The Effect of Different Organic Gelating Agents on Grain Size of ZnO Nanoparticles

Ş. KARAAL^{a,*}, H. KÖSE^a, A.O. AYDIN^a AND H. AKBULUT^b

^aDepartment of Chemistry, Arts and Sciences Faculty, Sakarya University, 54187, Sakarya, Turkey

^bDepartment of Metallurgy and Material Engineering, Faculty of Engineering, Sakarya University
54187, Sakarya, Turkey

In this work, sol-gel method was used in order to synthesize ZnO nanoparticles. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was used to obtain ZnO precursor solution. To investigate the effect of organic gelating agents on grain size, various organic gelating agents such as triethanolamine (TEA), glycerin (GLY), ethylene glycol (EG), citric acid (CA) and tartaric acid (TA) were used. X-ray diffraction analysis was used for phase identification and grain size calculation. ZnO powders were characterized by using Fourier-transform infrared spectroscopy, scanning electron microscopy and atomic force microscopy.

DOI: [10.12693/APhysPolA.125.338](https://doi.org/10.12693/APhysPolA.125.338)

PACS: 81.20.Fw, 81.07.Bc

1. Introduction

ZnO is a semiconducting material which has direct wide band gap of 3.37 eV and high excitonic binding energy of 60 meV [1]. It is one of the important metal oxide materials because of many potential applications, such as piezoelectric transducers, optical waveguides, conductive gas sensors, transparent conductive electrodes, solar cell windows [2]. Due to its excellent electrical and optical properties, ZnO is so useful in electronics and optoelectronic devices [3]. ZnO nanomaterials are extensively used as electrode active material because of their high electrochemical activity, e.g. Ni-MH cells, lithium cells, solar cells, fuel cells [4]. Recently, various methods have been employed to produce ZnO, including vapor decomposition, precipitation, thermal decomposition, and sol-gel process. Among these methods, the sol-gel process is more attractive due to providing good homogeneity, easy composition control, low process temperature, low equipment costs, and good optical properties [5, 6].

In nanoindustry, citric acid (CA) is often used in nanoparticle synthesis to control the size and morphology. Citrate ion can undergo a facile exchange with another surface functional groups and this makes citrate a good ligand in preparation of nanomaterials [7]. CA is used to obtain glassy gel precursor to synthesize ZnO nanoparticles [8]. So, gelating agents such as CA provide to form gel structure via chelation reactions. Like CA, triethanolamine (TEA) [9], glycerin (GLY) [10], ethylene glycol (EG) [11] and tartaric acid (TA) [12] can also be used as organic chelating agents. In this work, ZnO nanoparticles were fabricated via sol-gel method using different organic gelating agents such as TEA, GLY,

EG, CA and TA. It was specifically aimed to investigate the effect of different organic gelating agents on the ZnO nanoparticles for the possible applications such as solar cells and Li-ion battery electrodes.

2. Experimental

In the experimental stage, firstly, different sols were prepared by adding $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ precursor to 40 mL absolute ethanol. The solutions were stirred with a magnetic stirrer and heated to 50 °C. During the stirring at 50 °C, the solutions were cloudy. Certain amounts of TEA, GLY, EG, CA, and TA were added to five sols until forming the complex reaction between Zn^{2+} cation and organic gelating agents. After the addition of these gelating agents, the solutions became transparent. The resultant sols were dried at 150 °C in air after stirring and heating a few hours. Then, these dried powders were precalcined at 300 °C and subsequently calcined at a heating rate of 1 °C/min up to 500 °C and left at 500 °C for 2 h. Produced ZnO powder samples were coded as ZnO-TEA, ZnO-GLY, ZnO-EG, ZnO-CA, and ZnO-TA for the addition of TEA, GLY, EG, CA, and TA, respectively.

The produced nanoparticles were analyzed by scanning electron microscopy (SEM) (by JEOL-JSM 6060LV) and atomic force microscopy (AFM). AFM measurements were performed with a NTEGRA P9 (NTEGRA Prima) scanning probe system from NT-MTD, Moscow, Russia. Measurements were carried out in air with semi-contact mode. XRD analysis was performed with X-ray diffractometer (Rigaku D/MAX/2200/PC model device) using $\text{Cu } K_\alpha$ radiation ($\lambda = 1.54050 \text{ \AA}$) with 2°/min scanning speed using a grazing angle of 5°. FT-IR analysis was carried out on a UATR two Perkin-Elmer Fourier transformation infrared spectrometer. Phase analysis, nucleation and growth structures were investigated and the grain size of the resultant films was calculated.

