SYNTHESIS OF SUBMICRON POWDERS
OF ZnO AND ZnO-M_nO_m (M_nO_m = TiO_2, V_2O_5) BY SOL-GEL METHODS

Y. Dimitriev¹, Y. Ivanova¹, A. Staneva¹, L. Alexandrov²,
M. Mancheva², R. Yordanova³, C. Dushkin¹, N. Kaneva³, C. Iliev⁴

¹ University of Chemical Technology and Metallurgy
8 Kl. Ohridsky, 1756 Sofia, Bulgaria
E-mail: yanko@uctm.edu
² Institute of General and Inorganic Chemistry,
Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
³ Laboratory of Nanoparticle Science and Technology,
Faculty of Chemistry, Kl. Ohridsky University of Sofia,
1 James Boucher blvd., 1164 Sofia, Bulgaria
⁴ Geological Institute, Bulgarian Academy of Sciences,
1113, Sofia, Bulgaria

ABSTRACT

The present study is based on experiments using Zn-nitrate and Zn-acetate as precursors along with several variants of sol-gel technique which are widely popularized in the literature. The purpose is to check their applicability to ZnO-TiO₂ and ZnO-V₂O₅ binary mixtures as well as their photocatalytic activity towards model solutions. Comparative analysis of different schemes of preparation of ZnO and binary mixtures with the participation of TiO₂ and V₂O₅ show that the production of powders for photocatalytic applications depends on many factors. It has been shown that the introduction of small amounts of TiO₂ in presence of ethylene glycol leads to better results as compared to pure ZnO and a combination of ZnO and V₂O₅.

Keywords: sol-gel methods, photocatalytic activity, Zn-nanoparticles, TiO₂.

INTRODUCTION

The interest in studies of ZnO strongly increased during the past years due to the electric, optic and magnetic properties of this compound as well as to its relatively good chemical and thermal stability. Being characterized by multifunctionality, ZnO found application in various spheres already in the middle of 20th century. Its photocatalytic activity is among the reasons for which it is subjected to intense studies by physicists, chemists and technologists as it is a material suitable for creating a biologically pure environment. The methods of its preparation are accessible and economically advanta-

geous. Its properties, however, largely depend on the morphology and dimensionality of its particles. Zinc oxide has the unique ability to form different nanostructures from spheres, ribbons, pipes, sticks, tetrapods [1]. Regardless of the large number of investigations, the preparation of nanosized active particles especially by wet methods (which are more efficient and preferred for large applications) is still a challenge to scientists with respect to both obtaining reproducible structures and constant physicochemical parameters. There is no universal method for obtaining particles with various geometry and properties. Thus, spherical nanocrystals are prepared by spray pyrolysis and ther-
nal decomposition of zinc acetate [3, 4]. Precipitation from aqueous solutions results in prismatic and needle-like particles [5, 6]. On the other hand, varying the kind of precursor and the regime of thermal decomposition, it is also possible to obtain particles with different geometry [6-8]. Partly filled pipes have been synthesized using block polymers. Sol-gel methods have found application in the preparation of ZnO nanoparticles. Special attention in this case is paid to the kind of solvent with a view to achieving the desired particle geometry [9,10]. The photocatalytic activity of pure powdery zinc oxide has been investigated with respect to the decomposition of phenol[1], methyl orange [12], methylene blue [13], camphor and remazol red in water medium [14-16]. There is an opinion with respect to the decomposition of organic pollutants in water, that zinc oxide nanoparticles exhibit better properties towards the conventional ZnO and TiO₂ available on the market [16]. The photocatalytic activity of mixed ZnO-TiO₂ powders with respect to nitrophenol, formic and benzoic acid is proved [17-19]. The study of the photocatalytic activity of mixed systems of ZnO-WO₃ and ZnO-V₂O₅ [20-22] is also of special interest since the addition of transition element oxides which are also semiconductors, is expected to enhance the activity not only in the ultraviolet but also in the visible region.

The present study is based on experiments using zinc nitrate and Zn acetate as precursors along with several variants of sol-gel technique which are widely popularized in the literature. The purpose is to check their applicability to ZnO-TiO₂ and ZnO-V₂O₅ binary mixtures as well as their photocatalytic activity towards model solutions.

