

UDC 546.655.3/4

Synthesis of the Nanopowders of CeO₂ and ZnO with Controllable Particle Size by Means of Homogeneous Hydrolysis in the Presence of Hexamethylenetetramine

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(Received June 1, 2010)

Abstract

Synthesis of the nanopowders of CeO₂ and ZnO was carried out from the solutions of cerium (III) and zinc salts in the presence of hexamethylenetetramine. The effect of the major synthesis parameters including the molar ratio of the reagents and synthesis temperature on the micromorphology of the formed oxide powders was established. The possibility to vary the size of ZnO and CeO₂ nanoparticles under the hydrothermal microwave conditions was demonstrated.

Key words: zinc oxide, cerium dioxide, nanomaterials

INTRODUCTION

Wide band gap oxide semiconductors, including zinc oxide, titanium, cerium, etc., are widely used in modern technology, including in the production of high-performance semiconductor components (thyristors, varistors), UV filters, and solar panels. The transition of these oxides into the nano state is accompanied by changing a number of existing and emerging a number of new functional properties. In particular, decreasing the particle size down to that comparable to the radius of exciton, can result in the appearing quantum effects and, therefore, in significant changing the photo-physical and photochemical properties of materials. This naturally causes a considerable interest demonstrated in recent years with respect to nanomaterials based on wide band gap oxide semiconductors. Thus, zinc and titanium oxides are considered the most promising photocatalysts; therewith decreasing the particle size provides a significant increase in their photocatalytic activity. In turn, reducing the par-

title size of nanocrystalline cerium dioxide is accompanied not only by changing the band gap, but also by a significant increase in the oxygen non-stoichiometry level of the material, thereby a steep increase in the biological activity is observed [1].

Traditionally, zinc, cerium and titanium oxides are synthesized *via* precipitation by strong bases from solutions of metal salts, followed by the calcination of the precipitate formed. The precipitation of hydrated metal oxides usually occurs under a significant supersaturation, which often causes the directional variation of solid product micromorphology to be almost impossible. A good alternative is the use of reagents capable of slowly hydrolyzing to form hydroxyl ions, which allows one to control the supersaturation level as well as to avoid local concentration gradients. These agents first of all include urea and hexamethylenetetramine.

Hexamethylenetetramine (HMTA) is synthesized *via* the reaction between ammonia and formaldehyde in the liquid phase

$$6\text{CH}_2\text{O} + 4\text{NH}_3 \leftrightarrow \text{C}_6\text{H}_{12}\text{N}_4 + 6\text{H}_2\text{O} \quad (1)$$

Reaction (1) is reversible, so that HMTA is slowly hydrolyzed in aqueous solutions to form ammonium hydroxide [2]. A partial hydrolysis of HMTA occurs also in the case of the storing the reagent in a humid atmosphere. The mentioned property of HMTA is used in the synthesis of dispersed oxides and hydrated oxides of a number of transition metals, lanthanides and actinides, including iron (III) [3, 4], manganese [5], aluminum [6], Sc [7], rhodium [8], uranium [9, 10], zirconium [11], as well as complex oxides, in particular zinc gallate [12]. The authors of a number of papers consider that using HMTA instead of traditional precipitators allows obtaining oxide nanopowders with a smaller particle size and a larger specific surface (see, *e. g.*, [6]).

The number of papers devoted to the development of homogeneous precipitation methods in the presence of HMTA is relatively small, even in comparison with the same works based on the use of urea. In some publications (see, *e. g.*, [13]), it is considered possible to adjust the size of nanoparticles *via* changing the conditions for homogeneous hydrolysis reaction of metal salts.

The purpose of this work consisted in studying the effect of synthesis parameters in the presence of HMTA (including, under microwave hydrothermal conditions) on the morphological characteristics of ZnO and CeO₂ fine powders and nanopowders.

EXPERIMENTAL

In order to obtain ceria nanopowders as starting materials we used chemical purity grade (NH₄)₂Ce(NO₃)₆ and hexamethylenetetramine.

