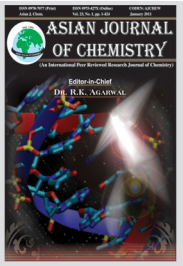
Asian Journal of Chemistry; Vol. 23, No. 5 (2011), 2184-2186

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Synthesize of ZnO Nanoparticle by Direct Reaction Between Zn and Water

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(*Received*: 30 August 2010; *Accepted*: 28 January 2011) AJC-9521

A simple technique was invented based on combining top-down and bottom-up approaches for synthezing ZnO nano-particles using only Zn and water as starting materials. In this method, Zn powder was milled using a planetary ball. Then the milled powder was pured in warm water. Zn was hydrolyzed and ZnO powder was self-assembled in two different morphologies: hexagonal flakes with average size of *ca.* 200 nm and rod morphology with average height of *ca.* 100 nm and average diameter *ca.* 20 nm. The specific surface area of the powder was 18025 m^2/g.

Key Words: ZnO, Nanomaterials, Mechanical activation, Hydrolysis and Powder technology.

INTRODUCTION

Due to their high specific surface area and quantum confinement effects, nano-structures exhibit different electrical, optical, chemical and thermal properties with respect to bulk-structures.

This versatility makes them highly applicable in nano-tools[1]. Among all of known nano-structures, ZnO has received more attention because, even in its bulk state, it has very useful properties (such as transparency in the visible range of light, high electrical stability, direct band gap (3.5 eV), being non-toxic, abundance in nature, *etc.*[2]) and has many application in industries (*e.g.* in solar cell, field emission, optoelectronic devices, sensors, catalysts, information storage, *etc.*[3,4]). Moreover, when the crystal surfaces, ZnO may be assemble in different from of nanostructures such as nanorods, nanotubes, nanobelts and nanosheets[3,5].

The structures are produced by means of various methods which can be commonly classified into two categories *viz.*, vapour phase process and solution phase route. Vapour phase methods include physical vapour deposition, vapour phase transport and some other methods[6,7]. However, these methods suffer from some disadvantages. They are performed at high temperature, require complex and costly equipment and accomplish only under certain, rigorous condition. Besides, these methods often use metal catalysts such as auto help and control the growth process[8]. Solution phase route methods include sol-gel and hydrothermal methods[9]. These methods have their own disadvantage too. They need expensive chemicals and use toxic, dangerous and costly organic solvents amine in solvothermal process. Moreover, they are very time-consuming.

Herein, a new route is presented for synthesizing ZnO nano-particles based on direct reaction between Zn and water. The most challenging problem in this method was elimination of thin layer of ZnO that prevents the reaction by surrounding the particles.

Meny efforts have been so far devoted to synthesize ZnO continuously, but they all failed to propose a convenient method. Growing ZnO on Zn foil, for example, stops after a while and only a thin layer of ZnO is produced[10]. Oxidation of Zn nano-particles, as another instance, works only when particles are sampler than 20 nm and, otherwise, only outermost 10 nm of particle reacts and prevents the core from oxidation[11].

In present work, mechanical activation was used for removal of surrounding ZnO layer. The activation was performed by milling Zn powder. The fresh surfaces are exposed when the power is immersed in water. The most important advantage of this using only Zn and water as starting materials instead of materials such as $Zn(CH_3COO)_2{\cdot}2H_2O$ or alcohol solutions. This method benefits from some other advantages. It dose not need costly equipments. Its efficiency is 100 %, eco-friendly and can be used for mass production. Furthermore, this method can be extended to other metal oxide systems[12].

EXPERIMENTAL

Zinc powder (95 % purity, Mesh-325, Merck Art. No. 1.28789) is used as starting material. Zinc was milled in a

planetary ball mill for 15 h and under 0.4 MPa argon atmosphere. Ball-to-powder weight ratio was 30:1 and rotational speed of mill was 300 rpm. The milled powder was poured in 250 mL of water at 75 °C and was stirred using a magnetic stirring machine for 5 h at constant temperature. The powder then characterized by X-Ray Diffraction (XRD, using Philips 3710W X-Ray diffract meter with CuK_α (λ = 1.54184 Å) radiation), scanning electron microscopy (SEM, using Cambridge S360) and Transmission Electron Microscopy (TEM, using Philips EM 2228S). Specific surface area of the powder was determined through nitrogen adsorption by Brunauer-Emmet-Teller method (BET-N_2 adsorption, Micromeritrics Gemini 20375).

RESULTS AND DISCUSSION

X-ray diffraction profile of resultant powder is shown in Fig. 1. It demonstrates the XRD peaks corresponding to hexagonal phase of ZnO (JCDS 36-14051). Sharp diffraction peaks indicate good crystallinity of the powder. Lattice constants were calculated to be a = 3.2543(1) Å, which are slightly larger than reported in the same JSPDS card number for bulk ZnO (a = 3.2498 Å and c = 5.2066 Å).

