Advanced Powder Technology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Effect of magnetized ethanol on the shape evolution of zinc oxide from nanoparticles to microrods: Experimental and molecular dynamic simulation study

Hamed Rashidi [a,*], Ali Ahmadpour [b], Mostafa Gholizadeh [c], Fatemeh F. Bamoharram [d], Fatemeh Moosavi [c]

[a] Department of Chemical Engineering, Shahrood Branch, Islamic Azad University, P.O. Box 36155-163, Shahrood, Iran
[b] Department of Chemical Engineering, Ferdowsi University of Mashhad, Mashhad, Iran
[c] Department of Chemistry, Ferdowsi University of Mashhad, Mashhad, Iran
[d] Research Centre for Animal Development Applied Biology – Department of Nanobiotechnology, Mashhad Branch, Islamic Azad University, Mashhad, Iran

ARTICLE INFO

Article history:
Received 7 May 2017
Received in revised form 6 November 2017
Accepted 15 November 2017
Available online xxxx

Keywords:
Zinc oxide
Solvothermal
Magnetic field
Electron microscopy
Molecular dynamics simulation

ABSTRACT

In the current research, ethanol was exposed to an external magnetic field, called magnetized ethanol, and then, used as a solvent in the solvothermal method to synthesize various ZnO structures. Moreover, the morphologies of the synthesized structures are compared with those obtained using ordinary ethanol. The attained results evidently demonstrated the formation of ZnO nanoparticles and microrods by using ordinary and magnetized ethanol, respectively. Moreover, X-ray diffraction (XRD) and scanning electron microscopy (SEM) were utilized for characterizing the synthesized ZnO structures. The XRD results demonstrated that the synthesized products are in Zincite hexagonal phase. Besides, molecular dynamics simulation suggested that the molecular mobility is diminished upon using the magnetic field. It was found that the interactions among ZnO particles were enhanced by the slight increase in the magnetic field while the number of interactions between ZnO and solvent was reduced revealing the magnetic-field-induced particle growth from the molecular level insight.

1. Introduction

Since the properties of final products depend on the particles' shape and size, the main objective in the synthesis of different materials is to control these two parameters. Due to the relatively high exciton binding energy (60 meV) and a wide direct band gap (3.37 eV), and also, its various shape-induced functions, zinc oxide has gained a great deal of attention. ZnO structures with various shapes and sizes have different applications ranging from catalysis for photo-catalytic degradation to solar cell preparation, gas sensors [1–8] and antibacterial properties [9].

In recent years, both fundamental and applied researches have been concentrated on the morphologically controllable synthesis of ZnO because of its unique electrical, acoustic and optical properties [10–13]. Various methods, such as mechanochemical, sol-gel, direct precipitation, azeotropic distillation, freeze drying, ethanol washing, chemical vapor deposition and hydrothermal processing have been used in the preparation of ZnO structures [9,14–27]. Because of their advantages such as low cost, simple routes and low-temperature processes, the hydrothermal and solvothermal techniques have been widely used for the synthesis of nanostructured materials like ZnO crystals [28–30].

In the solvothermal technique, the solvent plays a vital role in the properties of synthesized crystals. Besides, solubility and transport behavior of the precursors can be strongly affected by the properties of a solvent such as polarity and viscosity. Therefore, various crystalline compounds in different shapes and sizes could be produced by only changing the type of solvent [10–12,30–32]. The choice of proper solvent for crystallization might impose profound effects on the morphology of synthesized particles. Investigation on the solvent magnetization revealed that some unique properties could be generated in the solvent subsequently leading to the synthesis of altered structures.

In the recent years, the magnetic field has been used for enhancement of heat transfer coefficient in heat transfer applications like heat pipes which contain magnetic particles [33–36], while studies on the effect of magnetic field on solvent's properties are relatively rare. The effect of magnetic field on properties of water has been discovered in the early 1900s by Danish Physicist

* Corresponding author.
E-mail address: hrashidi@iau-shahrood.ac.ir (H. Rashidi).

https://doi.org/10.1016/j.apt.2017.11.022

Please cite this article in press as: H. Rashidi et al., Effect of magnetized ethanol on the shape evolution of zinc oxide from nanoparticles to microrods: Experimental and molecular dynamic simulation study, Advanced Powder Technology (2017), https://doi.org/10.1016/j.apt.2017.11.022

Hendricks Anton Lorenz [37]. In that research, protic solvents, i.e. water and ethanol, were exposed to a magnetic field. His observation demonstrated that by passing water through a magnetic field, the electron pattern in the ions was changed [38]. It is also reported that if water is exposed to an external magnetic field, different phenomena would occur. Magnetization of the solvent influenced the hydrogen bond distribution resulting in an increase in the water viscosity and enthalpy as well as a decrease in the surface tension [39–42].

