive X-ray detector Oxford Instruments INCA x-act. Photoemission (PE) spectra were measured using a hemispherical analyzer within an ESCALAB 250 Xi laboratory spectrometer (Thermo Fisher Scientific, UK).

3. Results and discussion

3.1. XRD analysis

The Fig. 1 shows an X-ray diffractogram of the composite powder CeO₂-Ag. According to XRD analysis, the composite contained two crystalline phases: CeO₂, cubic phase, S.G.: Fm-3m (225), PDF card No. 00-034-0394, period $a = 5.4113 \text{ \AA}$, $\rho = 7.215 \text{ g/cm}^3$ and Ag-3c, cubic phase, S.G.: Fm-3m (225), PDF card No. 03-065-2871, period $a = 4.0861 \text{ \AA}$, $\rho = 10.502 \text{ g/cm}^3$. When processing diffractograms, a model was used – CeO₂ was present in two fractions, large crystal and fine (not amorphous). Reflexes from large particles on the Fig.1 are indicated in green and conditionally named Cerianite-1, reflexes from small particles are indicated in red and named Cerianite-2. The result of XRD analysis showed: Cerianite-1, contents $\approx 12.5 \text{ wt.}\%$, coherent scattering region (CSR) = $74 \pm 12 \text{ nm}$, a period = $5.413 \pm 0.003 \text{ \AA}$, $\rho = 7.208 \pm 0.007 \text{ g/cm}^3$, $R_b = 5.902$; Cerianite-2, contents $\approx 82.5 \text{ wt.}\%$, CSR $\approx 4 \text{ nm}$, a period = $5.426 \pm 3 \text{ \AA}$, $\rho = 7.16 \pm 0.02 \text{ g/cm}^3$, $R_b = 2.896$; Silver-3c, \approx content $5 \text{ wt.}\%$, CSR = $51 \pm 3 \text{ nm}$, period $a = 4.087 \pm 0.002 \text{ \AA}$, $\rho = 10.50 \pm 2 \text{ g/cm}^3$, $R_b = 4.566$, $R_{exp} = 13.00$, $R_{wp} = 14.11$.

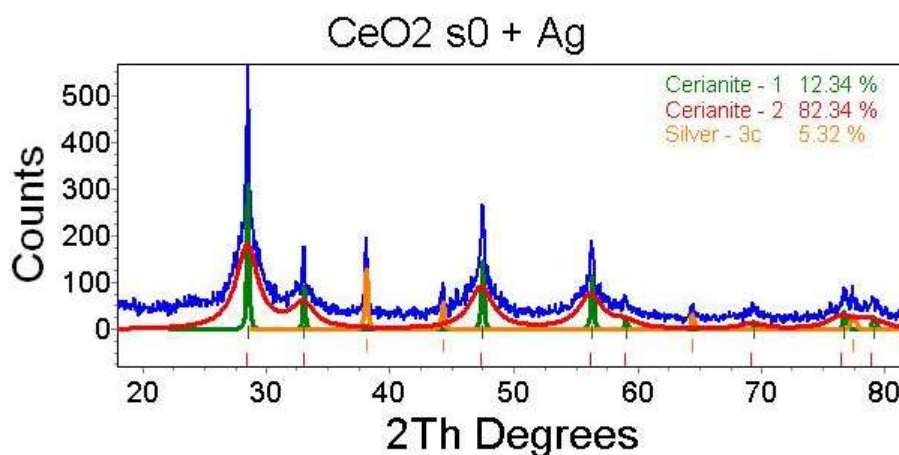


Fig. 1. XRD pattern of composite CeO₂-Ag.

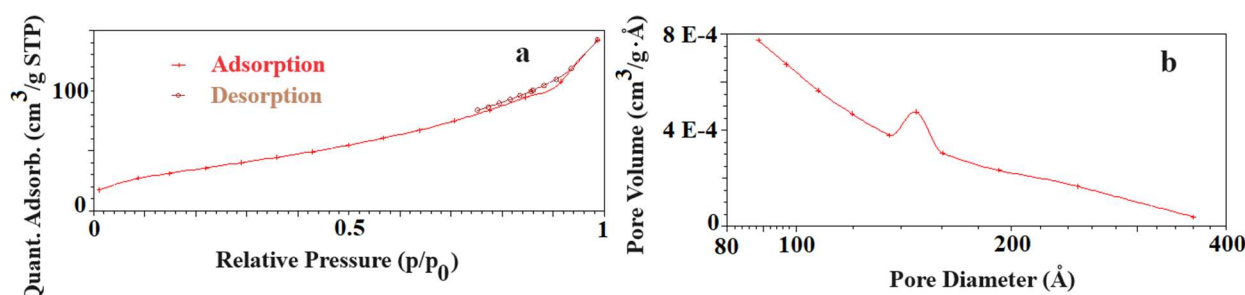


Fig. 2. For sample of CeO₂-Ag composite: a) Isotherm of adsorption and desorption; b) Pore size distribution.

3.2 BJH analysis

The Fig.2 shows the isotherms of the nitrogen desorption assembly and the pore size distribution in the CeO₂-Ag composite. The hysteresis loop on the adsorption desorption isotherm on the Fig.2a confirms the presence of mesopores in the composite. The composite had a wide pore size distribution ranging from 8 to 38 nm, with a maximum at a \sim of 15 nm. Comparison of the texture composite CeO₂-Ag with the corresponding characteristics of the individual samples of the pure CeO₂ NPLs (Table 1) obtained earlier in different evaporation modes showed that the texture parameters of the double composite were only slightly inferior to the CeO₂ NPLs in the pore volume, with the same order of pore diameter in both samples.

