OPTIMIZATION OF NANOSTRUCTURED ZnO-PARTICLE FABRICATION ROUTE WITH DIFFERENT ALCOHOLS AND VARYING SODIUM HYDROXIDE CONCENTRATION

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Abstract

Nanostructured zinc oxide particles are fabricated with the sol-gel technique. The influence of the sodium hydroxide concentration, type of alcohol, and temperature are investigated using fractional factorial experimental design. Parameter ranges were zinc acetate concentration from 0.5 M to 1.5 M, sodium hydroxide concentration from 0.8 M to 2.4 M, annealing time from 20 h to 60 h, and oven temperature from 40 °C to 100 °C. A white precipitate is obtained with slowly adding zinc acetate dehydrated onto sodium hydroxide, under agitation. Such precipitate is washed three times in deionized water and ethanol. The resulting particles are characterized by scanning electron microscopy. A highly homogenous production of nanostructured particles is obtained with $Zn(CH_3COO)_2$ *=0.5 M, NaOH=2.4 M, T=100 °C, t= 20 h.*

1 Introduction

Nanostructured zinc oxide, *ZnO*, has drawn a great deal of attention due to its various properties, such as: piezoelectricity, transparency in the infrared region, biocompatibility, opto-electricity [1], [2], [3], [4]. As a result, zinc oxide has found many applications in the industry, such as: electronics, pharmaceuticals, cosmetics, food packaging [5], [6], [7]. Such applications are related to the fact that *ZnO* is a wide bandgap semiconductor, and it is also a biocompatible material with a high isoeletric point, IEP. The *ZnO* IEP is about *9.5*, which makes it suitable for absorption of proteins with low IEP, as protein immobilization is primarily driven by electrostatic interaction [4].

Nanostructured *ZnO* powders and thin films are prepared using different techniques, such as: sol-gel synthesis, sputtering, chemical vapor deposition, spin coating, thermal evaporation [4], [5], [8], [9], [10], [11], [13], [14]. The synthesis *ZnO* nanoparticles can be achieved by precipitation from a solution with a soluble metal salt with hydroxide ions. Flower-shaped nanostructured particles have been produced using zinc acetate, $Zn(CH_3COO)_2$, and sodium hydroxide, *NaOH*, as precursors [4], [8], [9].

As is expected, temperature and reactant concentration influence the fabrication process [9], [10], [11], [16], [17]. With respect to nanostructure fabrication, temperature is an important factor that affects ZnO morphology, however most studies have concentrated in the high temperature range, such as *600 °C* to *900 °C* [19], [20]. Some reports deals with low temperature deposition (*50 °C, 90 °C, 180 ° C*) with different reactants (*NaOH*, methenamine, methanol) and fabrication techniques (horizontal tube furnace, refluxing, chemical vapor deposition) [4], [8], [9], [12], [13], [14]. This work is focused on the lower temperature range, up to *100 °C*, with aiming at achieving a low-cost fabrication route for industrial applications.

In this paper, a low-temperature homogeneous formation of ZnO particles with nanotextured surface is reported. The hydrothermal technique is used to produce the precipitate, and the influence of the *NaOH* concentration, zinc acetate concentration, temperature and time are investigated using fractional factorial experimental design. This paper is divided into four sections. This introduction is the first. Next the materials preparation is presented. Thirdly, the results are analyzed, and finally, the conclusions.

2 Materials and methods

2.1 Zinc oxide preparation

Nanostructured *ZnO* was prepared using an aqueous solution of zinc acetate dehydrate, $Zn(CH_3COO)_2$ (Merck) and sodium hydroxide, *NaOH* (Vetec) *100 mL*: *100 mL*. The procedure was carried out with slow dipping zinc acetate dehydrate onto sodium hydroxide on hotplate (*60 °C)*, under agitation, for *30 min*. The white precipitate produced was collected, washed with deionized water and ethanol (Merck) three times for each solvent, alternately. Next, the powder was dried in a furnace. Finally, the powder grain size and nanostructured surface were observed in a scanning electron microscope (JEOL – 6460). The process flow is presented in Figure 1.