*corresponding author; e-mail: sdombaycioglu@sakarya.edu.tr

3. Results and discussion

SEM micrographs of ZnO nanoparticles produced by adding different organic gelating agents presented in Fig. 1. As can be seen in Fig. 1a, ZnO powders which were prepared with the addition of TEA (ZnO-TEA) showed coarse-grained particles with nanorod-like morphology. For GLY added ZnO sample (ZnO-GLY), very fine, homogeneous and spherical nanosized particles were obtained, as seen in Fig. 1b. As can be seen from Fig. 1c, ZnO nanoparticles synthesized with EG (ZnO-EG) also showed spherical nanoparticles and very similar morphology with ZnO-GLY sample. In Fig. 1d, CA added ZnO sample (ZnO-CA) showed a plate-like morphology with a coarsening of ZnO nanoparticles, and agglomeration was also observed. Figure 1e indicated that ZnO nanoparticles, synthesized with TA addition (ZnO-TA) showed agglomerated nanoparticles and spherical particles seemed as grape-like morphology. As a result, ZnO samples added organic gelating agents, which have similar functional groups, represent similar morphology.

Fig. 1. SEM images of ZnO nanoparticle samples produced by different gelating agent additions: (a) ZnO-TEA, (b) ZnO-GLY, (c) ZnO-EG, (d) ZnO-CA, (e) ZnO-TA.

AFM analysis was applied to investigate the morphology of two ZnO samples. ZnO-TEA and ZnO-GLY samples, which have different morphologies, were used to obtain detailed information about the porosity of particles. In Fig. 2a and b, 3D AFM images of ZnO-TEA and ZnO-GLY samples can be seen, respectively. Both of the samples exhibit mesoporous structure with nanograins, which are also consistent with SEM images.

XRD method was used to characterize the crystal structure of ZnO nanoparticles. Figure 3 shows the XRD patterns of the nanoparticles produced by different organic gelating agents. The results show that there is no significant preferential nucleation and growth by changing organic gelating agents. XRD results of ZnO nanoparticles showed predominant crystal plane of (101), (100) and (002) planes [13]. XRD patterns of these samples are in agreement with the typical ZnO diffraction pattern (JCPDS No. 98-000-0111). The strongest peak

Fig. 2. AFM images of ZnO samples produced by the addition of gelating agents: (a) ZnO-TEA and (b) ZnO-GLY.

for each case is the (101) plane and peaks of ZnO indicated the broadest diffraction (101) peak which suggests that the nanoparticles are very small in size [14]. Therefore, the intensity of peaks gives information about grain size. As can be seen from Fig. 3, ZnO-TEA showed the sharpest diffraction peaks and ZnO-TA showed the broadest diffraction peaks. It is concluded that ZnO-TA has minimum grain size and ZnO-TEA has maximum grain size.

Fig. 3. XRD results of ZnO nanoparticles produced with various gelating additions.

Scherrer's formula (Eq. (1)) was used to calculate the grain size of the ZnO nanoparticles by using XRD data

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

In this formula, D is the mean grain size of crystalline structure, λ is X-ray wavelength, β is full width at half maximum (FWHM) or integral breadth of XRD peak and θ is the Bragg angle. Grain size of samples determined by Scherrer's formula for the (101) plane of ZnO crystal can be seen in Table. Maximum grain size (75 nm) was obtained from the first sample ZnO-TEA. Minimum grain

size (35 nm) was obtained from the ZnO–TA sample. ZnO nanoparticles synthesized by adding organic gelating agents, which have similar functional groups, represent similar grain structures, which were also proved by SEM micrographs.

Fig. 4. FTIR spectra of ZnO samples produced by the additions of (a) ZnO–TEA, (b) ZnO–GLY, (c) ZnO–EG, (d) ZnO–CA, and (e) ZnO–TA.

TABLE

Grain size of ZnO particles obtained from sols with different gelating agents.

Samples	Gelating agent	Grain size [nm]
ZnO–TEA	TEA	75
ZnO–GLY	GLY	47
ZnO–EG	EG	46
ZnO–CA	CA	36
ZnO–TA	TA	35

Figure 4 shows the FTIR spectra of pristine ZnO samples. Fourier transform infrared spectra are generated by the absorption of electromagnetic radiation in the frequency range of 350 to 4000 cm^{-1} . Different functional groups and structural features in the molecule absorb at characteristic frequencies. The frequency and intensity of absorption are the indication of the band structures and structural geometry of the molecule [15]. The broad bands of the characteristic peaks assigned to the ZnO appear between 350 and 600 cm^{-1} from the stretches of Zn–O bonds in Fig. 4a–e.

4. Conclusions

ZnO nanoparticles were fabricated via sol–gel method with different organic gelating agents such as TEA, GLY, EG, CA, and TA. XRD, FTIR, SEM and AFM analyses

were performed to investigate the morphologies, phase analysis, nucleation and growth structures of nanosized ZnO samples. XRD and FTIR analyses confirmed to ZnO crystal structure, SEM and AFM images indicated nanosized and mesoporous nature. The calculated grain size of ZnO particles with Scherrer's formula was supported with SEM and XRD results. According to calculations of grain size, ZnO–TA nanoparticles showed minimum grain size (35 nm), whereas ZnO–TEA showed maximum grain size (75 nm). Consequently, ZnO nanoparticles synthesized by adding different organic gelating agents, which have similar functional groups, represent similar results for the XRD, SEM, and FTIR analyses. The results obtained from XRD, FTIR, SEM, and AFM are compatible with each other and the results show that nanosized ZnO particles can be used for application of electrodes such as sensors, solar cells and Li-ion batteries.

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