The concentration of ammonium hexanitratocerate (IV) in the initial solutions was equal to 0.00394 M, the concentration of HMTA amounted to 0.0038, 0.0118, 0.0394, 0.0935, 0.1576 M.

The deposition of ceria was performed from solutions with a molar ratio of Ce/HMTA equal to 1 : 1, 1 : 3, 1 : 10, 1 : 24, 1 : 40.

The weighed sample portions of the starting materials were dissolved in distilled water (180 mL) and held thermostated in an open glass cell at 30, 60 and 90 °C. In the course of this procedure the solution was stirred with a magnetic stirrer. The duration of the synthesis at 60 and 90 °C was 1 h (the speed of rotation 1500

min⁻¹), the temperature accuracy was ±1 °C. In addition, in order to investigate the influence of the synthesis duration upon ceria particle size (IV), we performed the synthesis at 60 °C during 27 h at the molar ratio between the reactants equal to 1 : 10.

The resulting sediments were washed four times with distilled water with intermediate centrifugation (6000 min⁻¹) and dried at 50 °C during 24 h in a drying oven.

Hydrothermal microwave (HTMW) processing the solutions of ammonium hexanitratocerate (IV) and HMTA was carried out with the help of Berghof Speedwave MWS-3+ apparatus. We used poly(fluoroethylene) autoclaves with 100 mL volume capacity (filling level of the autoclave amounted to 50 %). The temperature of the suspension under treatment was monitored by IR pyrometer (accuracy of the temperature determination at 150 °C was equal to ±1 °C), the pressure inside the reactor was measured using an optical pressure sensor (the accuracy of pressure determination at 150 °C, was equal to 1 atm). Heating power was equal to 700 W, the rate of the temperature increase amounted to 40 °C/min. The synthesis was performed at 180 °C during 1 h.

After the experiment the autoclave was removed from the furnace and cooled down to a room temperature. The product obtained was isolated by centrifugation, washed several times with distilled water, and dried then during 24 h in air at the temperature of 50 °C.

Upon obtaining zinc oxide *via* homogeneous hydrolysis in the presence of HMTA, we used Zn(NO₃)₂ · 6H₂O (“ch.” grade) and HMTA (“kh. ch.” grade).

The synthesis under pre-hydrothermal conditions was carried out as it follows: zinc nitrate and HMTA solutions heated up to the temperature of isothermal exposure equal to 75, 85, 90 or 95 °C, (the concentration of zinc nitrate solution being 0.05 and 0.1 M, the molar ratio of the reactants 2 : 1, 1 : 1, 1 : 2, 1 : 5, 1 : 10; the HMTA concentration being of 0.05, 0.1, 0.2, 0.5, and 1.0 M) was stirred and heated at the predetermined temperature during 1, 2, 3, 5, 15, 30, 60, 150 min.

The synthesis of ZnO by HTMW processing was performed under the conditions similar to those described above. The rate of heating up

to the temperature of isothermal exposure during hydrothermal synthesis amounted to 2 °C/min. the treatment temperature, °C: 105, 115, 125, 135, 150, 170. The duration of treatment, h: 0.5, 1, 2, 4, 8, 24. In the course of HTMW synthesis, the heating power ranged within 350–1400 W; the synthesis temperature was equal to, °C: 105, 115, 125, 135, 150, 170; the process time was 30, 60 and 120 min.

After the synthesis the suspensions obtained were centrifuged, washed once with distilled water, centrifuged again and dried at 30–60 °C.

The XRD phase analysis of the samples was carried out using a Rigaku D/MAX 2500 diffractometer (CuK_α radiation) at the goniometer rotation speed ranging within 1–2 grad/min. The identification of the diffraction peaks was performed using JCPDS database. The XRD method was used to determine the size of coherent scattering regions (CSR). In order to determine the values of diffraction peak broadening we fitted the peaks by Lorentzian functions:

$$y(x) = y_0 + \frac{2A}{\pi} \frac{\omega}{4(x - x_0)^2 + \omega^2}$$

where A is the area under the peak, ω is the width at the half-height, x_0 is the peak centre position. The value of the physical broadening was calculated by the formula

$$\beta_{hkl} = \sqrt{\beta_{\Sigma}^2 - s^2}$$

where s is instrumental broadening ((0.09±0.01)°2θ). As a reference sample for determining the instrumental broadening we used single-crystal sapphire. The calculation of the size of coherent scattering region was performed using Scherrer formula:

$$D = K\lambda/\beta_{hkl}\cos\theta$$

Here K is the shape factor of the particles taken equal to 1; λ is X-ray wavelength equal to 0.154056 nm; β_{hkl} is the physical broadening of diffraction peak, rad. units; θ is the position of the diffraction peak. The relative error of CRS determination was equal to 5 %.