Table 1. Texture characteristics of NPles pure CeO₂ and binary composites CeO₂-Ag.

Sample	SSA, m ² /g	V _{pore} , cm ³ /g	D _{pore} , nm
CeO ₂ -Ag	126.5	0.111	18.6
CeO ₂ -1	158.3	0.505	17.8
CeO ₂ -2	129.3	0.350	23.8

3.3. SEM analysis

On Fig. 3 shows SEM images of the surface of double nanocomposite CeO₂-Ag made with different magnification. The synthesis product (Fig. 3a) had a form of 3D spatial nanostructures in the form of "clouds" made by agglomerates of NPles CeO₂ less than 10 nm, which were coated with placers of individual and chain NPles Ag, spherical in size from 10 to 200 nm (Fig. 3a,b), without obvious signs of the formation of Ce-O-Ag chemical bonds. Figure Fig. 3c shows individual spherical NPles Ag of 20 and 50 nm, consistent with XRD analysis results. NPles Ag are characterized by a smooth surface, which allows them to be easily distinguished against the background of cerium oxide agglomerates characterized by a rough-looking surface.

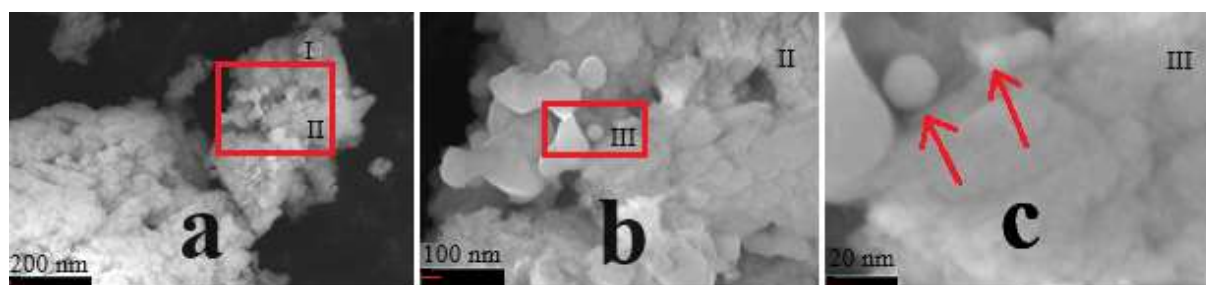


Fig. 3. SEM images of composite CeO₂-Ag with a different magnification (a) of the agglomerate of the composite CeO₂-Ag (I) of about 4–5 μm with a scattering of metal NPles Ag (red rectangle) of the surface of oxide NPles CeO₂; (b) Red rectangle II agglomerate region on the Fig.3a at greater magnification; (c) Rectangular area III (red rectangle on Fig. 3b) at greater magnification. Two spherical NPles Ag sizes from 20 to 50 nm (shown by red arrows) are clearly visible.

3.4. XPS analysis

The results of elemental analysis of the surface of CeO₂-Ag composite NPles by X-ray photoemission spectroscopy (XPS) are given in the Table 2. The Ag content of the composite turned out to be small (1.29 at.%), with a high concentration of carbon, probably adsorbed on the developed surface of the composite from the surrounding atmosphere. The atom ratio [O/Ce] = 3.22 deviated significantly from stoichiometric in the assumption that only CeO₂ was present in the final product. Excess oxygen is spent on the formation of CO₂, but it is not enough at such a high carbon concentration (31.49 at.%). It can be assumed that the composite CeO₂-Ag contains oxygen vacancies in a high concentration, which can compensate for the lack of oxygen atoms. This assumption confirms the presence of oxygen vacancies in the CeO₂ NP produced by the PEBE method, as previously shown in work [5].

Table 2. Chemical composition of the samples CeO₂-Ag by XPS.

Sample	Concentration, at. %				
	[O]	[Ce]	[C]	[Ag]	[O/Ce]
CeO ₂ -Ag	51.30	15.92	31.49	1.29	3.22

4. Conclusion

For the first time, using the radiation-chemical method, was carried out the synthesis of a mesoporous nanocomposite "cerium-silver dioxide" in aqueous AgNO₃ solution in the presence of NPles CeO₂ previously synthesized by PEBE method.

Element analysis data by XPS and XRD analysis confirmed the presence of Ag in the composition of the composite at a low concentration (1.29 at.% and 5.3 wt.%), which indicates a inhibition of the process of formation of NPles Ag in the presence of NPles CeO₂ in suspension. The synthesis product was free of related impurities and had a form of 3D spatial nanostructures in the form of "clouds" made by agglomerates of NPles CeO₂ less than 10 nm, which were coated with placers of individual and chain NPles Ag, spherical in size from 10 to 200 nm, without obvious signs of the formation of Ce-O-Ag chemical bonds. The presence of metal nanoparticles Ag and semiconductor CeO₂ makes it possible to count on the appearance of plasmon resonance in such heterophasic structures. Nevertheless, deposition of NPles Ag resulted in a sharp reduction in the SSA of the precursor-pure CeO₂ from 190.0 to 126.48 m²/g in the composite.

SEM images and good texture parameters (BET SSA = 126.5 m²/g, pore volume = 0.111 cm³/g and Pore Size = 18.6 nm) confirmed the mesoporous type of the resulting composite, indicating the prospect of its use as an adsorbent in cleaning water of contaminants or nanocontainer in various biomedical applications.

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