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The effect of the synthesis route on the grain size and morphology of ZnO/Ag nanocomposite

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Ag/ZnO nanocomposite powders have various applications as contact materials. There are some methods for synthesizing them such as chemical vapor deposition (CVD), co-precipitation, spray-pyrolysis, sol-gel, laser ablation and hydrothermal routes. In this study, Ag/ZnO nanocomposite powders have been synthesized by three various co-precipitation techniques. The nanocomposite powders obtained were evaluated by scanning electron microscopy (SEM), X-ray diffraction (XRD), simultaneous thermal analysis (STA), X-ray fluorescence (XRF) and energy dispersive X-ray spectroscopy (EDS). The experimental results showed that the size of the nanocomposite samples was in the range of 50-100 nm. Finally, it was found that the optimum route for preparing Ag/ZnO nanocomposite powders was the dropping funnel method.

Key words: Ag/ZnO, Co-precipitation, Nanocomposite, Grain size, Morphology.

Introduction

Contactors, motor starters, circuit breakers and relays are switchgears that control and regulate the electrical power. [1] Silver metal oxides (Ag/MeO), especially silver cadmium oxide (Ag/CdO), have attracted much attention in the electrical and electronics industries due to their high thermal and electrical conductivities, low contact resistance, high welding adhesion resistance, and high resistance to arcing, high hardness and strength [2-4]. However, dangerous pollution problems have occurred with toxic cadmium vapor released into the environment during the fabrication. Scientists are engaged to develop further research into environmentally friendly materials, such as Ag-ZnO [5], Ag-La_2O_3 [6], Ag-Yb_2O_3 [1] and Ag-SnO_2 [7, 8].

In recent decades, silver tin oxide has been used instead of toxic Ag/CdO contact materials. Of course, silver tin oxide has some drawbacks such as high temperature rise and being more difficult to process [9]. Ag/ZnO contact material has been used to replace silver tin oxide (Ag/SnO_2) in order to compensate its shortcomings [2, 10]. Chemical and physical features and the oxide vapor pressure of Cd and Zn are similar. The electrical contact resistance of Ag/ZnO is lower than that of Ag/CdO and is a potential candidate to replace Ag/CdO as a new contact material [11].

Several methods have been reported to prepare Ag/ZnO materials, such as co-precipitation, hybrid induction and laser heating techniques [12], photo reduction [13, 14], impregnation photolysis [15], flame spray pyrolysis [16], ultrasonic spray pyrolysis [17] etc.

The Co-precipitation method is considered to be a better choice, since it is simple and its particle size is small, uniform and controllable [18].

In this study, Ag/ZnO contact materials were fabricated by co-precipitation method. The purpose of this paper is to investigate the effect of the synthesis route on crystal size and morphology of Ag-ZnO nanocomposite.

Three routes of the co-precipitation were used for synthesizing the nanocomposite powders and the grain size and morphology of powders were compared. These routes were DF (dropping funnel), DM (direct mixing) and DS (direct spraying). The results showed that the dropping funnel method is the most appropriate route for preparing fine particles.

Experimental procedure

Materials

Silver nitrate ($AgNO_3$), zinc nitrate hexa hydrate (Zn $(NO_3)_2.6H_2O$) and sodium carbonate (Na_2CO_3) were purchased from the Merck company and used without any further purification.

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Sample preparation

The starting materials for the preparation of Ag and ZnO powders were silver nitrate ($AgNO_3$) and zinc nitrate hexahydrate ($Zn (NO_3)_2.6H_2O$), respectively. The preparation steps were as follows: 12.5 mmole $Zn (NO_3)_2.6H_2O$ and 83.4 mmole $AgNO_3$ were dissolved in water and mixed together homogenously. The mixture was poured into a Na_2CO_3 solution with three different methods. First, the mixture of $AgNO_3$ and $Zn (NO_3)_2.6H_2O$solution were poured into the Na_2CO_3 solution suddenly (direct mixing method-DM). In the second method, the mixture of $AgNO_3$ and $Zn (NO_3)_2.6H_2O$ solution were sprayed into Na_2CO_3 solution (direct spraying method-DS). In the third method, the precursors of $AgNO_3$ and $Zn (NO_3)_2.6H_2O$solution were poured drop-wise into an aqueous solution of Na_2CO_3 and the reaction was carried out under vigorous stirring at room temperature (dropping funnel method-DF). Silver and zinc carbonate were filtered and washed and then dried in an oven. The following reactions will occur initially:

$$2AgNO_3+Na_2CO_3\rightarrow Ag_2CO_3+2NaNO_3 \quad (1)$$

$$Zn(NO_3)_2+Na_2CO_3\rightarrow ZnCO_3+2NaNO_3 \quad (2)$$

Calcination at 400 °C for 4 h converts the carbonates to Ag-ZnO nanocomposite.