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the samples were performed using a PYRIS Diamond TG/DTA thermal analyzer (PerkinElmer). For the experiment, we used alundum and platinum crucibles. The portions of the samples were equal to 10–80 mg. We used a linear polythermal heating mode with the heating rate amount-

ing to 10 °C/min to up to temperature ranging within 900–1100 °C.

In order to analyze the micromorphology CeO₂ and ZnO nanopowders by means of transmission electron microscopy (TEM) we used a Leo 912 AB Omega electron microscope with the accelerating voltage equal to 100 kV. Before the investigation, the samples were placed on a copper mesh 3.05 mm in diameter coated by polymer film. Images were obtained in a transmission mode at magnification up to 500 000. In obtaining the electron diffraction (ED) images, we used a restricting aperture 0.4 μm in diameter.

Basing on the TEM data we determined the characteristic size of the particles obtained. For this purpose, we used several images of the same sample obtained at the same magnification; those characterize different sites of the sample. We measured the area of particles exhibited in the photographs, and then measured the diameter of the particles in the assumption that they are isotropic. Basing on the data obtained from measuring the particle diameter we plotted a histogram of particle size distribution. The resulting distribution was approximated by a Gaussian function according to the method of least squares, and then we determined the characteristic size of the particles and the standard deviation value from the parameters of the approximating function.

In order to analyze the micromorphology of ZnO powders by scanning electron microscopy (SEM) we used a Leo Supra 50 VP electron microscope (the magnification ranging within 5000–200 000) at the accelerating voltage ranging within 1–10 kV. In order to provide an efficient charge flow, the surface of the samples was sputtered by carbon.

The measurement of the specific surface area for ZnO powders was performed *via* low-temperature nitrogen adsorption using analyzers Sorbtometr-M and ATX-06 (grade A helium being used as a carrier gas). Prior to the measurements we performed degassing the samples under nitrogen within the temperature range of 50–200 °C during 30–120 min. Mass used portions is 100–500 mg. The nitrogen sorption was carried out at –196 °C, the desorption at –50 °C. The partial pressure of nitrogen was determined using a katharometer whose temperature was maintained at 45 °C. After power

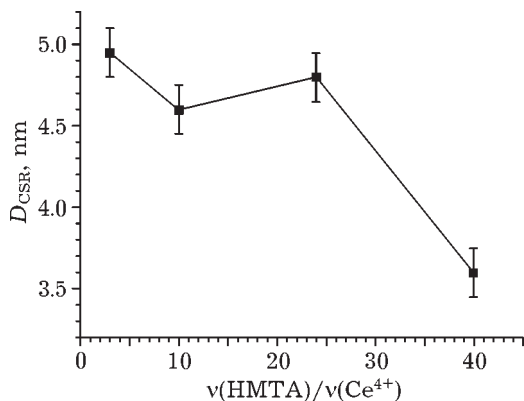


Fig. 1. Size of coherent scattering region for CeO_2 (D_{CSR}) depending on the molar ratio between HMTA and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (v) in the initial solution at the reaction temperature equal to 60°C .

turned on the device was heated during 30 min up to establishing a steady-state temperature of the thermal conductivity detector. Before measurements, the instrument was calibrated to improve the accuracy of pressure determination. The specific adsorption of nitrogen was measured at its partial pressure ranging within 0.05–0.40 bar (eight points), then basing on the data obtained we calculated the specific surface area of powders using Brunauer–Emmett–Teller (BET) model for six points (0.05–0.30 atm).