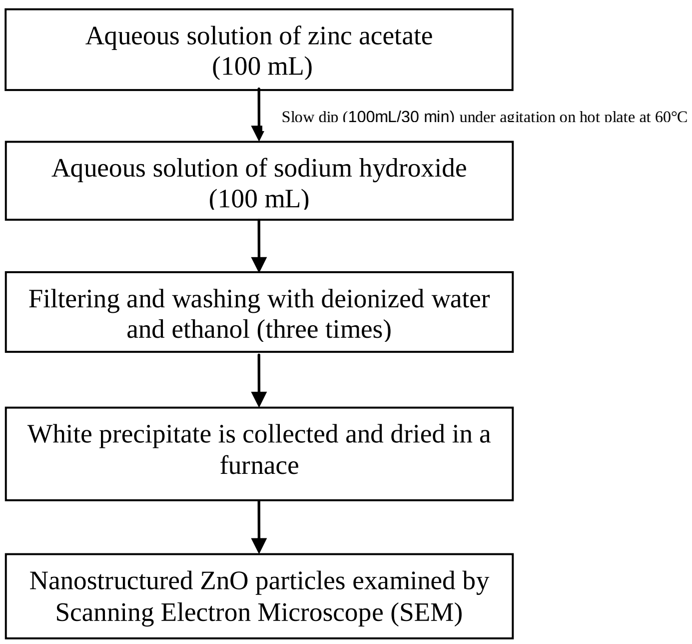

Figure 1. Process flow for production of nanostructured zinc-oxide particles.

2.2 Experimental design

The goal is to get a homogeneous production of nanostructured zinc oxide particles at low temperatures (up to *100 °C*) for biosensor and packaging applications. A 2^{4-1} fractional factorial experimental design was prepared to speed up the search for the optimum condition [15]. The independent variables are: zinc acetate concentration, sodium hydroxide concentration, time and temperature in the furnace, all combinations are presented in Table 1.

Run	Factors			
	ZnAc (M)	NaOH (M)	Time (h)	Temperature (°C)
01	-1 (0.5)	-1 (0.8)	-1 (20)	-1 (40)
02	+1 (1.5)	-1 (0.8)	-1 (20)	+1 (100)
03	-1 (0.5)	+1 (2.4)	-1 (20)	+1 (100)
04	+1 (1.5)	+1 (2.4)	-1 (20)	-1 (40)
05	-1 (0.5)	-1 (0.8)	+1 (60)	+1 (100)
06	+1 (1.5)	-1 (0.8)	+1 (60)	-1 (40)
07	-1 (0.5)	+1 (2.4)	+1 (60)	-1 (40)
08	+1 (1.5)	+1 (2.4)	+1 (60)	+1 (100)
09	0 (1.0)	0 (1.6)	0 (40)	0 (70)
10	0 (1.0)	0 (1.6)	0 (40)	0 (70)

Table1. 2^{4-1} fractional factorial experimental design with coded and real values.

2.3 ZnO nano with different alcohols

Considering the best condition obtained from the experimental design in Table 1, a new study was carried out by changing the washing step. Besides ethanol and deionized water, the other solvents chosen for this additional evaluation were methanol, and n-propanol..

3 Results and discussion

The SEM images for the various experimental conditions are presented in Figure 2, and Figure 3. By visual inspection, one can see that nanostructured zinc oxide particles are produced in the low temperature range studied (*20 °C* up to *100 °C*). The best shaped nanostructured zinc oxide was achieved with condition Run 03 (ZnAc= *0.5 M*, NaOH= *2.4 M*, T= *100 °C* and t= *20 h*). It is observed that a lower ZnAc with high NaOH favor the nanostructured surface formation.

Next, the washing and drying step were examined. In the first experiment, ethanol and deionized water were used three times each. Keeping conditions as in Rund 03, the washing step was modified with three new combinations: methanol and deionized water, n-propanol and deionized water, just deionized water (six times). The goal was to observe the influence of the organic solvent during washing process. The results are present in Figure 3. There are no major differences among the various treatments.