$$Ag_2CO_3\rightarrow Ag_2O+CO_2 \quad (3)$$

$$ZnCO_3\rightarrow ZnO+CO_2 \quad (4)$$

$$Ag_2O\rightarrow Ag+1/2O_2 \quad (5)$$

Sample characterization

X-ray diffraction

XRD of all powders was carried out in a diffractometer, using Cu-Kα radiation (1.5406 Å). For qualitative analysis, XRD diagrams were recorded in the interval $10° \leq 2\theta \leq 110°$ at a scan speed of 2 °minute^{-1} giving a step size of 0.03 ° and a step time of 1 s.

Simultaneous thermal analysis (STA)

The thermal behavior of the nanocomposite was studied by simultaneous thermal analysis (STA). A thermo analyzer (STA; Polymer Laboratories PL-STA 1640) that started from room temperature up to 600 °C with a heating rate of 10 K minute^{-1} was used to record the conventional thermo analytical curves (DTA and TGA).

Scanning electron microscopy

The powder samples were coated with a thin layer of gold by sputtering (EMITECH K450X, England) and then the microstructure of the powder sample was observed in a scanning electron microscope (SEM; Philips XL30) that operated at an acceleration voltage of 25 kV.

X- Ray fluorescence (XRF)

The composition of the synthesized powders was analyzed by XRF. Samples with a particle size of ≤ 20 μm were selected and converted into glassy disks by melting in Pt-Au 5% crucibles (with the addition of a ux mixture containing 80 wt. % lithium metaborate and 20 wt.% lithium tetraborate). Composition measurements were performed in a Philips PW2404 sequential X-ray uorescence spectrometer equipped with a rhodium X-ray tube.

Results and discussion

Reaction mechanism

It was demonstrated that due to quick mixing of respective solutions to the precipitant, an instantaneous super-saturation occurs which leads to coarser particles. While by adding the solution drop-wise to the reaction media, there were a greater number of suitable places for nucleation. Hence, the nanosized powders were achieved which led to increased specific surface area of the particles. Moreover, the shape of powders changed from flaky to round shape. This phenomenon can improve the flowability of the powders. The difference in the mentioned morphology can be observed in Fig. 1.

SEM observations

As observed in Fig. 1 (a, b, c) the DF method can be considered as a suitable method for preparation of Ag/ ZnO nanocomposite powder because the finest grain

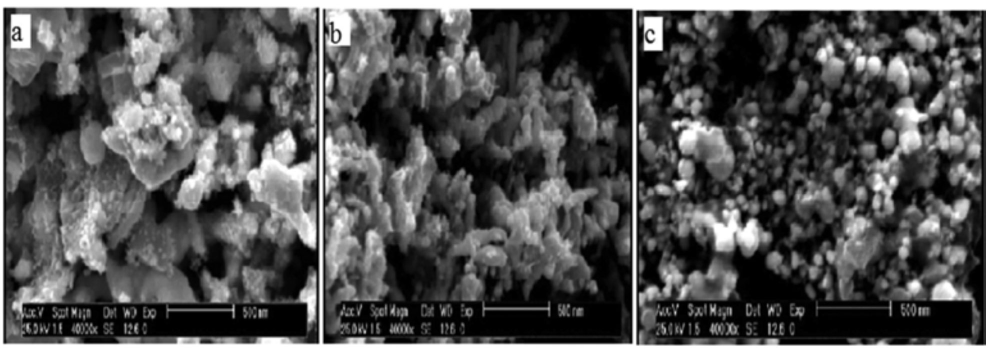

Fig. 1. SEM images of samples with 40000 times magnification a (DM method), b (DS method) and c (DF method)