RESULTS AND DISCUSSION

According to the XRD phase analysis, the homogeneous hydrolysis of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ in the presence of HMTA under the conditions chosen results in the formation of single-phase cerium (cerianite, PDF No. 34–394). The analysis of XRD profiles allows one to conclude that the CeO_2 diffraction peaks are strongly broadened, which could be, to all appearance, connected with a small size of the particles forming CeO_2 .

Let us consider the data obtained in processing the XRD patterns for CeO_2 synthesized at 60°C with different Ce/HMTA molar ratio (1 : 3, 1 : 10, 1 : 24, 1 : 40). Figure 1 demonstrates the size of coherent scattering regions (CSR) for CeO_2 , depending on the composition of the initial solution. It is seen that with increasing the excess of the precipitant the average particle size demonstrates a decrease from 5.0 to 3.6 nm.

The results obtained in the processing of the XRD data are in good agreement with the TEM data. Indeed, the average size of the particles synthesized from the solutions with Ce/HMTA molar ratio of 1 : 3 and 1 : 24, are almost identical being about 5 nm, whereas the size of the particles obtained from the solutions with Ce/HMTA molar ratio = 1 : 40, is about 4 nm.

With increasing the temperature of CeO_2 synthesis up to 90°C , the ratio between the initial reagents exerts a greater effect on the particle size of the reaction product. So, with a small surplus HMTA (1 : 3) the particle size of CeO_2 is about 7 nm, which is much higher than the value for particles obtained from a similar solution at 60°C . With increasing the excess of HMTA to the ratio values of 1 : 10, 1 : 24 and 1 : 40, the CeO_2 particle size in powders synthesized at 90°C , neatly decreases down to 4.9, 4.9 and 4.2 nm, respectively. It should be noted that the particle size of CeO_2 films deposited from the solution with Ce/HMTA molar ratio equal to 1 : 10 and 1 : 24, at 60 and 90°C , do not differ amounting to about 5 nm.

Figure 2 demonstrates the results of processing the XRD patterns of the samples synthesized from the solutions with different Ce/HMTA ratio at the temperature values ranging from 30 to 180°C . It can be seen that with increasing the synthesis temperature, a natural increase in the CSR of CeO_2 occurs. Under the pre-hydrothermal conditions, the size of particles synthesized at identical temperature values, is close enough to each other, whereas in the case HTMW synthesis at 180°C there is a

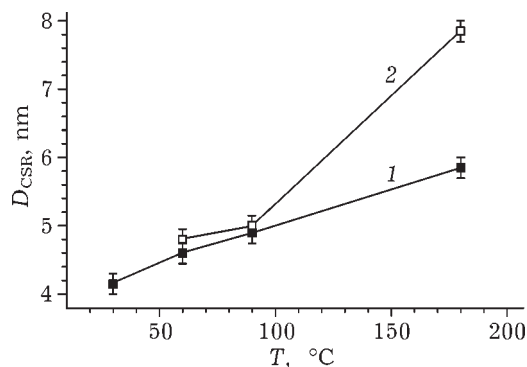


Fig. 2. Particle size (D_{CSR}) of nanocrystalline cerium dioxide depending on the temperature of homogeneous precipitation. Ce/HMTA ratio in the original solution: 1 : 10 (1), 1 : 24 (2).

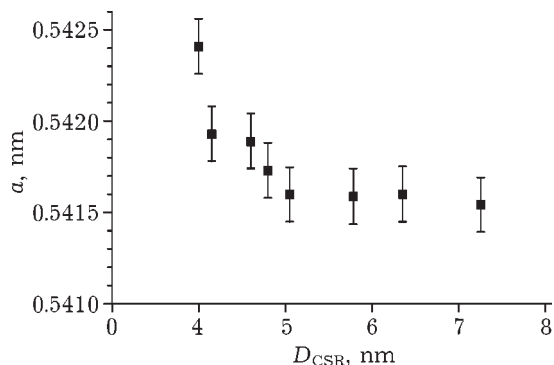


Fig. 3. Cell parameter (a) depending on CeO_2 particle size (D_{CSR}) for samples synthesized by means of homogeneous hydrolysis.

significant difference between the sizes of CSR for the samples synthesized from the solutions with different molar HMTA excess.

