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SYNTHESIS, CHARACTERIZATION AND OPTIMUM REACTION CONDITIONS FOR NANOSTRUCTURED ZINC OXIDE

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ABSTRACT. In the present paper were established the optimum conditions for the synthesis of Ag-doped ZnO nanopowders. The 0.05% Ag-doped ZnO nanopowders were successfully synthesized by coprecipitation, followed by a washing-drying-calcination treatment. It was found that the optimum conditions for the preparation with high yield and high surface area were as follows: pH value 6.9-7.1, calcination temperature 400 - 500 °C and calcination time 2 h, respectively. The obtained nanopowders were investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and specific surface. The silver doping improves the antibacterial activity of ZnO nanopowders. Therefore the materials based on the obtained nanopowders represent an attractive opportunity for the construction industry.

Keywords: zinc oxide, silver, synthesis, coprecipitation, characterization.

INTRODUCTION

In the past decades, the synthesis and characterization of “so-called” nanoparticles have attracted much attention, not only for the fundamental scientific interest, but also for many technological applications [1–4]. These particles have distinctly different electrical, optical, mechanical and chemical properties in comparison with their corresponding bulk material.

The interior mould attack has become a problem of increasing importance. The medical researchers and phisicians have been observing more and more respiratory and allergic complaints arising from exposure to moulds. Also, paint on outside attack must be taken into account [5, 6].

In recent years, ZnO and ZnO-based powders have been extensively studied due to their properties and technological applications [7]. As well known, zinc oxide has a long history of usage for pigments and protective coatings on metals [8]. Zinc oxide is a very important material due to the interesting

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characteristics (fluffy white, density 5.61 g/cm^3, melting point 1975^{o}C) [9]. ZnO is cheaper than other white oxides and insoluble in water, a very important property of the quality of a pigment.

As well known, silver and silver ions exhibit an excellent antibacterial activity against many types of bacteria, even at lower concentrations, and do not cause adverse health effects [10, 11]. Recently, several inorganic antibacterial materials containing silver and silver ions have been successfully prepared and some of them are already commercialized products. These materials are more chemically durable, discharge slowly the silver ion and more slowly affected by light. Therefore, it is rational that introduction of silver ions into ZnO may improve antibacterial capacity of ZnO.

Until now, several methods, such as the mechanical mixing method [12], sol-gel process [13, 14], thermal hydrolysis [15] and coprecipitation [16] have been used to prepare metal-doped ZnO nanopowders.

The coprecipitation method seems to be the most attractive due to its easy control, without requiring expensive and complex equipments. Coprecipitation is the process whereby the fractional precipitation of a specified ion in a solution results in the precipitation not only of the target ion but also of other ions existing in the solution. The additional precipitation of unwanted ions represent an impediment to the analytical process [17]. Some of the most commonly substances used in coprecipitation operations are hydroxides, carbonates, sulfates and oxalates. pH is evidently an important factor in this type of process.

During last years our interests were focused on the preparation and characterization of new ZnO-based nanopowders [18]

The objective of the present study is to continue our research related to determining the optimum parameters for the synthesis of Ag-doped ZnO nanopowders *via* coprecipitation and the properties of the obtained nanoparticles. The obtained nanopowders have a low doping metal content (0.05 wt.%) in order to avoid cytotoxicity and not to affect the white color of the powders. The materials that incorporate these nanopowders may be used in construction industry, increasing the security of living, durability and comfort.

RESULTS AND DISCUSSION

Preparation

Establishing the adequate conditions for complete precipitation from zinc solution is not a simple process due to the amphoter character of Zn. In order to obtain the desired material, the zinc hydroxide is dissolved in a small excess of sodium or potassium hydroxide resulting in the corresponding alkali metal zincate. Because the zinc hydroxide is soluble in the presence of ammonium ions, different complex ions resulted too. Therefore, the solution pH is an important factor for the process.

The zinc hydroxide in the presence of alkaline carbonates form some basic zinc carbonates as $(CO)_3Zn_4(OH)_2$. Thus, it was appeal to the simultaneous precipitation of Zn^{2+} and Ag^{+} using an alkaline carbonate. The obtained carbonates were calcinated at an appropriate temperature resulting in a homogenous mixture of oxides containing particles of small dimensions.

The degree of precipitation control was realized by titration of the unprecipitated cation from the solution resulted after filtration, at controlled pH values. Thus, the quantity of precipitated Zn^{2+} could be calculated as the difference between initial and final content from the filtrate filled up to constant volume. The experiments were realized at different pH values, *i.e*. 6.0-8.0. In Figure 1 are presented the values for the zinc remained unprecipitated in solution. The optimum precipitation pH value is 6.9-7.1.