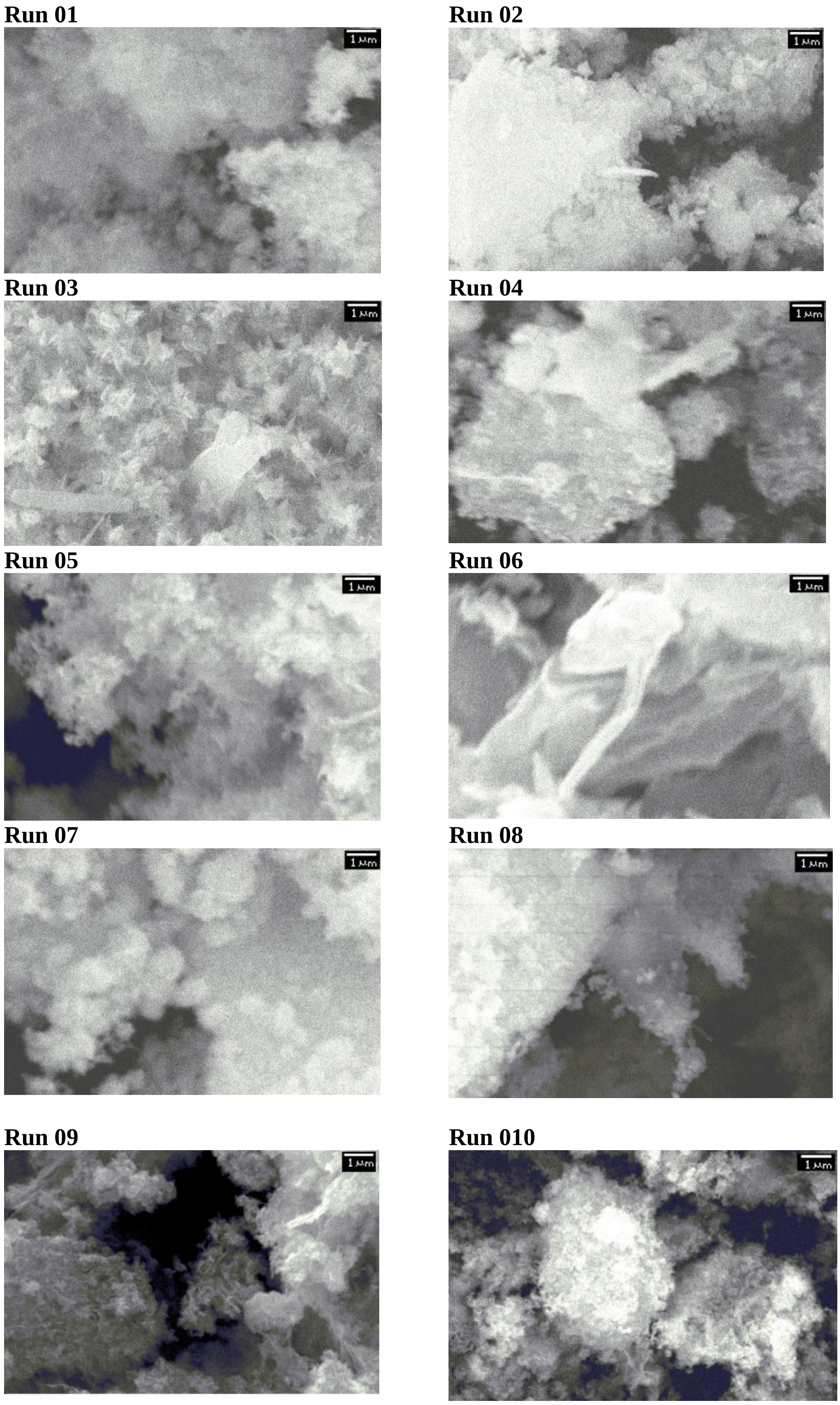

Figure 2. SEM images of nanostructured ZnO particles for conditions in Table 1.

