

## Effect of organic compounds on morphologies ZnO nanostructures

MARYAM SABBAGHAN

*Department of Chemistry, Faculty of Science, Shahid Rajaee Teacher Training University, P.O. Box 167855-163 Tehran, Iran*  
[sabbaghan@srttu.edu](mailto:sabbaghan@srttu.edu)

**ABSTRACT.** This paper reviews effects of organic compounds for synthesis of ZnO by reflux method as well as systematic investigation on the relationship between the structures of organic compounds on ZnO nanostructures morphology. The characteristic results revealed that using different template not only prevent a drastic increase in the crystallite size of the zinc species but also provide suitable conditions for the oriented growth of primary nanoparticles with especial morphology. It was found that the formation of ZnO with various morphologies could involve the role of preformed "nucleus" and used templates to control the growth rate of various facets of these preformed nuclei. Depends on organic compounds and concentration of sodium hydroxide different morphologies of ZnO nanostructures were obtained. Three categories of organic compounds, carbohydrates, surfactant and ionic liquids were investigated as template.

**Keywords:** Morphology, ZnO nanostructures, ionic liquid.

### 1. INTRODUCTION

As their unusual physical and chemical properties differ from those of bulk materials owing to the size-quantization effect and extremely large specific surface area, nano-structured materials have raised a lot of interest [1]. These nanomaterials have novel electronic, structural, and thermal properties which are of high scientific interests in basic and applied fields. Among them, ZnO have been paid attention for their unique properties, such as electric conductivity, optical transparency, piezoelectricity and near-UV emission [2]. ZnO with a great band (3.3– 3.6 eV) is an important n-type semiconductor, with the large excitation binding energy of 60 meV at room temperature [3]. Also ZnO nanostructures have a great advantage to apply to a catalytic reaction process due to their large surface area and high catalytic activity

[4]. Since zinc oxide shows different physical and chemical properties depending upon the morphology of nanostructures, not only various synthesis methods but also the physical and chemical properties of synthesized zinc oxide are to be investigated in terms of its morphology. Herein, the effect of various organic compounds especially ionic liquid on morphology of ZnO nanostructures by a simple reflux method will be reviewed from our recent researches.

## 2. METHODS FOR SYNTHESIS OF ZNO

Several routes have been developed to synthesize ZnO nanostructures such as a wet polymerization, sol-gel, sol-gel combustion, precipitation, hydrothermal, solvothermal, CVD, thermal oxidation and electrochemical depositions. Recently, ZnO nanoparticles were prepared by ultrasound, microwave-assisted combustion method, two-step mechanochemical-thermal synthesis, anodization, co-precipitation, and electrophoretic deposition [5]. Therefore, development of new, simple, cost-effective, and large-scale synthetic routes to high quality ZnO nanostructures has been becoming increasingly important. Compared with the above methods, the reflux method has the advantage of low synthesis temperature and simple processing, and obtaining powder with especial morphology and uniformity that has been used here. Zinc acetate pentahydrate and sodium hydroxide were used as precursors and water as solvent [6-7]. The structural and optical properties of these ZnO particles are investigated by using X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Visible absorption.

## 3. EFFECT OF ORGANIC COMPOUNDS ON MORPHOLOGY

A wide variety of techniques have been exploited to fabricate ZnO nanostructures. Zinc oxide nanoparticles with different morphologies were synthesized by controlling different parameters of the precipitation process such as solution concentration, pH, washing medium, and reaction time. One of the important factors was used included template-confined synthesis routes. It was found that the formation of ZnO with various morphologies could involve the role of preformed "nucleus" and used templates to control the growth rate of various facets of these preformed nucleuses. When only  $Zn^{+2}$  was used (without any template), ZnO nanoparticles were formed (S1). With using template, ZnO nanoparticles with smaller crystallite size and various morphologies were obtained in this condition.

