Nanoparticles of Zinc Oxide Obtained by Water in Oil Microemulsion System

A.M. Pineda-Reyes  
Doctorado en Nanociencias y Nanotecnología  
CINVESTAV-IPN  
CD-México  
anamaria.pineda.reyes@gmail.com

M. de la L. Olvera-Amador  
Departamento de Ingeniería eléctrica-SEES  
CINVESTAV-IPN  
CD-México  
molvera@cinvestav.mx

Abstract- This work reports results obtained from synthesis of zinc oxide powders via microemulsions of type water in oil through of two routes. The formation of microemulsions as confined reaction media to the synthesis involves the combination of emu oil, zinc acetate, and sodium hydroxide as precipitating agent. To reach the thermodynamic stability and find the hydrophilic-lipophilic balance of the microemulsions, Span-Tween 80 was used. Synthesized zinc oxide powders were characterized by X-ray diffraction and electron microscopy transmission. ZnO powders presented a hexagonal wurtzite structure. Electron microscopy transmission images showed that synthesized powders presented a spherical morphology and nanometric-sized crystallites around 14 nm.

Keywords-Zinc Oxide; W/O microemulsion; nanoparticle synthesis.

I. INTRODUCTION

The remarkable properties of zinc oxide (ZnO) and the versatility of its morphology, among other characteristics of great importance for industrial applications, have increased the interest in obtaining nanostructured ZnO. This material is considered as one of the most important metallic oxide at the nanoscale-level, particularly due to its electrical and optical properties [1].

ZnO is a II-VI semiconductor that in thin film form, usually presents a hexagonal wurtzite structure, an n-type conductivity, a direct and wide band gap (~ 3.3 - 3.4 eV), and large free exciton binding energy (~ 60 meV) [1].

The growth of ZnO crystals can be prepared as powders, films or bulk form [2-4]. Some of the different nanostructures types reported until now are nanowires, nanorods, nanobelts, nanosprings, nanotubes, nanodonuts, and nanopropellers, among others; depending on the method of synthesis or growth technique [3,5-6]. Several research groups have used different preparation methods, such as sol-gel process, homogeneous precipitation, spray pyrolysis, thermal decomposition by microwave heating, and conventional hydrothermal method, among others [1]. The synthesis via microemulsions has been very versatile and reproducible, because it allows controlling the nanoparticles size with a reduced distribution compared to chemical methods [7]. The precipitation of various materials by microemulsions has allowed obtaining particle sizes of less than 10 nm and low polydispersion [8].

The use of microemulsions allows preparing nanoparticle with morphology and size homogeneous, which are of great interest for their tiny size and large surface area per unit volume. Microemulsions are considered as microreactors or nanoreactors due to their dynamic structure and spherical droplets shape, where reactions take place between the precursor and the precipitating agent. The reaction occurs as consequence of the constant coalescence and redispersion, promoting a process of fusion and fission of droplets [9,10].

Microemulsions are optically isotropic mixtures, thermodynamically stable, transparent or translucent, and with a spontaneous formation [7], which are constituted from two liquids, one oily and other aqueous phase, that can be stabilized with one or more surfactants [10,11]. In case of having a continue oily phase, and an aqueous phase containing the metallic salt or the reducing agent, the microemulsion is called “water in oil”.