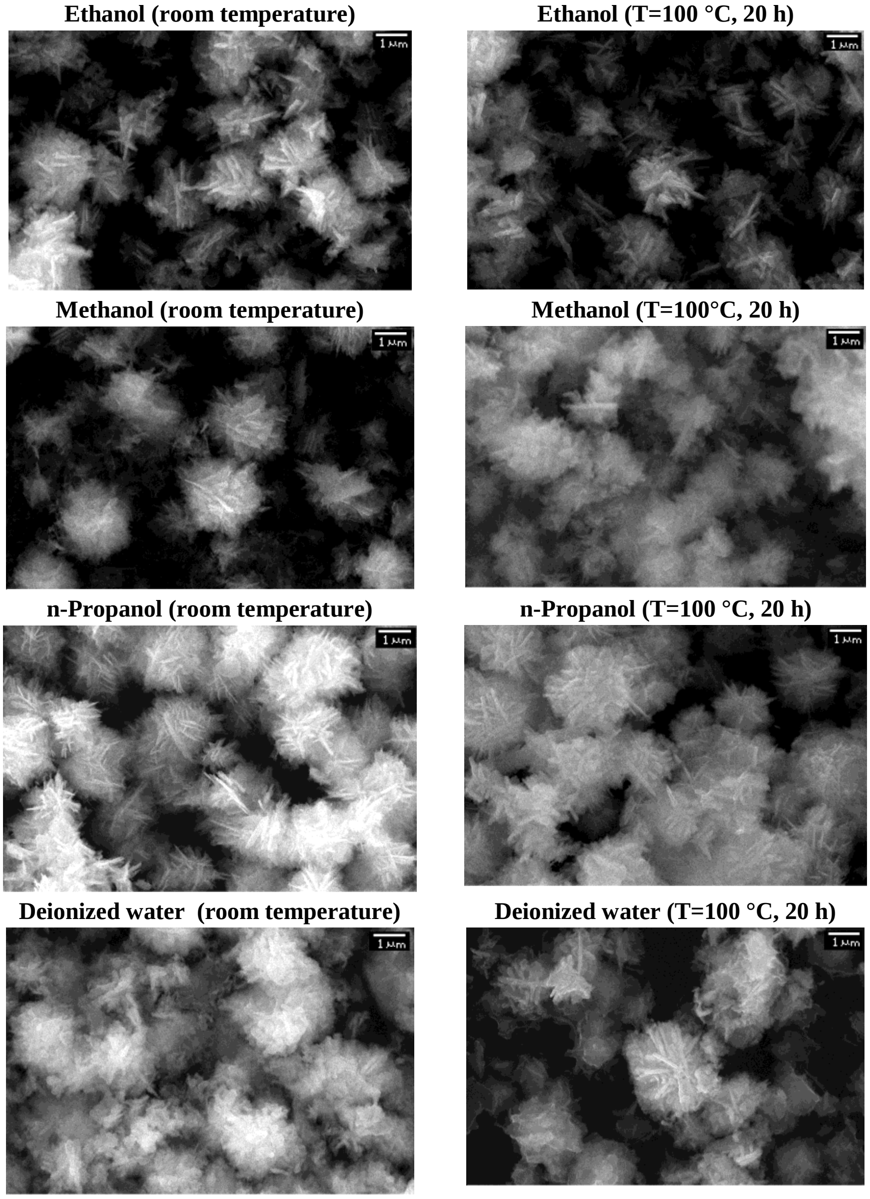

Figure 3. SEM images of nanostructured ZnO particles with dendritic-like structures on the surface for different alcohols and deionized water.

4 Conclusions

A highly homogenous production of nanostructured particles is obtained. The best result was achieved with ZnAc= 0*.5 M*, NaOH= *2.4 M*, T= *100 °C* and t= *20 h.*). It is observed that a lower ZnAc with high NaOH favor the nanostructured surface formation. Further investigations are being carried out to improve this optimization.

For the conditions selected, there is no noticeable influence of the type of solvent on the nanostructured zinc oxide particles produced. There is also no noticeable effect of the drying temperature. Although at higher temperatures, previous reports have shown that increasing the temperature will reduce the particle size, while increasing the length of the dendritics on the particle surface.

By achieving nanostructured ZnO particle production at low temperature, one obtains a lower cost route for the application of this material. The produced powder is now under investigation for biosensor and packaging applications.

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