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Mass transfer effect on the electrosynthesis of zinc oxide nanostructures

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ABSTRACT

The paper deals with electrosynthesis of zinc oxide nanostructures under controlled mass transfer rate. The results of this works show that mass transfer is a main factor to control and change the morphology of zinc oxide nanostructures from the nanosheets to the nanoparticles. Electrosynthesis was done by direct oxidation of zinc anode by exerting pulsed current in the solution containing sodium sulfate and sodium sulfide. At diffusion mass transfer (DMT) control zone, zinc oxide is synthesized in nanosheet form with 30 nm average thickness. By adding convection mass transfer (CMT), the length and width of nanosheets are strongly decreased and their thicknesses slowly increased to form nanoparticles. At higher convective mass transfer rates (more than 0.14 $cm^2 s^{-1}$), by increasing CMT rate, average particles sizes of the samples are decreased.

KEYWORDS

Electrosynthesis;
Pulsed current;
Zinc oxide;
Nanostructure;
Mass transfer.

INTRODUCTION

In recent decade, there are great interests on nonstructural zinc oxide (ZnO), because it has wide direct band gap, strong excitonic binding energy and promising application for UV-laser with low threshold[1], field emission array[2], surface acoustic device[3], transistor and biosensor[4] in nanoscales. Different ZnO nanostructures such as nanowire, nanorod, nanobelt, nanotube, and various fascinating nanostructures such as hierarchical and tetrapod nanowisker, nanocomb, and nanopin have been synthesized through different routes[5].

ZnO nanostructures were synthesized by different physical and chemical methods. The chemical methods have more performances than physical methods in controlling of particles sizes and morphology. Several chemical methods for the synthesis of zinc oxide and mixed metal oxides have been reported e.g. preparation of fine zinc oxide by means of spray pyrrolysis[6], sol-gel technique[7] and thermal decomposition[8]. The synthesis of zinc oxide from organic solutions has also been reported, e.g. precipitation from alcohols and amines[9-11]. In major of these studies, the control of particle shape and the rate of particle growth have been considered in order to avoid the formation of large particles.

On the other hands, electrochemical synthesis of nanoparticles has received a great deal of attention in the past several years. This is probably because

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electrosynthesis has a low cost reaction condition that can be carried out under smooth condition and the properties of nanoparticles can be controlled by several factors such as current amplitude, applied potential, temperature and solution composition[12]. Pulsed current electrosynthesis is a modified method versus the conventional galvanostatic method. There are several reports which show that the pulsed current electrosynthesis is more adequate than the direct current[13].

There is not any attention about the mass transfer controlling during synthesis and electrosynthesis of zinc oxide nanostructures. In this work, we have applied a pulsed current method for the direct synthesis of nanostructured zinc oxide in the presence of sodium sulfide as pH adjuster, sodium sulfate as ionic strength adjuster and poly vinyl pyrolidone (PVP) as structure director. We have tried to investigate the effect of mass transfer during pulsed electrosynthesis of ZnO nanostructures on the morphology and particles sizes of the final sample.

EXPERIMENTAL

All materials and reagents were purchased from Merk of Fluka. Double distilled water was used in all experiments. All the electrochemical experiments were carried out by an electrolyzer equipped with pulse system (BTE 04, Iran). A scanning electron microscope with EDX instrument from Philips (XL30, Netherlands) was used for the studying of morphology and particles sizes of the samples. X-ray diffraction (XRD) studies were performed by a Decker D_8 instrument.

Before each electrodeposition, three similar pure zinc electrodes were dipped in the diluted HNO_3 for 30 min and then rinsed with double distillated water to remove any surface species Electrosynthesis was done by using one zinc electrode as anode and two zinc electrodes as cathode on two sides of anode. Zinc oxide nanostructures were directly synthesized by pulse anodic oxidation of pure zinc electrode which coupled with two pure zinc cathodes in aqueous solution containing sodium sulfide, sodium sulfate and Polyvinyl pyrolidone (PVP). Oxidation was done by applying the pulsed galvanostatic method. All sampled were synthesized under conditions including 0.001M sodium sulfide, 0.1 M sodium sulfate, 12.7 pH, 0.5 %wt PVP as structural additive, 45 °C solution temperature, 0.5 mA cm^{-2} pulsed current amplitude, 1 s pulse time and 1 s relaxation time. The synthesized sample was filtered, washed with water and acetone and then dried at 80 °C. The rate of mass transfer was controlled during electrosynthesis and several ZnO samples were synthesized by using different mass transfer rates.

