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Production of Spherical Ag/ZnO Nanocomposite Particles for Photocatalytic Applications

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***Abstract*—**Noble metal participation in nanostructured semiconductor catalysts has drawn much interest because of their improved properties. Recently, it has been discussed by many researchers that Ag participation in TiO_2, CuO, ZnO semiconductors showed improved photocatalytic and optical properties. In this research, Ag/ZnO nanocomposite particles were prepared by Ultrasonic Spray Pyrolysis(USP) Method. 0.1M silver and zinc nitrate aqueous solutions were used as precursor solutions. The Ag:Zn atomic ratio of the solution was selected 1:1. Experiments were taken place under constant air flow of 400 mL/min at 800°C furnace temperature. Particles were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS). The crystallite sizes of Ag and ZnO in composite particles are 24.6 nm, 19.7 nm respectively. Although, spherical nanocomposite particles are in a range of 300-800 nm, these particles are formed by the aggregation of primary particles which are in a range of 20-60 nm.

***Keywords*—**Ag/ZnO nanocatalysts, Nanotechnology, USP

I. Introduction

NANOTECHNOLOGY is one of the leading research areas in the world that deeply knowledge of physics, chemistry, biology and materials science is required [1]. Nanomaterials are widely used in the space and aircraft, automotive, IT, environmental, textile and catalytic applications [2].

There are 2 main approaches to produce nanostructured / nanosized materials. These are Top-Down and Bottom-Up approaches. Each approach has advantages and disadvantages [3]. These play an important role for selecting the approach. Top-Down approach is based on the sizing down the material by giving external mechanical, chemical energy [4,5]. The main production methods related to top-down approach are high-energy mechanical milling [6], electrodeposition [7] and lithography/etching [8]. On the other hand, sol-gel [9], chemical vapor deposition (CVD) [10], aerosol based methods [11] are outstanding examples for bottom-up approach.

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Besides all nanomaterial production methods, Ultrasonic Spray Pyrolysis (USP) method comes forward with its advantages. This method is industrialized, economic method that enables to produce the wide-ranging nano products. The mechanism of this method contains four steps. The first step is aerosol generation in the ultrasonic atomizer. Aerosols are obtained from aqueous solutions of metal salts and transferred into the reaction furnace. Then, shrinkage of the aerosol droplets comes due to the evaporation. Following step is the chemical reaction at desired temperature in the furnace. Final step is the formation of solid particles [11-13]. In this method, particles produced are likely spherical, non-agglomerated, pure and narrow size distributed. Moreover, the method enables not only to produce spherical particles, but also to coat any specific substrates [12,14].

ZnO is one of the widely studied metal-oxide nanostructured semiconductors with a wide band gap of 3.2 eV as well as CuO, TiO_2 etc. [15]. Doping and making composite are widely studied ways of reducing metal oxide semiconductor band gap [16]. Within modification techniques of ZnO, there is not so much study about their composites. According to literature, composite materials could also improve the response of nanostructure under the light irradiation; increase the interface charge transfer [17].

In this research, Ag/ZnO nanocomposites were produced via USP method. X-Ray Diffraction (XRD), Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM-EDS), were used to characterize particles obtained.

II. Experimental

The high-purity metal salts used in this method were silver nitrate, $AgNO_3$ (Merck) and zinc nitrate hexahydrate, $Zn(NO_3)_2.6H_2O$ (Fluka). Atomic Ag:Zn ratio was 1:1. 0.1M Ag^+ and Zn^{2+} containing aqueous solution were prepared using deionized water. 1.3 MHz ultrasonic generator (RBI) was used to atomize the corresponding solution aerosol. Air was selected as a carrier gas and applied into the reaction furnace with a constant flow of 400 mL/min. The reaction temperature was chosen 800°C. The general overview of the USP system is shown in Fig. 1.

XRD analysis was performed with Philips 1700 X-ray Diffractometer, JEOL FEG-SEM were used to obtain SEM pictures and elemental analysis. All samples got ultrasonic treatment to prevent possible agglomeration before taking measurements.