### 3.1 NATURAL COMPOUNDS

In our research ZnO nanostructures with a diversity of different morphologies, as

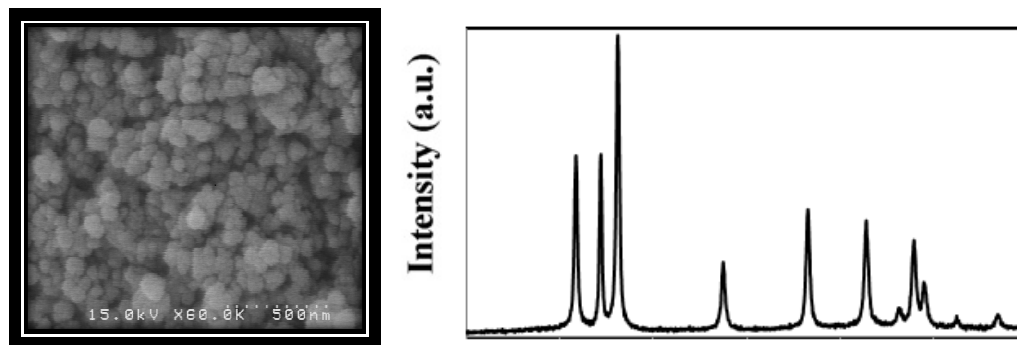


Figure 2. SEM images and XRD pattern of ZnO nanoparticles (S1)

nanoparticles, nanocauliflower and nanosheet-like have been fabricated by using sucrose, methyl cellulose and casein respectively in reflux method. It seems sucrose prevents the agglomeration of ZnO particles. Methyl cellulose as a kind of nonionic compound with heat gelatification property causes to have cauliflower morphology. Ultimately Casein as phosphoproteins is much like that of denatured globular proteins. The high number of proline residues in caseins causes particular bending of the protein chain and inhibits the formation of close-packed, ordered secondary structures. This structure cause to ZnO nanosheet-like morphology was obtained (S1-3, Figure 1) [6].