RESULTS AND DISCUSSION

In all synthesizes, the synthesis conditions which noted in the experimental section were exactly used. Some initial synthesizes were done to specify the suit-

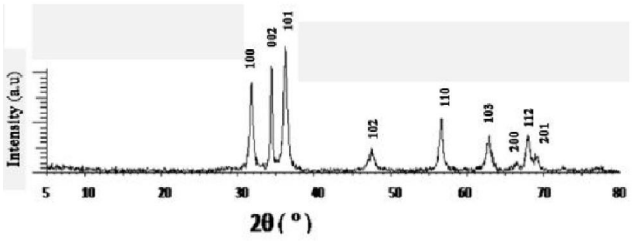

Figure 1 : XRD patterns for the synthesized ZnO nanoparticles

TABLE 1 : Experimental conditions of different ZnO samples and the obtained specifications for the synthesized nanostructures

CMT type	CMT rate (cm^2 s^{-1})	Sample morphology	Length (nm)	Width (nm)	Thickness (nm)	Diameter (nm)
Without CMT	0	Nanosheet	1140	914	30	---
Ultrasonic (90 W)	0.02	Nanosheet	913	502	45	---
Ultrasonic (180 W)	0.04	Nanosheet	559	415	70	---
Ultrasonic (450 W)	0.1	Nanosheets & nanoparticles	449	348	82	114
Ultrasonic (630 W)	0.14	nanoparticles	---	---	---	175
Ultrasonic(810 W)	01.8	nanoparticles	---	---	---	145
Stirring(100 rpm)	0.2	nanoparticles	---	---	---	99
Stirring(100 rpm)	0.4	nanoparticles	---	---	---	46