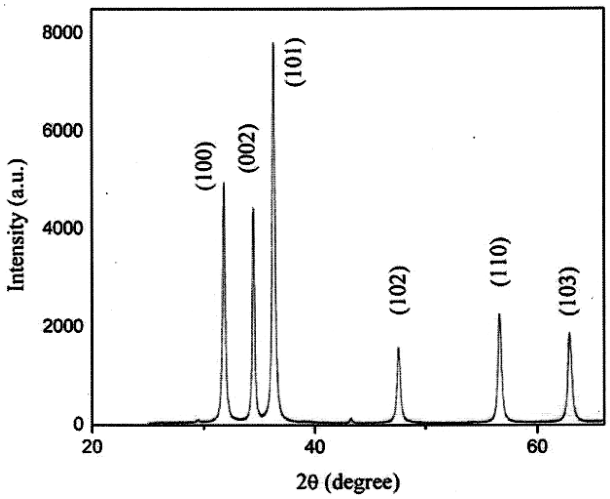

Fig. 1. XRD Pattern of activated Zn powder after being immersed hot water

Synthesized ZnO had two types of morphologies: hexagonal flakes and rod structure. Fig. 2 shows SEM image of a set of hexagonal flakes which are densely stacked with average size of *ca.* 200 nm. Finer rod structures are pictured in the TEM image of Fig. 3. The rods have average length of *ca.* 100 nm and average diameter of *ca.* 20 nm. Specific surface area of powder was obtained to be 18.25 m^2/g.

A simple mechanism can be proposed for synthesizing ZnO through reaction between activated Zn and warm water: Zn particles react naturally with oxygen or water. However, a layer of oxide or hydroxide surrounds the particle after a while and thickens gradually.

Therefore, oxide/hydroxide agent is very unlikely to pierce into the particle and reaction stops, consequently. As soon as the milled powder is immersed water bare surface of Zn particles is exposed to water and reaction begins:

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2 \quad (1)$$

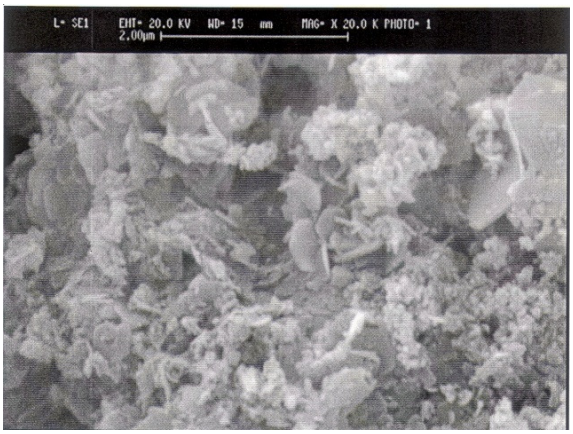

Fig. 2. SEM image of ZnO powder. Planar hexagons are clearly depicted

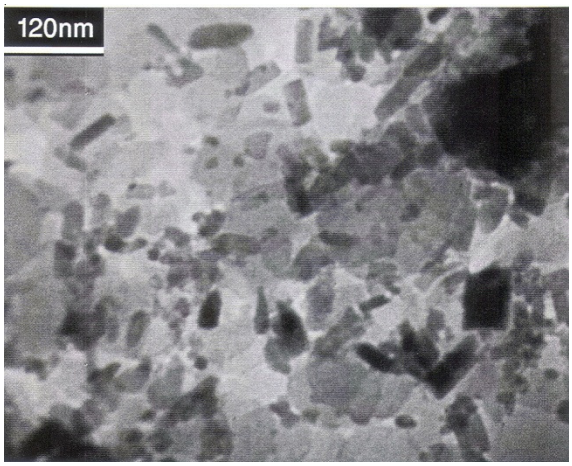

Fig. 3. TEM image of ZnO powder

Direct contact of Zn with warm water causes the kinetics of reaction to be rapid. Therefore, hydrogen generated in this reaction flows outward the Zn particles. Zinc particles, ejecting the hydrolyzed particles and preventing $Zn(OH)_2$ passive layer to be formed. Consequently, the inner atoms of Zn are incessantly brought in direct contact with water and the reaction proceeds until efficiency of 100 % is achieved. Suspended particles of zinc hydroxide are hydrated through reaction (2) and zinc oxide is synthesized. However, in contrast with reaction (1) which is exothermic, reaction (2) is endothermic[13] for this required heat is supplied by warm water.

$$Zn + 2H_2O \rightarrow ZnO + H_2O \quad (2)$$

These ZnO species form ZnO seeds. The seeds agglomerate to form hexagonal planar nuclei. From the crystal nature of wurtzite ZnO, it is known that Zn atoms are tetrahedral coordinated with four oxygen atoms. Thus, one face of the hexagonal sheet is Zn rich and forms the (0011) planes and the opposite face is the $(000\bar{1})$ oxygen rich plane. According to the rule on ZnO crystal growth mechanism, put forward by Zhong *et al.*[14], the growth rate in [0001] direction is the fastest and the velocities of crystal growth in the different directions are as following:

$$V[0001] > V[01\bar{1}\,\bar{1}] > V[01\bar{1}\,\bar{0}] > V[01\bar{1}\,1] > V000\bar{1}]$$

Therefore, ZnO nanoparticls normally prefer to grow or aggregate along <0011> direction.

Conclusion

A novel method was presented for synthesizing nano-sized ZnO particles by setting a direct reaction between water and activated Zn powder. The particles were formed in two morphologies: hexagonal planes and rods. The activation was performed by mechanical activation of Zn powder. Ball milling removes the oxide layer surrounding the Zn particles. The activated Zn powder was hydrolyzed with efficiency of 100 % as soon as it immersed in warm water. This method benefits from some advantages including simplicity, using no expensive or toxic materials and needing no metal catalysts.

ACKNOWLEDGEMENTS

The authors are thankful to the Materials and Energy Research Center for the support of this work.

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