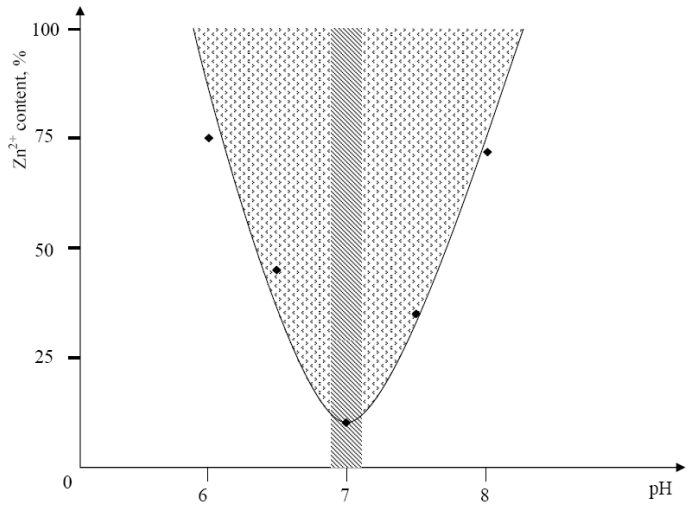

Figure 1. Relationship between the pH of solution and Zn^{2+} content.

It was found experimentally that the optimal synthesis method can be divided into two parts: one is the preparation of the precursor by the coprecipitation method and the other one is the formation of silver doped ZnO nanopowders by calcination (Figure 2) [18].

The zinc oxide diffraction peaks start to appear after the powder was calcinated at 380^{o}C. With the increase of thermal treatment temperature, the microcrystallites are formed more obviously and also the diffraction peaks become more intense.

The commercial ZnO has a wurtzite crystal structure. Literature data demonstrate that ZnO crystals begin to nucleate at about 380^{o}C, and then ZnO crystal growth is completed at about 800^{o}C [19].

At 600ºC X-ray diffraction analysis of the prepared Ag-doped ZnO nanopowder show sharp diffraction peaks corresponding to the hexagonal wurtzite structure: 31.8º (1 0 0), 34.5º (0 0 2), 36.4º (1 0 1), 47.7º (1 0 2), 56.7º (1 1 0), 62.9º (1 0 3), 66.4º (2 0 0), 68.2º (1 1 2) and 69.3º (2 0 1).

The typical silver diffraction peaks were not observed, mainly because the low dosage of silver ions.

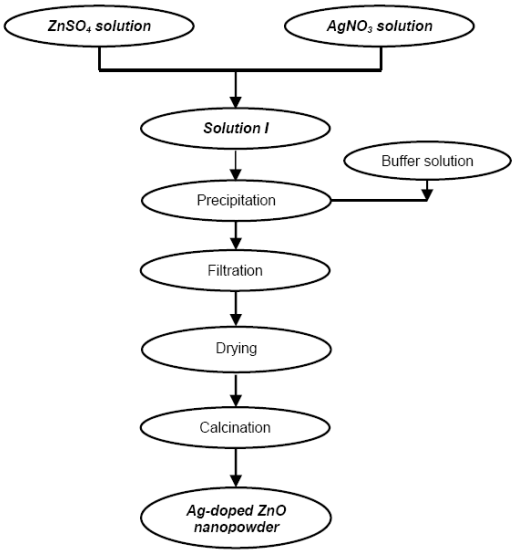

Figure 2. Flow diagram for the synthesis of Ag-ZnO nanopowders.

Structural characterization

X-ray diffraction spectra

Figure 3 shows the XRD patterns of the samples calcinated at different temperatures.

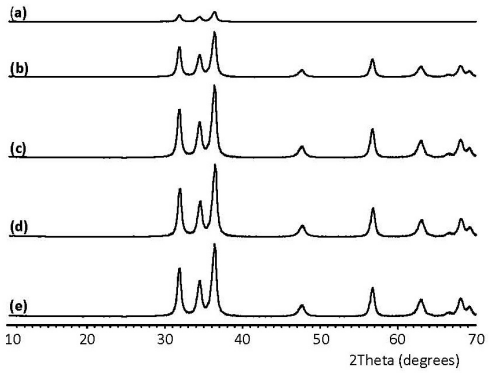

Figure 3. XRD patterns of the ZnO nanopowders calcinated at different temperatures: (a-e) 300, 380, 400, 450 and 600ºC, respectively.