Several authors like Lim et al. report that ZnO can be obtained by a microemulsion method. They have processed ultrafine powders with an average particle size of 150 nm, prepared from a microemulsion of Zn(NO₃)₂ solution, petroleum spirit and poly(oxyethylene)₅ nonyl phenol ether (NP₅) [12]. Singhal et al. reported the synthesis of ZnO with a particle size of 11.5 and 13.9 nm from zinc oxalate (Zn-AOT), by a microemulsion of Zn-AOT, isooctane and ethanol [13]. Kaneko et al. obtained ultrafine ZnO particles using a microemulsión of nonylphenyl ether (NP-6), cyclohexane and ammonia of zinc di-n-butoxide (ZDB) [14]. Hingoran et al. synthesized ultrafine polycrystalline ZnO nanoparticles with particle size ranging from 5 to 40 nm. They developed the synthesis by mixing two water/oil (W/O) microemulsions of cetyl trimethyl ammonium bromide (CTAB), n-octane, and as aqueous phase, a system containing a solution of zinc nitrate and the other of ammonium carbonate [15]. Romo et al. reported particles between 8.5 and 30 nm in a bicontinuous
microemulsion stabilized with a mixture of sulfosuccinate sodium bis (2-ethylhexyl) and sodium dodecyl sulfate (2/1 wt/wt), zinc nitrate 0.7 M and sodium hydroxide [8].

The aim of this work is present initial results about the synthesis of ZnO via a microemulsion by using zinc acetate as zinc precursor and sodium hydroxide as a precipitating agent, at a reaction temperature of \(60^\circ C\). The product obtained was dried and calcined at moderate temperatures and short times. The powders were characterized by X-ray diffraction; whereas morphology and particle size were evaluated by transmission electron microscopy (TEM).

II. EXPERIMENTAL PROCEDURE

A. Preparation of ZnO nanoparticles by water-in-oil microemulsions

The composition of the microemulsions was determined with the aid of a pseudo-ternary phase diagram, at a temperature of \(60^\circ C\); each vertex of the diagram represents 100\% of the system components. The vertices are emu oil, a binary mixture of surfactants Span and Tween 80 of HLB 9.7, and the 0.5 M aqueous solution of zinc acetate \([\text{Zn(CH}_3\text{COO)}_2\cdot\text{H}_2\text{O}]\) as precursor or sodium hydroxide (NaOH) 1 M as precipant agent. Both materials were of analytical grade. The phases present in each system were visually evaluated by their isotropic nature and optical clarity, considering that stable microemulsions are those formulations that presented a good optical transparency [16]. The data in the phase diagram was determined by varying the surfactant/oil ratio (SOR for its acronym in English, surfactant oil ratio), water/oil (WOR for its acronym in English, water oil ratio) and the balance hydrophilic-lipophilic (HLB for its acronym in English hydrophilic, lipophilic balance).

B. Zinc oxide powder synthesis

The ZnO powders were synthesized by two microemulsion routes, the first route used two microemulsions of same composition, one contains the metal salt and the second reducing agent, both microemulsions were mixed to allow exchange of reactants between micelles where is carried out the reaction through the collisions of Brownian motion, the attractive van der Waals forces and repulsive osmotic and elastic forces. [7].

Whereas in the second route was used a single microemulsion containing metal salt and the reducing agent was added directly dropwise to the microemulsion system. In both cases the reaction was developed at \(60^\circ C\) and stirred at 1200 rpm. The systems were kept in dark for 24 hours. Afterwards, the mixtures were centrifuged at 7500 rpm for 15 minutes for several times with a mix hot water, acetone or hexane, in order to separate the oil and surfactant residues from the precipitate, as well as water soluble salts obtained of the reaction. The precipitates were dried during 1 hour at \(100^\circ C\), and then calcined at \(400^\circ C\) for 2 hours.

C. Zinc oxide powder characterization

The powders were analyzed by X-ray diffraction (XRD) to identify the structure from a diffractometer system (PANalytical, model XPERT-PRO) by using the Cu-\(\alpha\) radiation (\(\lambda=0.15406\) nm). The spectra were taken in the 2\(\Theta\) mode, in the 20 to 80\(^\circ\) range, with a 0.02\(^\circ\)/min scan increment. The morphology of the ZnO powders was determined by transmission electron microscopy in a Jeol ARM200F with a field emission gun at an acceleration voltage of 200 kV. Samples for TEM analysis were prepared by dissolving an appropriate amount of ZnO powder in isopropyl alcohol and placing in a thin layer on a formvar\textsuperscript{®}-coated carbon grid.