The influence of magnetic field on macroscopic features and microscopic structures of water has been previously studied by Xiao-Feng and Bo [43]. They have detected some variations in the water properties once exposed to the magnetic field. They have also measured the changes in surface tension, contact angle, viscosity, rheology, refractive index, dielectric constant and electrical conductivity of the magnetized water by using infrared, Raman, visible light, ultraviolet and X-ray techniques. It has been shown that although the distribution of molecules and transition probability of valence, bonded and inner-layer electrons were varied, the constitution of molecules and atoms remained unchanged. In addition, the magnetic field has been found to be responsible for the reduction of the contact angle, surface tension force, and hydrophobicity of water while the refractive index, dielectric constant and electric conductivity of water were increased. The viscosity of magnetized water could be enhanced by increasing the intensity of magnetic field and magnetized time. Likewise, the effect of magnetic treatment on the surface tension reduction of water was investigated by Amiri and Dadkhah [42]. They have reported a reduction in the surface tension of pure water with increasing the number of times water passes through the magnetic field. An 8% reduction in the surface tension of magnetically treated water is reported elsewhere [44]. Rohani and Entezari have investigated the synthesis of manganese oxide nanocrystals in the presence of magnetic field. They have demonstrated that larger and smaller sizes of nanoparticles could be obtained with and without magnetic treatment, respectively [45]. In addition, the external magnetic field retards the nucleation process which accelerates the crystal growth leading to an increased amount of rod-like structure.

We have recently investigated some applications of magnetization in various processes [38,39,46–49]. To the best of our knowledge, among all magnetized solvents, the role and behavior of magnetized ethanol have been vastly overlooked, and no capability has been mentioned for this popular solvent. As a result, there is a great interest to delineate the effect of magnetized ethanol on material synthesis. In continuation of our previous works on the synthesis of various ZnO structures as well as applications of magnetized solvents [38,39,47,50–54], and also due to the importance of ZnO structures in nanotechnology, photocatalysis, and several other industries, the major aim of the current work is to investigate the influence of induced magnetic field applied to ethanol on the morphology of zinc oxide prepared by the solvothermal technique.

For a deeper understanding of the processes, classical molecular dynamics (MD) simulations is also performed to determine the extent of enhanced hydrogen-bonding and local environmental structures [55–57], indicating that MD simulation is a powerful tool to decipher the local features at the molecular level. In addition, MD helps the researchers to understand different properties including macroscopic and microscopic ones. However, the formation of rod structures in a specific solvent has not been investigated by MD simulation so far. Assessment of the magnetization process from the molecular viewpoint was also performed to explore the size and configuration of particles in ethanol illustrating the effect of the aspect ratio and the particle-particle interactions on the aggregate structures of ZnO rod-like particles.

2. Materials and methods

2.1. Solvent magnetizing apparatus

A permanent magnet in a compact form was used. This equipment was a coaxial static magnetic system (AQUA CORRECT, H.P. S Co., Germany) with the field strength of 0.6 T. The two ends of this equipment were connected to the liquid pump and the solvent reservoir. Solutions could flow through a coaxial static magnet and return to the solvent reservoir. Therefore, the solution might pass throughout the magnetic field several times in a closed cycle (Fig. 1).

2.2. Synthesis method

Zinc acetate dehydrate and ethanol (both analytical grades) have been purchased from Merck Company. Zinc acetate dehydrate (0.02 mmol) was dissolved in ethanol (ordinary/magnetized) (30–40 mL) under vigorous stirring. Ethanol was magnetized at various times (1 pass, 10 min, and 120 min) in the case of magnetized ethanol. After mixing for about 10 min, the reaction mixture was transferred into the Teflon-lined stainless steel autoclave (50 mL), which was maintained at 130 °C for 48 h followed by cooling naturally to the room temperature. To remove all impurities, the white precipitates were separated by centrifuge, washed several times with deionised water and ethanol and then dried at 60 °C for 8 h to get a white fine powder. This powder was used for further characterizations.

2.3. Measurements and analysis

The crystal structure of Zinc oxide samples was characterized by X-ray diffraction (XRD, Bruker D8 Advance) using Cu-Kα radiation (λ = 1.5406 Å). The surface morphology of powders was studied using scanning electron microscope (SEM, LEO 1450 VP, Zeiess, Germany). Furthermore, the energy dispersive X-ray spectroscopy (EDS, 7353, Axford, England) was used for the elemental analysis. FTIR spectroscopy, within the wave number range of 850 and 4000 cm^{-1}, was employed with a Bruker 500 scientific spectrometer. The conductivity of solvent was determined using an Accumet AR20.

2.4. Simulation details

By employing a hybrid density functional theory incorporating Becke's three-parameter exchange with Lee, Yang and Parr's (B3LYP) correlation functional [58,59], density functional theory (DFT) calculation for ethanol system was performed using Gaus-

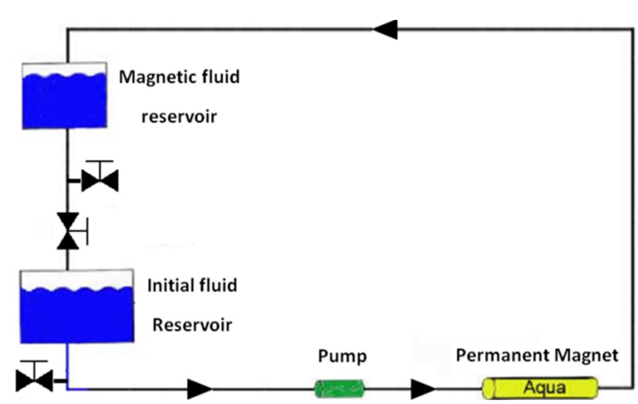

Fig. 1. The schematic of solvent magnetization apparatus.

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