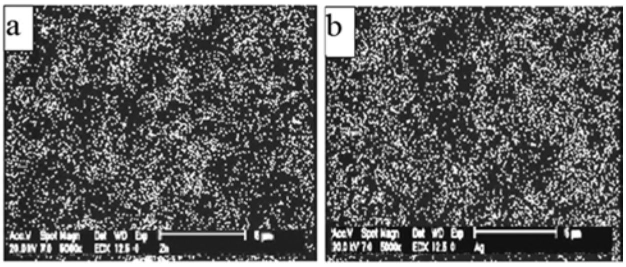

Fig. 2. EDX images of distribution of Zn (a), Ag (b) in Ag/ZnO composite in DM method.

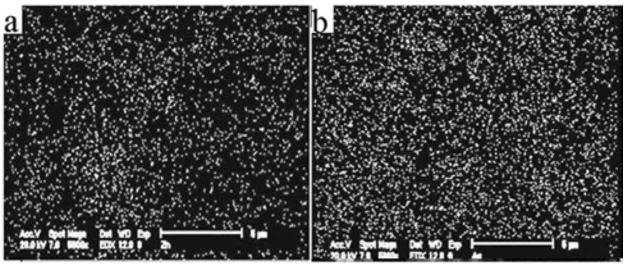

Fig. 3. EDX images of distribution of Zn (a), Ag (b) in Ag/ZnO composite in SD method.

sizes were achieved by this method. The mean grain size in this method is around 60 nm and the range of particle size is between 50-100 nm.

EDS analyses

Figs. 2 and 3 show the EDS patterns of Ag/ZnO nanocomposite samples from the DM and SD methods. It can be seen that Ag and Zn elements do not have a uniform distribution in the matrix. The results obtained of EDS patterns (Figs. 2 and 3) show that the samples contained two elements of Ag and Zn. In the DM and SD methods the nucleation does not occur as well as in the DF method that can be seen in Fig. 4. Therefore, the DF method is a better route as far as uniform distribution of ZnO in the Ag matrix is concerned. It is worth mentioning that a uniform distribution is one of the most important properties in the preparation of Ag/ ZnO nanocomposites [18, 19].

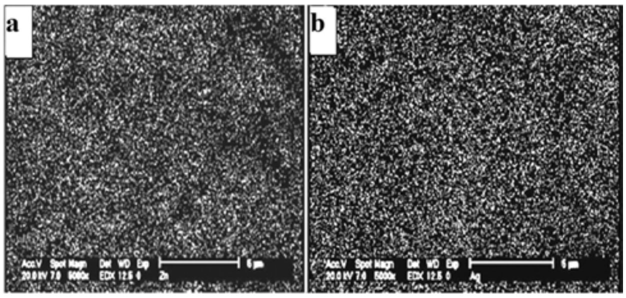

Fig. 4. EDX images of distribution of Zn (a), Ag (b) in Ag/ZnO composite in FD method.

Table 1. Calculation of grain size by Scherrer'sformula

Method	Grain size
DM	276 nm
DS	90.7 nm
DF	57.38 nm

Crystallite size

The crystallite sizes of the Ag-ZnO powders were determined by XRD analyses. It was calculated from the line broadening of the (111) Ag diffraction line according to the Scherrer's equation:

$$D = \frac{k\lambda}{\beta Cos\,\theta_B} \quad (6)$$

where D is the crystallite size, λ is the wavelength of Cu Kα_1 radiation, and β is the corrected width at half maximum of the diffraction peak. The grain size of samples is shown in Table 1. Since by adding the solution drop-wise to the reaction media facilitates the condition for nucleation so nanosized powders were achieved which in turn increased the specific surface area of particles. Super saturation constitutes the thermodynamic driving force for all the precipitation and crystallization processes [20].