Specific surface

The temperature heat treatment is the factor that mostly influences the formation and growth of crystalline particles obtained from precipitates after calcination. The diffusion in solids, the mobility of constituent particles and their possibility of migration to interfaces increase as temperature increases. The control of particle size increasing is realized indirectly by determining specific surface of the calcinated product at the temperatures of interest.

The studies were realized on precipitates calcinated at 300, 400 and 600°C. The results of the specific surface area analyses are reported in Table 1.

Table 1. Specific surface area of the powders calcinated at different calcination temperatures.

Temperature (°C)	Specific surface area (m^2/g)	Average diameter (nm)
300	70.8-74.3	14.39-15.10
400	49.8-51.5	20.90-21.39
600	20.46-28.6	52.27-62.40

Fourier transform infrared spectroscopy

In FTIR spectra of the samples undoped and doped ZnO (calcinated at 400°C) were observed bands with maximum well defined, centred at 593, 555, 547, 522, 517, 503, 500, 490 cm^{-1} (Figure 4).

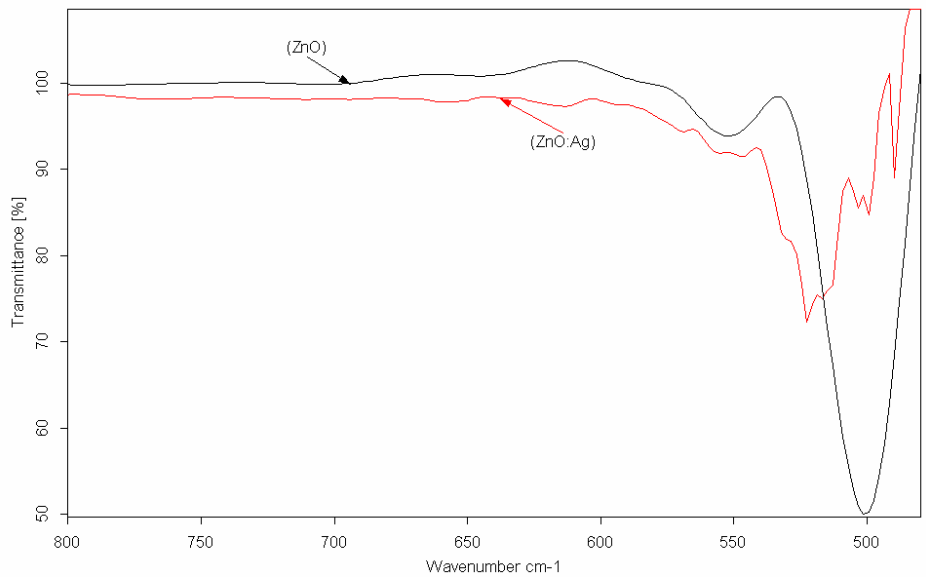

Figure 4. FT-IR spectra of undoped ZnO and Ag - doped ZnO nanopowder, calcinated at 400ºC.

The FTIR spectra of undoped ZnO powders show a high intensity broad band around 490 cm^{-1} due to the stretching mode of Zn–O bond. A similar band was also observed in doped ZnO powder.

The absorption bands observed in the low energy region is formed by the stretching vibration modes of Zn–O and Ag–O bonds (593 and 490 cm^{-1}) [20].

In the FTIR spectra for doped ZnO sample, in comparison with undoped ZnO spectra, we can see a slight displacement of characteristic Zn-O band, concurrent with modification of the peaks and appearance of the new bands which can be attributed to the Zn-O-Ag bonds.

The broad absorption band from 490-600 cm^{-1} indicates the presence of Ag in the ZnO powder and this could be due to a small concentration of silver.

The materials based on these nanopowders could be used in public spaces which necessitate high quality standards and special technical requirements (hospitals, surgeries, bathrooms, food processing facilities, storage rooms, laboratories, nurseries, schools, sport rooms, etc.). General advantages and benefits in the use of materials based on these nanopowders are: environmentally friendly, significant reduction of moos and algae, improvement of the air quality, housing comfort and healthy dwelling, inexpensive, long-term prevention, convenient and easily synthesizable.

CONCLUSIONS

The synthesis of Ag-doped ZnO samples by coprecipitation is simple, stable, repeatable and inexpensive. Several parameters that may influence the synthesis have been discussed. It has been concluded that the optimum reaction conditions are: pH: 6.9-7.1, calcination temperature: 400-500 °C and calcination time: 2 h. The silver concentration must be enough small not to influence the pigment color. The characterization of the obtained samples by specific techniques clearly indicates nano-sized particles.

These nanopowders may be incorporated into a coating in order to obtain materials with superior characteristics for the construction industry.