It is known that with decreasing the particle size of cerium dioxide, increasing the degree of oxygen non-stoichiometry is observed together with the unit cell parameters (see Fig. 2, a). In addition, for macrocrystalline dioxide cerium the unit cell parameter is equal to 0.541 nm, and when the particle size decreases down to several nanometres, this parameter could increase, according to different data, up to 0.545–0.561 nm [13].

The results of calculating the lattice parameters of the samples we synthesized are demonstrated in Fig. 3. One can see that the CeO_2 unit cell parameter exhibits power dependence on the particle size, and with increasing the particle size from 3.5 to 7 nm the unit cell parameter decreases from 0.5423 to about 0.5417 nm. The most significant decrease in the cell parameter is observed within the range of 3.5–4.5 nm, and then this value remains constant within the calculation error.

Thus, varying of the molar ratio between the reactants as well as the reaction temperature for the homogeneous hydrolysis of ammonium hexanitratocerate (IV) in the presence of HMTA allows one to vary within a significant range the size CeO_2 nanoparticles formed and their oxygen non-stoichiometry.

A similar influence of the synthesis parameters upon the dispersion level of the fusion products is observed for zinc oxide.

According to the XRD phase analysis, heating the zinc nitrate and HMTA solutions at 75 °C

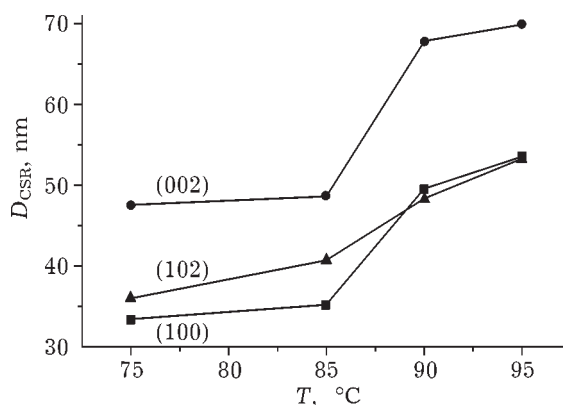


Fig. 4. Size of CSR in ZnO samples obtained by the hydrolysis of 0.05 M $\text{Zn}(\text{NO}_3)_2$ solution in the presence of 0.05 M HMTA solution during 30 min depending on the temperature of synthesis.

and at higher temperature values results in the formation of single-phase zinc oxide. The size of the ROC exhibits an increase with increasing the temperature of the reaction (Fig. 4), which is associated with gradual growing the ZnO particles formed under low supersaturation conditions. According to the XRD data, the growth occurs mainly in the direction (002), which is quite typical for ZnO [14] being indirectly confirmed by SEM data.

In a complete accordance with the RGA and TEM data, increasing the synthesis temperature neatly results in decreasing the specific surface of the powders obtained from 25 to 15 and 2 m^2/g at 75, 85 and 95 °C, respectively. A significant reduction in the specific surface area

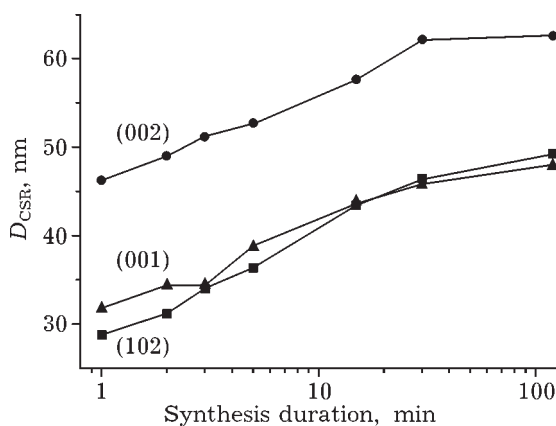


Fig. 5. Size of CSR for ZnO powders synthesized at 90 °C within the range of 1–120 min from 0.1 M $\text{Zn}(\text{NO}_3)_2$ and 0.1 M HMTA solutions depending on the duration of the synthesis.