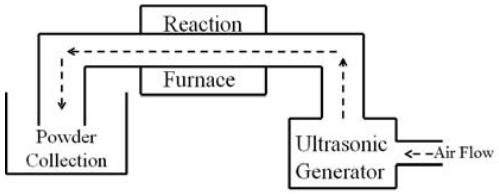

Fig. 1 General overview of USP system

III. Experimental Design

To produce Ag/ZnO nanocomposite, one of the important factor is solubility of Ag in ZnO. It can be referred from the literature that the maximum silver solubility in ZnO is % 0.76 mole at 1200°C [18]. Slight amounts of Ag in ZnO makes Ag solutes present with ZnO structure.

Reaction equations are as follows:

$$AgNO_3 \Rightarrow Ag + NO_2 + \frac{1}{2}O_2 \quad (1)$$

$$Zn(NO_3)_2 \Rightarrow ZnO + 2NO_2 + \frac{1}{2}O_2 \quad (2)$$

For the reactions (1) and (2); the Gibbs free energy change and reaction equilibrium constant were calculated via HSC. Fig. 2 shows the Gibbs free energy change with respect to temperature and Table I is for temperature dependent reaction equilibrium constant.

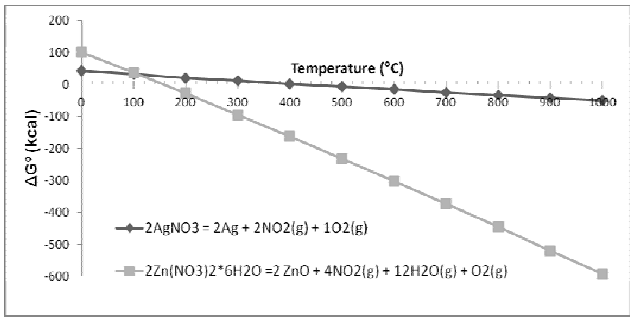

Fig. 2 Gibbs free energy changes calculated from HSC

TABLE I
Reaction Equilibrium Constants Calculated from HSC

Temperature (°C)	$K_{AgNO3/Ag}$	Temperature (°C)	$K_{Zn(NO3)2/ZnO}$
0	2.07×10^{-35}	**0**	3.11×10^{-81}
100	2.63×10^{-19}	**100**	2.16×10^{-22}
200	3.24×10^{-10}	**200**	1.05×10^{13}
300	6.60×10^{-5}	**300**	1.34×10^{36}
400	2.56×10^{-1}	**400**	5.92×10^{52}
500	9.9×10^{1}	**500**	2.76×10^{65}
600	8.8×10^{3}	**600**	3.04×10^{75}
700	2.8×10^{5}	**700**	4.93×10^{83}
800	4.56×10^{6}	**800**	3.75×10^{90}
900	4.33×10^{7}	**900**	2.87×10^{96}
1000	2.98×10^{8}	**1000**	3.75×10^{101}

The Gibbs free energy of decomposition reaction of $Zn(NO_3)_2$ is possible after about 150 °C. Furthermore, $AgNO_3$ decomposition reaction takes place after about 400°C. Ag/ZnO nanocomposite will form at reaction temperature of more than 400 °C as proven by thermodynamics. On the other hand, kinetic parameters are one of the important factors that should be considered. Table I shows the reaction equilibrium constants which are strongly related to reaction rate constants. Data presented in the table point out that, after 800 °C the change in the equilibrium constant is fixed for both reactions and there is no need to increase temperature for the termination of decomposition reaction.

IV. Results and Discussion

Crystal structure of the particles prepared was characterized by the XRD. The pattern of particles is shown in Fig. 3. Face centered cubic Ag (JCPDS Card no: 01-087-0597) and hexagonal ZnO (JCPDS Card no: 01-089-7102) were obtained in composite structure. Crystallite size of the particles were calculated with Debye-Scherrer formula using (111) peak (2θ =39°) of Ag and (101) peak of ZnO (2θ =36°). Crystallite size of Ag is 24.6 nm whereas for ZnO is 19.7 nm.