XRD analyses

Fig. 5 depicts the XRD patterns of Ag/ZnO

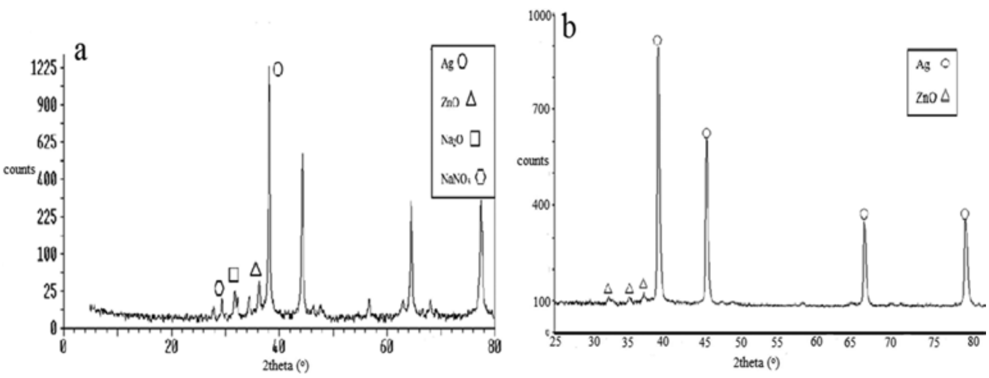

Fig. 5. XRD patterns of the Ag/ZnO nanocrystallites synthesized by the co-precipitation method. a) Not washed with adequate water b) washed with adequate water several times

Table 2. XRF result of final powder (weight percent)

silver	Zinc Oxide	Impurities
91.4%	7.8%	0.8%

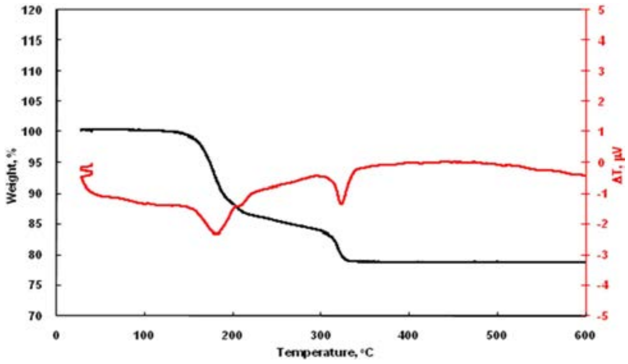

Fig. 6. TG-DTA curves of the precursor.

nanocomposite powder obtained. In Fig. 5(a), XRD pattern indicates that the peaks of $NaNO_3$ and Na_2O appeared. $NaNO_3$ is soluble in water and it shows that there was not adequate washing in the first stage of fabrication. In Fig. 5(b) the impurities were removed with further washing and there were no Na_2O peaks in the XRD pattern. The hexagonal structure of ZnO is exhibited by the typical pattern. Peaks associated with Ag were observed at 39 °, 44.6 °, 64.9 ° and 78.2 ° [18]. Peaks associated with ZnO were observed at 31.77 °, 34.44 ° and 36.27 °.

XRF analyses

The XRF data are given in Table 2. Ag and Zn can be seen in the final product confirmed by the XRD and EDS results. The amount of impurity in the composite was low and there was a relatively good agreement between the theoretical calculations and the XRF results. In this sample the content of ZnO is 9.7 wt.%, which is basically close to the actual amount of 10 wt.%.

Thermal analysis

A TG-DTA curve of the nanocomposite powders obtained (DF method) is illustrated in Fig. 6. For the Ag/ZnO nanocomposite, weight losses were observed at 160 °C, between 200 °C and 300 °C, and < 400 °C. The first period of mass loss (< 200 °C) corresponds to desorption of physically adsorbed water. This process gives a strong endothermic peak at about 160 °C and continues to about 300 °C. A strong endothermic peak at about 320 °C corresponds to an obvious weight loss in the TG curve and the weight remained constant when the temperature was higher than 320 °C. This indicates the complete decomposition of the carbonate and hydroxyl of the precursor [18].

Conclusion

In conclusion, Ag/ZnO nanocomposites were successfully synthesized via a chemical co-precipitation method. The precursor was a mixture of $AgNO_3$ and $Zn(NO_3)_2.6H_2O$. The DF (dropping funnel) method was a convenient method for synthesizing Ag/ZnO nanocomposite. The finest grains were produced by this method, the mean grain size was around 60 nm and the range of particle sizes is between 50-100 nm. A more uniform distribution occurred in the DF method than with the other methods.

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