EXPERIMENTAL SECTION

The Ag-doped ZnO nanopowders were prepared by the coprecipitation method similar to that one previously reported [18].

All reagents were purchased from commercial suppliers and used without further purification. There were used precipitant solution of different pH values, *i.e*. 6.0-8.0) and the calcination temperatures were: 300, 380, 400, 450 and 600ºC, respectively).

The obtained powders were investigated using powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and specific surface studies. X-ray diffraction (XRD) patterns of these powders were measured on

the SHIMADZU 6000 diffractometer using a CuKα radiation source (40.0 KV, 30.0 mA) and a graphite monochromator. The samples were characterized by FTIR measurements using a model Tensor 27 Bruker spectrometer, in the wavelength range 4000-400 cm^{-1}, after 64 scans, with resolution of 4 cm^{-1}. The specific surface was determined using a modified BET installation.

The detailed preparation process can be described as follows: firstly, under vigorous stirring, the aqueous solution of zinc sulfate was added into silver nitrate aqueous solution. Subsequently, a buffer solution was used to adjust the pH of the reaction system to about 6.9-7.1. The resulted precursor of Ag-doped, $Zn_5(CO_3)_2(OH)_6$ precipitate, was thoroughly washed with distilled water and dried at room temperature (for more than 24 h) and then thermally decomposed under static air atmosphere to give silver doped zinc oxide. The calcination temperature was relatively low, in the range of 400-500 ^oC and the calcination time was 2 h, after which the material was cooled in the furnace and a white powder was obtained. A similar procedure was used for other pH and calcination conditions.

REFERENCES

1. G. Schmid, "Nanoparticles: From Theory to Application", Wiley-VCH, Weinheim, **2004**.
2. K.J. Klabunde, "Nanoscale Materials in Chemistry", Wiley-Interscience, New York, **2001**.
3. A.P. Alivisatos, *Science*, **1996**, *271*, 933.
4. Zhong Lin Wang, *J. Phys.: Condens. Matter*, **2004**, *16*, 829.
5. S. E. Henshon, "Mildew on the Wall", Royal Fireworks Publishing Company, New York, **2004**.
6. F.H. Kayser, K.A. Bienz, J. Eckert, R.M. Zinkernagel, "Medical Microbiology", Ed. Georg Thieme Verlag, Stuttgart, **2005**.
7. S.R. Dhagea, R. Pasrichab, V. Ravia, *Materials Letters*, **2005**, *59*, 779.
8. G.E. Weismantel, "Paint Handbook", Ed. McGraw-Hill, New York, **1981**.
9. C.G. Macarovici, D. Macarovici, "Chimia oxizilor dubli si utilizarile lor", Ed. Academiei Republicii Socialiste Romania, Bucuresti, **1975**.
10. A. Panacek, L. Kvitek, R. Prucek, M. Kolar, R. Vecerova, N. Pizurova, V.K. Sharma, T. Nevecna, R. Zboril, *J. Phys. Chem. B*, **2006**, *110*, 16248.
11. H.J. Lee, S.Y. Yeo, S.H. Jeong, *J. Mater. Sci.*, **2003**, *38*, 2199.
12. P.B. Joshi, N.S. S. Murti, V.L. Gadgeel, V.K. Kaushik, P. Ramakrishnan, *Journal of Materials Science Letters*, **1995**, *14*, 1099.
13. B. Houng and C.-J. Huang, *Surf. Coat. Technol.*, **2006**, *201*, 3188.
14. M.J. Alam, D.C. Cameron, *J. Vac. Sci. Technol.*, A, *Vac. Surf. Films*, **2001**, *19*, 1642.

15. Y. Liu, C. Liu, Q. Rong, Z. Zhang, *Appl. Surf. Sci.,* **2003**, *220*, 7.
16. O.D. Jayakumar, H.G. Salunke, R.M. Kadam, M. Mohapatra, G. Yaswant, S.K. Kulshreshthaa, *Nanotechnology*, **2006**, *17*, 1278.
17. P. Patnaik, "Dean's Analytical Chemistry Handbook", 2nd ed. McGraw-Hill, **2004**.
18. O. Cadar, C. Roman, L. Gagea, I. Cernica, A. Matei, *Revista Romana de Materiale*, **2007**, *37 (4)*, 316.
19. T. Masaki, S.J. Kim, H. Watanabe, K. Mizamoto, M. Ohno, K.H. Kim, *J. Cer. Proces. Res.*, **2003**, *4 (3)*, 135.
20. A.S. Tas, P. J. Majewski, F. Aldinger, *J. Am. Ceram. Soc.*, **2000**, *83*, 2954.