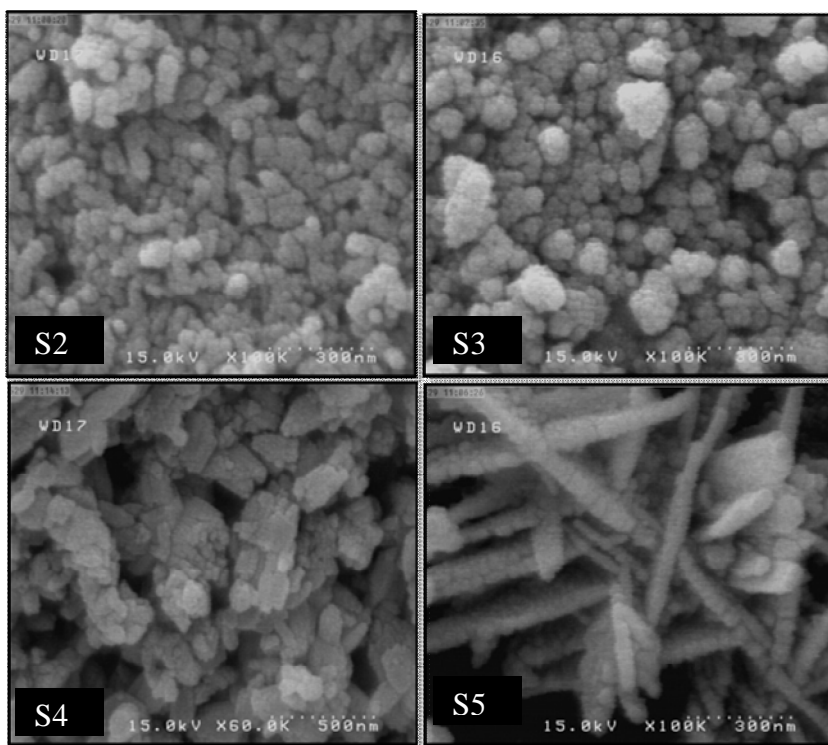


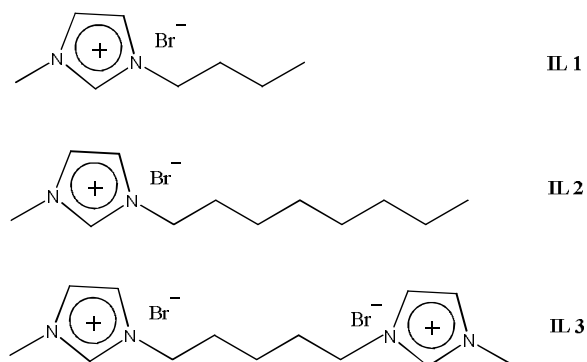
Figure 2. SEM images of ZnO nanoparticles (S2) nanoparticle (S3)nanocauliflower (S4) nanosheet-like (e) nanorod-like.

### 3.2 SURFACTANTS

Sodium dodecylsulfate (SDS) as an anionic surfactant was used as template in reflux method. These template sheet-like micelles of SDS that make nanoparticles grow along this template which serves as the nuclei for the nanoparticles growth as nanorod-like (S5, Figure 1) [6].

### 3.3 IONIC LIQUIDS

Ionic liquids (ILs) have been developed to a central point of interest in both academia and industry [7]. Particularly, ionic liquids can act as solvents, reactants and templates for fabrication of inorganic materials [8]. Room-temperature ionic liquids based on imidazolium cations have attracted considerable attention in recent years because of the possibility that these substances can serve as environmentally benign media, in place of volatile organic compounds. The structures of the ILs 1–3 used in our researches are shown in Scheme 1.



Scheme 1. Chemical Structure of Ionic Liquids

Figure 2 shows the typical SEM images of the samples obtained by the reflux method with using different ILs. With using IL1 as template, ZnO nanosheets with smaller crystallite size were obtained. The results indicate that the best condition for nano sheet morphology was ratio 4:1 of NaOH/Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O and 4:1 IL/Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (S6). Also using the longer alkyl chain at position-1 of imidazole ring or using dicationic ionic liquid with a definite concentration cause the more width of nano sheet (S7-S8). The growth unit for ZnO crystal is considered to be Zn[OH]<sup>-4</sup>. At the same time, with the electrostatic interaction between this complex and ILs, some surfaces of the growth units are modified by the complex ions.

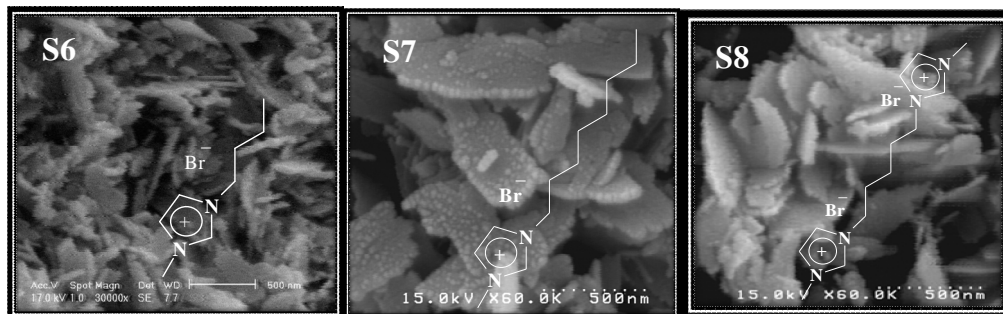


Fig. 3. SEM images of 2D ZnO nanostructures

#### 4 CONCLUSIONS

In summary, Changes in the morphology of ZnO nanostructures could be affected by using the different templates. The growth mechanism of these samples could involve the role of preformed nucleus and the used templates to control the growth. 1D ZnO morphologies of nanocrystalline ZnO particles have been synthesized using sodium dodecylsulfate. 2D ZnO nanostructures were obtained with using ionic liquids or casein. Changes in the dimensions of ZnO nanosheets could be affected by using the different ionic liquids. Nanocauliflower morphology has been fabricated by using casein in reflux method.

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