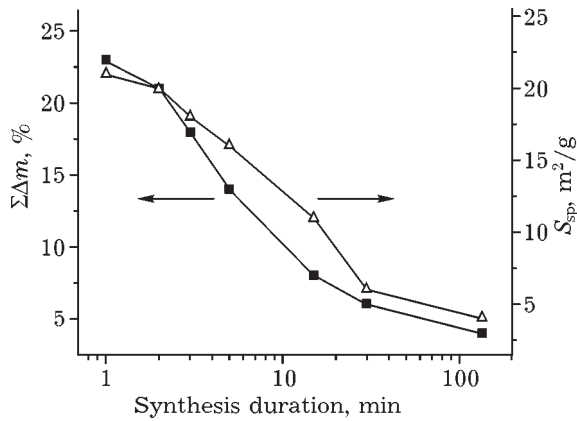


Fig. 6. Total mass loss ($\Sigma\Delta m$) and the specific surface area of powders ZnO, synthesized at 90 °C within the range of 1–120 min from solutions 0.1 M $\text{Zn}(\text{NO}_3)_2$ and 0.1 M HMTA solutions depending on the duration of the synthesis.

with a relatively small increase in the size of the ROC inherent in ZnO particles, to all appearance, could indicate that in the samples there are some impurities of XRD amorphous zinc hydroxo derivatives characterized by high specific surface values.

In order to study the dynamics of ZnO particle growth under isothermal conditions, we synthesized a series of samples with varying the processing time at a constant temperature (90 °C) and the concentration of the reagents (0.1 M). Figure 5 demonstrates that with increasing the duration of the synthesis the CSR size monotonically increases from 30 to 47 nm in the directions (100) and (101) and from 47 to 63 nm in the direction (002). It should be noted that the samples synthesized within the range of 1–3 min are not single-phase; their XRD patterns present exhibit low-intensity diffraction peaks corresponding to zinc hydroxocarbonate. With further increasing the duration of the synthesis, the corresponding peaks in the XRD patterns disappear, and the product synthesized is presented by single-phase ZnO.

With increasing the duration of the synthesis at the constant temperature of the reaction mixture, the growth of zinc oxide particles is accompanied by a monotonic decrease in the specific surface value. Figure 6 demonstrates the total mass loss of and the specific surface of samples depending on the duration of the synthesis. One can see that these values exhibit

sympatric change. This means that the reduction of the specific surface of the samples is primarily connected with the decomposition of residual XRD amorphous zinc hydroxo compounds with a high specific surface area, being only to a small extent caused by the growth of ZnO particles.