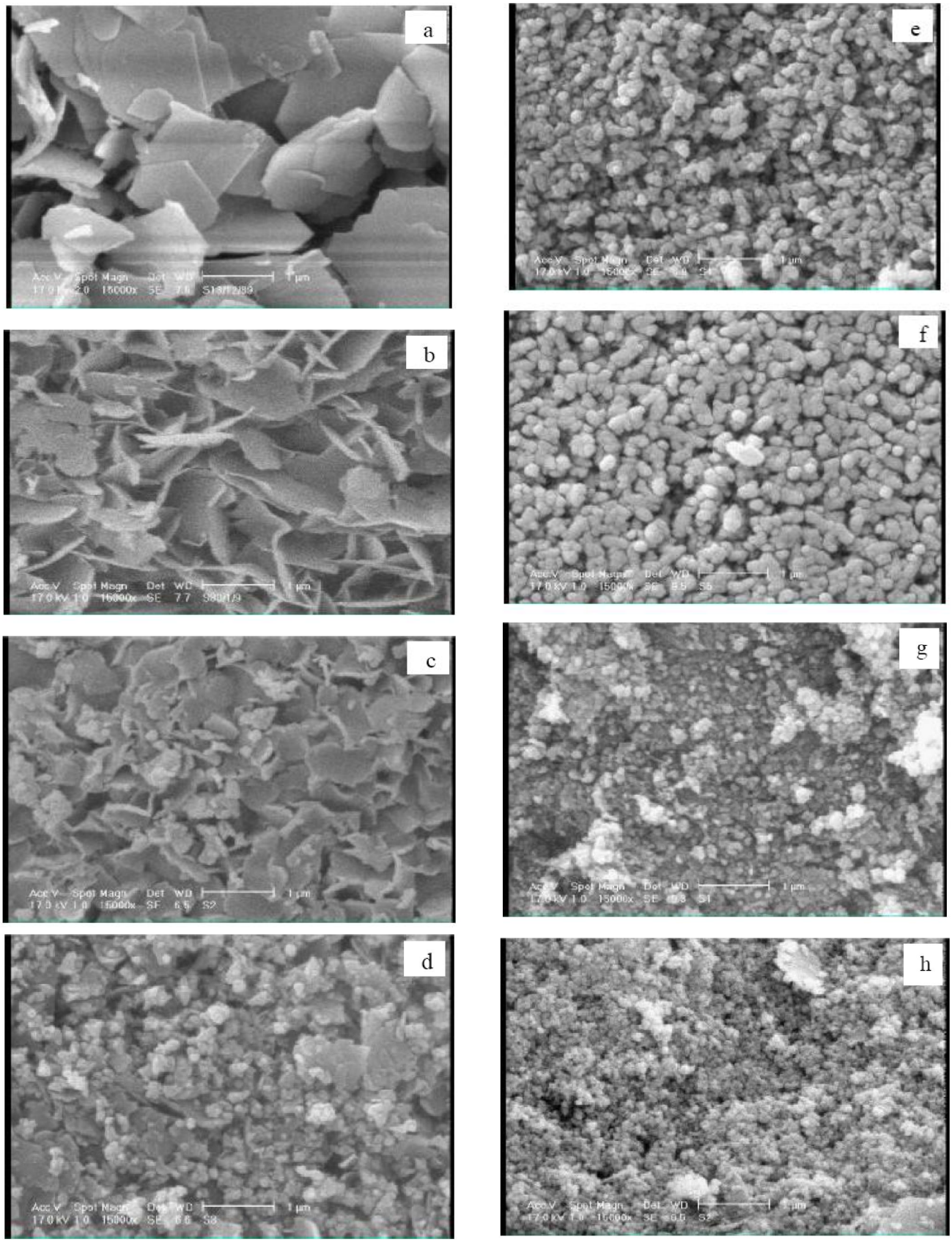

Figure 2 : SEM images of the ZnO samples synthesized at different CMT rates (according to experimental conditions noted at TABLE 1)

able pH adjuster. The results showed sodium sulfide can act as the best pH adjuster to synthesis ZnO nanostructures. Figure 1 shows the XRD patterns of ZnO sample synthesized in the presence of sodium sulfide as pH adjuster. The XRD patterns of the samples showed that the synthesized sample have no sulfide species (such as zinc sulfide) as impurity.

In the main part of this study, some synthesizes were performed under the same conditions. Nevertheless, the mass transfer rate was controlled to investigate its effect on the morphology and particles sizes. It is obvious that the diffusion mass transfer (DMT) can not change or control by operator. One person can only control the convection mass transfer. Convective mass transfer (CMT) through a temperature gradient or stirring the solution is created. Thus, by controlling the temperature and stirring the solution, the convective mass transfer rate can be controlled. All experiments were performed under controlled temperature (45 °C) to eliminate the effect of temperature gradient in a convective mass transfer. Under constant temperature, the CMT rate is dependent on the solution stirring.

In this study, the CMT was produced by controlled stirring of the synthesis solution and using ultrasonic irradiation. All samples were synthesized under specified conditions including 0.001M sodium sulfide as pH adjuster, 0.1 M sodium sulfate as supporting electrolyte (ionic strength adjuster), 12.7 pH, 0.5 %wt PVP as structural additive, 45 °C solution temperature, 0.5 mA cm^{-2} pulsed current density (pulse height), 1 s pulse time (t_{on}) and 1 s relaxation time (t_{off}). Eight samples were synthesized at different convective mass transfer rates including. TABLE 1 shows the summary of experimental convection rates and the obtained morphology and particles sizes. The morphologies and the particles sizes of the samples which noted at TABLE 1 were obtained from SEM images. Figure 2 shows the SEM images of the different ZnO samples which synthesized under different CMT rates. As it can be seen in Figure 2 and TABLE 1, CMT rate is a very important parameter to change the shape and dimensions of the ZnO particles. In the synthesis solution, Na_2S is treated with water to produce homogenously hydroxide ions. By exerting current pulse, the zinc anode is oxidized to form Zn^{2+} ions. The chemically produced hydroxide ions are transferred to the anode surface. The hydroxide ions and the electrochemically produced zinc ion are combined to form zinc hydroxide nanoparticles at the surface of anode. Zinc oxide is more stable than zinc hydroxide at 45 °C, so that zinc oxide is easily converted to zinc oxide. In the explained mechanism, the transfer of hydroxide ions from the solution into the anode surface is the rate controlling step of the mechanism. The rate of this step strongly depends on the DMT and CMT rates. During all electrosynthesis processes, the DMT rate is same. Therefore, the observed differences between ZnO samples are related to CMT differences. The formation of nanosheets is performed with two-dimensional growth while, the nanoparticles have similar growth in three dimensions. Two-dimensional growth needs a low rate of mass transfer. In the absence of CMT, DMT make this propose (the sample synthesized without stirring), because DMT is carried out only in vertical direction with respect to the anode surface (Fick's first low in mass transfer). By adding CMT to DMT cause to increase the mass transfer rate and disturb two-dimensional growth. By increasing the CMT rate, the growth rate in thee dimensions will be similar so the nanoparticles are formed.

CONCLUSIONS

Mass transfer rate during electrosynthesis of ZnO nanostructures is a very important parameter to control the morphology and the particles sizes of the samples.

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