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SYNTHESIS OF ZnO NANOPOWDER PREPARED IN NATURAL POLYMER MEDIA

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Zinc oxide nanopowders are an important metal oxide with unusual semiconducting properties and wide application in various fields, such as catalysis, optic, pigment, piezoelectric devices, chemical sensors, cosmetic ingredients, medicine. Due to the large numerous of toxic chemicals and extreme environment employed in the chemical production of ZnO nanopowders, green chemistry methods employing the use of different biological materials (plants, fungus, bacteria, algae) and natural polymers (gelatin, starch, different proteins) have been adopted [1-3]. Besides that, the use of natural sources in the synthesis of nanomaterials can have a low cost and eco-friendly approach.

We studied the green chemical approach for fabrication method using natural polymer agar and the physical and chemical characteristics of zinc oxide nanopowders.

Agars are known as water-soluble, gel-forming polysaccharide extracts from agarophyte members of the Rhodophyta. Agars are usually composed of repeating agarobiose units alternating between 3-linked β -D-galactopyranosyl (G) and 4-linked 3,6-anhydro- α -L-galactopyranosyl (LA) units. This disaccharide regularity may be marked or modified in a number of ways by substitution of hydroxyl groups with sulfate hemiesters and methyl ethers in various combination and more rarely with a cyclic pyruvate ketal as 4,6-O-[(R)-1-carboxyethylidene] acetal and sometimes by

additional monosaccharides [4]. Typical constituents found in agar group polysaccharides are shown on Figure 1.

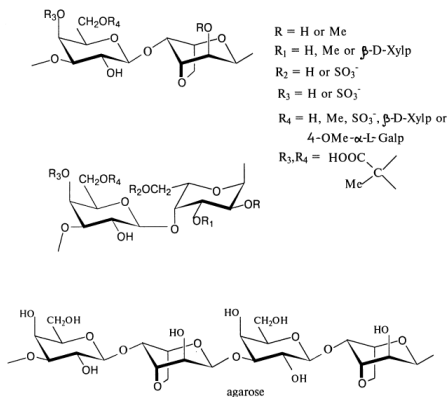


Fig. 1. Structural features of the agar group polysaccharides

ZnO nanopowders were synthesized by sol-gel technique with agar as a green stabilizer. Deionized water was used as solvent. The zinc nitrate solution was added to the agar solution, and the container was moved to a water bath. The temperature of the water bath was fixed at 80°C. Stirring was continued for 12 h to obtain a brown-yellowish gel (Fig. 2). The final product was calcined at 500, 600 and 700°C in air for 2 h to obtain ZnO nanoparticles.



Fig. 2. Schematic illustration of ZnO sintering process by sol-gel method

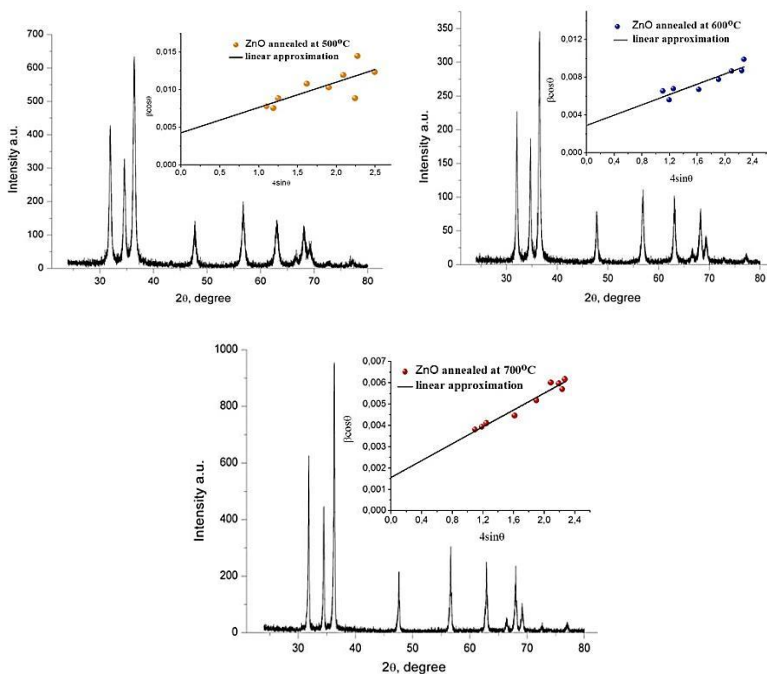


Fig. 3. XRD pattern and Williamson-Hall analysis of ZnO nanopowders prepared in agar media prepared at different calcinations temperature

Fig. 3 shows XRD patterns and Williamson-Hall plots of zinc oxide nanopowder synthesized at 500°C, 600°C, 700°C. It is seen that the diffractograms were possible to record the reflexes characteristic of zinc oxide with Miller – Bragg indices (100), (002), (101), (102), (110), (103), (200), (112), (201), which correspond to the angles $2\theta = 31.8^\circ; 34.5^\circ; 36.3^\circ; 47.7^\circ; 56.7^\circ; 63.0^\circ; 66.5^\circ; 68.1^\circ; 69.2^\circ$, respectively. According to the X-ray phase analysis, it was found that single-phase ZnO is formed at 500°C (JCPDS card # 89-7102). The tensile strain and the particle size increase with an increasing the heating temperature from 500 °C to 700 °C.