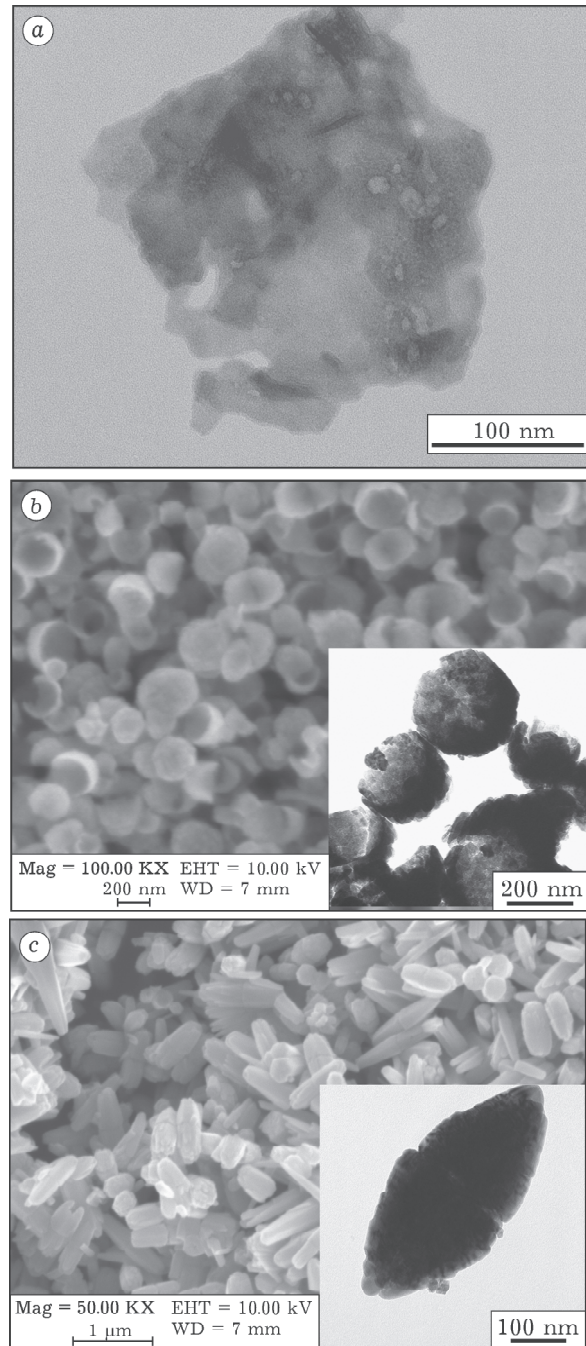


Fig. 7. SEM and TEM micrographs for powders obtained *via* slow hydrolysis of a of 0.1 M $\text{Zn}(\text{NO}_3)_2$ solution in the presence of HMTA (0.1 M) at 90 °C during 0 (a), 3 (b) and 30 min (c).

A significant effect of the duration synthesis on the micromorphology of ZnO particles obtained is registered basing on electron microscopy data, too (Fig. 7). In the case of the synthesis duration ranging within 3–5 min, the products consist of monodisperse hollow hemispherical aggregates being of 200–400 nm in diameter, composed of crystallites with the size ranging within 20–40 nm (see Fig. 7, b), which is in a good agreement with agrees well with RGA data. With increasing the duration of synthesis up to 15–120 min, one can observe the formation of ZnO rods; 200–500 nm in diameter and 0.5–3 μm long (see Fig. 7, c). The proximity of the characteristic diameter of the particles obtained in the synthesis with different duration, block structure inherent in the resulting ZnO rods (see Fig. 7, c, inset), as well as the fact that a short-time synthesis results in a low (less than 1 % of the theoretical) yield of the product, allows drawing a conclusion that hemispheres formed within the first 3–5 min of the synthesis act as primary particles, wherefrom larger particles of zinc oxide further grow according to the mechanism of autocatalysis [15].

In order to study the potentialities of further increasing the dispersion level of materials synthesized we performed a systematic investigation of the micromorphology of ZnO powders obtained *via* HTMW synthesis from 0.1 M Zn(NO₃)₂ and 0.1 M GMTA solutions at higher temperature values (105–170 °C).

The XRD data for the samples obtained *via* homogeneous hydrolysis of zinc nitrate in the presence of HMTA under HTMW processing, indicate that the synthesis temperature exerts almost no effect on the CSR size inherent in the samples. Thus, the size of CSR in the (100) and (101) directions are equal to 35–40 nm, whereas for the direction (002) this value ranges from 50 to 60 nm. It should be noted that the size of CSR for the samples obtained *via* HTMW synthesis using HMTA is relatively small compared to the size of the crystallites in the powders obtained *via* zinc hydroxide hydrothermal treatment.

Indeed, according to the low-temperature nitrogen adsorption (Fig. 8), the specific surface area of the samples obtained even at low temperature values of HTMW synthesis (105 °C)

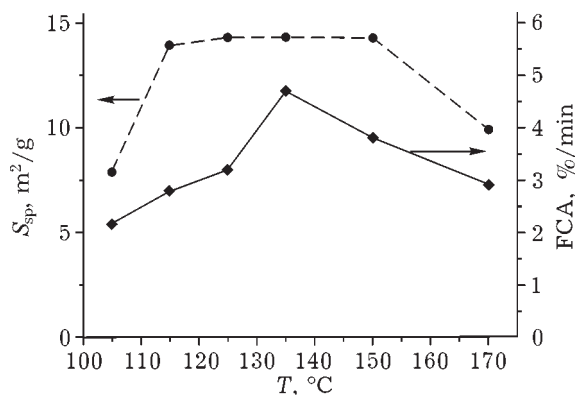


Fig. 8. Specific surface of ZnO samples and their photocatalytic activity (FCA) depending on the temperature of HTMW synthesis from 0.1 M Zn(NO₃)₂ and 0.1 M HMTA solutions during 30 min.