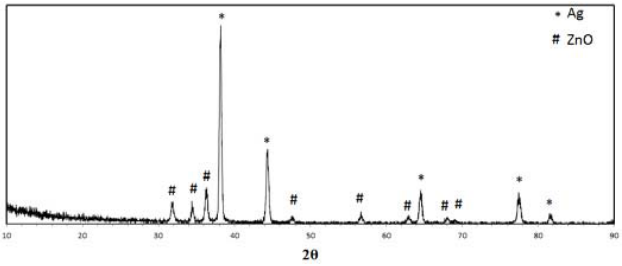

Fig. 3 XRD pattern of Ag/ZnO nanoparticles

The morphology of the particles produced was observed by SEM. SEM picture of particles is presented in Fig. 4. In this figure, particles so called secondary particles are submicron sized ranging from 300 nm to 800 nm and nearly spherical. High magnification image of particles clearly shows that primary particles ranging 20-60 nm aggregates and forms the secondary particles.

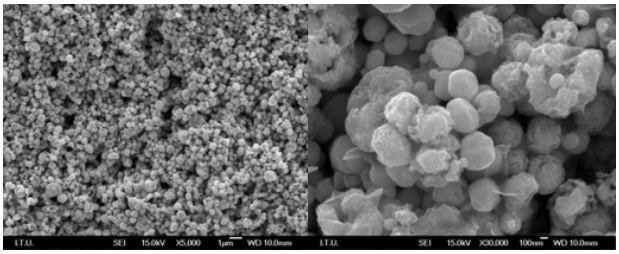

Fig. 4 SEM pictures of Ag/ZnO nanocomposite particles

Fig. 5 gives comparison between backscattered electron images and secondary electron images. Backscattered electron imaging gives the compositional distribution of the particles. The relatively brighter areas are high molecular weight Ag rich areas, whereas darker areas should indeed be low molecular weight ZnO rich areas.

Composition image exhibits that brighter and darker areas are not obviously segregate that indicates homogeneous distribution of Ag and Zn in the nanocomposite particles. SEM-EDS analysis shows that Ag:Zn ratio in nanocomposite particles is 0.998, which nearly same with desired composition in corresponding solution.

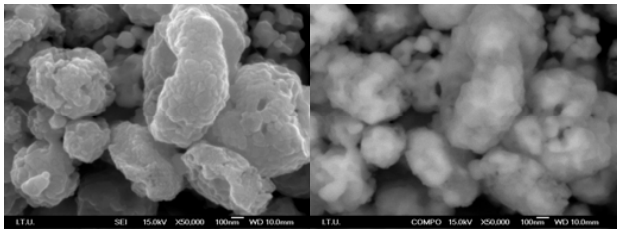

Fig. 5 Compositional distribution of particles (a) SEI and (b) BEI

Comparing the results of the study on Ag/ZnO nanocomposite particles by USP method conducted by Gürmen et al. shows that solution concentration and carrier gas flow rate have significant influence on the particle size, morphology and crystallite size. Finer crystallite sizes were obtained by decreasing of solution concentration [19]. In addition to that, aggregation of the primary particles increased due to the lower gas flow rate, which causes the longer reaction/sintering time in the heated zone. It is obviously seen from the results that nanocomposite particles have homogeneous composition which verifies the advantage of USP method for the production of desired nanocomposite particles

V. Conclusion

Spherical Ag/ZnO nanocomposite particles were successfully produced via USP method with 0.1M precursor solution at 800°C reaction temperature. Thermodynamic and kinetic background of decomposition reactions was also discussed. XRD results showed nanocomposite particles compose of hexagonal ZnO with 19.7 nm crystallites and FCC Ag with 24.6 nm crystallites. As a support to XRD, SEM-EDS showed only Ag, Zn and O elements. SEM also enabled us to predict particle morphology. Spherical secondary particles of 300-800 nm particle size were obtained using this method and consist of primary particles of 20-60 nm particle size. The distribution of Ag and ZnO in the secondary particles is homogeneous, and the ratio of Ag:Zn is nearly same with desired amount. USP method is a suitable process for Ag-ZnO preparation in a lab-scale and controllable particle properties of nanocomposites give a chance to investigate their effects on photocatalytic activity.

Acknowledgment

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