III. RESULTS

A. Pseudoternary phase diagram

Figure 1 shows the region where the solution/oil/surfactant ratio was appropriate, defined by its clear, stable, and transparent or translucent formulation, deducting the appropriate percentages for the formation of microemulsions from emu oil, Span-Tween 80 (1/1, wt/wt) and aqueous solutions of 0.5 M zinc acetate or 1 M sodium hydroxide, at \(60^\circ C\). Whereas beyond this region, the systems were turbid and non-homogeneous. The region of the phase diagram suggests the formation of microemulsions with concentrations between 10-21 \text{wt} \% of aqueous solution and 30-80 \text{wt} \% of surfactant. As mentioned earlier,
transparent or translucent microemulsions determine the region between microemulsions and not microemulsions. However, the type of structure was not possible to be identified, only by this isotropy in the microemulsions, despite their transparency [7]. Additionally, if the percentage of the aqueous phase is above 15%, it is suggested the formation of bicontinuous microemulsions [7].

B. Zinc oxide powder synthesis

The stable microemulsions of the phase diagram, were used to carry out the precipitation reaction. In the first route all precipitation reactions were not obtained ZnO powder. The above may suggest that the formed structure is not bicontinuous type, which, in the absence of coalescence between the drops there is no chemical reaction to form the ZnO. In the second route where one microemulsion system contained the metal salt and the reducing agent was dropped into the microemulsion, all the microemulsions were observed precipitation reactions obtaining ZnO powders, according to the following reaction (1). These suggesting that some of the microemulsions maintained their micellar structure, by observing homogeneous during the reaction for 24 hours.

\[
\text{Zn(CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \rightarrow \text{ZnO(s)} + 2\text{CH}_3\text{COONa} + 3\text{H}_2\text{O} \quad (1)
\]

From here and according with the second route, one of the system was selected to perform the characterization analysis, it was with 11 wt % aqueous phase and oil/surfactant ratio at 1.54.

C. Scanning electron transmission microscopy analysis

Figure 2 shows TEM micrographs at different magnifications of ZnO powders obtained from a
microemulsion 11 wt % aqueous phase of zinc acetate and oil/surfactant ratio at 1.54, calcined at 400° C. Nanoparticles with a homogenous size distribution are observed in Fig. 2a. Image 2b shows a poorly defined nanoparticle with a spherical morphology; this might be due to the type of structure formed in the microemulsion "droplets or micelles" used as nanoreactors that provide a confinement effect that limits the particle nucleation and growth; allowing specific size and shape by the droplet size of the microemulsion [9]. In the figure 2c, a crystallite size of 14 nm, approximately, is observed, and a crystalline growth is confirmed.

D. Structural characterization

An X-ray diffraction pattern of the selected sample is shown in figure 3, according to the powder ZnO synthesized at 60° C, namely, calcined at 400°C for 2 h. The results reveal that all peaks present corresponding to the hexagonal wurtzite structure, according to JCPDS 01-076-0704 crystallographic card. No additional phase is observed, indicative of pure ZnO powder. The spectra presented a preferential orientation of the growth in the peak (101) at ~36.15°. Non extra peaks, corresponding to another Zn phase was observed, that means that the Zn2+ ions contained in the microemulsion were decomposed to form the ZnO phase. It is worthy to note that the two peaks presented at low angle in all the spectra (~ 21° and 23°) correspond to the plastic covering the powders during the X-Rays analysis.

Additionally, the result in the diffraction pattern show that the microemulsion processing zinc oxide powders of high crystallinity and structure ordered at long range.

I. CONCLUSIONS

Using reverse microemulsions, identified in the ternary phase diagram of emu oil, Span-Tween 80 and aqueous solution of Zn(CH3COO)2·H2O), crystalline ZnO nanoparticles with a hexagonal wurtzite structure were processed. The crystal-size of ZnO was around 14 nm, with a homogeneous distribution. Results obtained from transmission electron microscopy analysis and X-ray confirmed the presence of ZnO in heat treated powders at 400° C.

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