Reflexes on diffractogram (500 °C) were indexed in hexagonal syngony (space group $P6_3mc$) and unit cell parameters are calculated: $a = 3.2363 \pm 0.0061 \text{ \AA}$, $c = 5.2127 \pm 0.0225 \text{ \AA}$, volume $V = 47.281 \pm 0.383 \text{ \AA}^3$, number of formula units $Z = 2$. Unit cell parameters of ZnO nanopowder synthesized at 600 °C: $a = 3.2404 \pm 0.0017 \text{ \AA}$, $c = 5.1914 \pm 0.0038 \text{ \AA}$, $V = 47.209 \pm 0.083 \text{ \AA}^3$; at

700 °C: $a = 3.2516 \pm 0.0005$ Å, $c = 5.2100 \pm 0.0012$ Å, $\rho = 6.7$ g/cm³, $V = 47.706 \pm 0.027$ Å³.

The average crystallite size and micro-strain of the present powder were estimated using Williamson-Hall (W-H) method. The two equations presented below assume that the size (β_D) and strain (β_ϵ) broadening represent the total integral breadth (β_{hkl}) of a Bragg peak. The theta dependences of the size and strain broadening in the W-H analysis are described by the following equations:

$$\beta_{hkl} \cos \theta_{hkl} = \frac{K\lambda}{D_{hkl}} + 4\epsilon \sin \theta_{hkl}$$

where D_{hkl} (nm) is the average size of crystallites along the direction normal to the diffraction plane (hkl), ϵ is the strain, K is the shape factor equal to 0.9, λ is the x-ray wavelength 0.15406 nm of Cu_{Kα} radiation, β_{hkl} is the integral breadth of the peak related to the diffraction plane (hkl) and θ_{hkl} is the Bragg angle in radians for the crystallographic plane (hkl). From the XRD data, β_{hkl} was obtained by Lorentzian peak fit using the PeakFit 4.2 software.

The $\beta_{hkl} \cos \theta_{hkl}$ term was plotted against $4\sin \theta_{hkl}$ for the orthorhombic perovskite LuFeO₃. After performing linear fit of the data points, it was estimated the average crystallite size from the y-intercept ($K\lambda/D_{hkl}$) and lattice strain from the slope (ϵ), as shown in Fig. 3.

The crystalline size of the ZnO nanoparticles calcined at temperatures of 500, 600, and 700 °C were found to be 32 ± 2 , 61 ± 2 , and 87 ± 2 nm, respectively. The angular coefficient of the line is positive. This indicates that tensile stresses act in ZnO samples.

From the obtained data of powder X-ray diffraction, their analysis and processing, it can be stated that with increasing heat treatment temperature, the parameter a of the unit cell of zinc oxide increased slightly, while the parameter c remained practically unchanged within the experimental error. The calculated value of the X-Ray density of the sample calcined at 700°C decreases by only 0.6% relative to the sample calcined at 500°C. This fact may indicate the redistribution of defect centers in the cationic (zinc) and anionic (O) sublattices with increasing temperature. Also, as the temperature increased, the size of the coherent scattering regions increased approximately threefold: from 32 nm (500°C) to 87 nm (700°C), while the magnitude of microdeformations ϵ decreased.

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АЛКІЛЮВАННЯ КЕТЕНАМІНАЛЕЙ ІЗ ЗАСТОСУВАННЯМ УЛЬТРАЗВУКОВОГО ВИПРОМІНЮВАННЯ

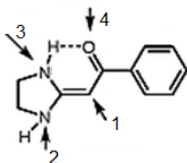
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Гетероциклічні кетенамінали (ГКА), які можна також віднести до циклічних 1,1-ендіамінів, є універсальними проміжними сполуками в органічному синтезі. Цікавою особливістю цих сполук є їх будова. В молекулах кетенаміналей є 4 нуклеофільні центри: два атоми Нітрогену аміногруп, атом Оксигену карбонільної групи та α -атом Карбону.



Супряження електронно-донорних аміногруп та електронно-акцепторної карбонільної групи призводить до значного підвищення електронної густини на α - атомі Карбону та сильної поляризації подвійного зв'язку C = C, внаслідок чого нуклеофільність α -атома Карбону набагато вища, ніж на атомах Нітрогену аміногруп.