is much higher than the specific surface for ZnO samples synthesized under pre-hydrothermal conditions from the solutions with the same concentration (2–5 m²/g). This could be connected with the fact that under the conditions of the rapid microwave heating of the reaction mixture occurring uniformly across the range of the entire volume up to the temperature higher than 100 °C one can attain a much more higher supersaturation level of the solution than for the synthesis under pre-hydrothermal conditions within the temperature range of 75–95 °C. This provides a higher nucleation rate and, therefore, results in a greater dispersion level of the samples. In turn, a high anisotropy level of the particles synthesized prevents their aggregation and, therefore, results in reducing the surface area of the material. The synthesized powders consist of rod-shaped zinc oxide particles 200–1000 nm in 30–150 nm length and diameter, and the particle size of ZnO is much smaller compared to the size of the particles obtained under pre-hydrothermal conditions.

Increasing the temperature of HTMW processing from 105 to 115 °C results in a significant increase in the specific surface area (from 7 to 14 m²/g). At the same time, further increasing the temperature up to 150 °C, exerts almost no effect on this value which varies within the instrumental error of measurement (from 13.9 to 14.3 m²/g). Increasing the treatment temperature up to 170 °C results in a slight decrease in the specific surface area (9.9 m²/g), which could be caused by the growth of zinc oxide

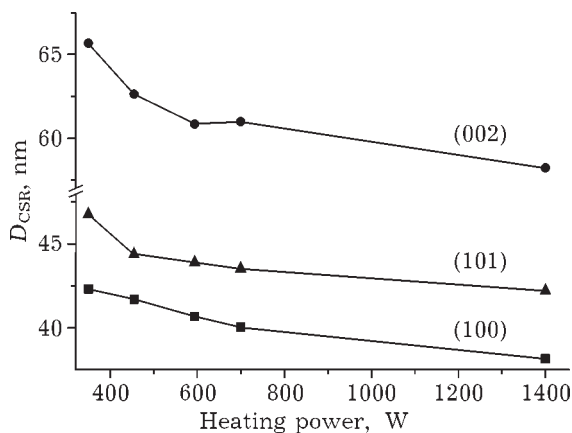


Fig. 9. Size of CSR for ZnO depending on microwave heating power.

particles according to the dissolution-crystallization mechanism.

Conducting a series of experiments with HTMW synthesis at 135 °C during 0.5–4 h demonstrated that the duration of the synthesis has no significant effect either on the surface area or the size of the crystallites. Thus, with increasing the duration of the synthesis up to 4 h value of S_{sp} ranges from 13.5 to 14.8 m²/g, whereas the particle size remains almost unchanged (about 35 nm).

A much more important factor is presented by the rate of heating of the solution up to the temperature of isothermal holding, determined by the power of microwave heating. Just this quantity determines the supersaturation level of the solution in the course of the treatment, which should affect the micromorphology of ZnO. Indeed, according to the XRD data, increasing the heating power of the solution from 350 to 1400 W results in monotonic decreasing in the size of CSR (Fig. 9). Reducing the size of the ZnO particles synthesized can also be observed according to the SEM data, therewith the increase in the heating power from 350 to 1400 W provides reducing both the length of the particles and their diameter.

CONCLUSION

Thus, within the framework of the present it was demonstrated that the homogeneous hydrolysis in the presence of hexamethylenetetramine represents a promising method for the synthesis of nanocrystalline ZnO and CeO₂ powders with controlled particle size. The influence of main synthesis parameters, including the molar ratio between reactants and the synthesis temperature upon the micromorphology of the oxide powders formed was established. It was demonstrated that performing the synthesis under microwave hydrothermal conditions allows additionally varying the size of ZnO and CeO₂ nanoparticles.

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