**EXPERIMENTAL**

**Zn nitrate precursor.** Three schemes were used to prepare ZnO/TiO₂ mixtures. The first two schemes

![Fig. 1. Flow diagram for preparation of ZnO powder by Zn-nitrate and Ti-butoxide (sample 7A).](image1)

![Fig. 2. Flow diagram for preparation of ZnO/TiO₂ powder by Zn-nitrate and Ti-butoxide (sample 10).](image2)
applied Zn(NO$_3$)$_2$$\cdot$6H$_2$O, CH$_3$COOH and Ti-butoxide Ti[O(CH$_2$)$_3$CH$_3$]$_4$ (Figs. 1, 2) in different ratio (samples 7A and 10). The components were dissolved at room temperature under intense stirring to achieve complete dissolution and occurrence of hydrolysis processes. This was followed by evaporation, drying and calcinations of the samples at 400-420°C. In the third diagram (Fig. 3), the Ti-butoxide content was reduced and ethylene glycol was introduced instead of acetic acid (sample 7B). The procedure of Chopali et al. [23] was followed in order to obtain an initial homogeneous polymer solution.

**Zn acetate precursor.** According to the scheme proposed (Fig. 4), evaporation and calcination of a solution with the participation of propanol and acetic acid was applied (sample 3A). The next scheme (Fig. 5) is a modification of the method proposed by Nondelaers et al. [24] for preparation of ZnO nanoparticles. The reagents used were: Zn(CH$_3$COO)$_2$$\cdot$2H$_2$O, citric acid
C(OH)(COOH)(CH₂COOH)₂ and 25 % ammonia solution (sample 4A). The aqueous solution of Zn-acetate was mixed with citric acid which, being a complex forming factor, prevents precipitation and helps the coordination of metal ions. The ammonia solution maintains a constant pH of 8.5 to the complete deprotonation of the acid. Additional introduction of NH₄VO₃ led to the preparation of binary ZnO/V₂O₅ composition (Fig. 6).

Drying and calcination proceeded stepwise, maintaining a maximum temperature of 420°C (sample 4B). The last combination studied was again ZnO/TiO₂ mixture (Fig. 7) using Zn-acetate, Ti-butoxide and ethylene glycol as a precursor (sample 11).

The phase formation processes were followed by Bruker D8 Advance X-ray phase analysis. The main short range order structural units of the submicron pow-
Fig. 7. Flow diagram for preparation of ZnO/TiO₂ powder by Zn-acetate and Ti-butoxide and etylene glycol (sample 11).

Fig. 8. X-ray diffraction patterns of: a) sample 7A; b) sample 7B; c) sample 10.

Results and discussion

Phase and structure analysis

Fig. 8 shows the X-ray patterns of TiO₂ containing samples. With increasing TiO₂ content, peaks characteristic to Zn₃TiO₄ are visible in addition to ZnO. Besides, a weak amorphous halo appears (sample 7A). When the TiO₂ content decreases, the only phase observed is ZnO (sample 7B, 10). It is worth noting that the sample containing small amounts of TiO₂ and ethylene glycol in the initial solution has the finest crystalline structure (sample 10). The calculated particle dimensions are of the order of 5-7 nm. The powders obtained from acetates (samples 3A, 4A, 4B and 11) exhibit the peaks of ZnO (Fig. 9). According to calculations made by the Scherrer method the powder dimensions in this case are 190 - 200 nm. All IR- spectra of the calcined samples show characteristic bands at 420, 480 cm⁻¹ which can be ascribed to the vibrations of ZnO₆ polyhedra (Figs. 10 and 11). The presence of
two peaks at 400-530 cm\(^{-1}\) can be attributed to the different geometry of the crystals (a transition from spherical to prismatic microstructure) [3].

According to SEM, during the calcination all samples are characterized by a trend to aggregation. Typical examples are shown in Fig. 12. Sample 7A shows formation of hexagonal flat crystallites whereas in sample 10 there are aggregates with a pronounced relief surface.

**Photocatalytic activity**

Figs. 13 and 14 show the results from photocatalytic experiments for all the samples investigated. The photocatalytic reaction takes place in a shorter time with samples 4A (obtained according to the scheme in Fig. 5) and 10 (obtained as shown in Fig. 2). However, samples 7B and 3A show the highest degree of malachite green decomposition during the first 30 minutes, which is probably due to the fact that these samples have a higher aggregation degree and during the reaction the active sites on the particle surfaces are consumed. Thus, a short additional mechanical activation with a view to improving the material may lead to a higher photocatalytic activity.
Fig. 11. IR-spectra of: a) sample 3A; b) sample 4A; c) sample 4B; d) sample 11.

Fig. 12. SEM micrographs of: a) sample 7A; b) sample 7B; c) sample 10.

Fig. 13. Photocatalytic activities of: a) sample 7A; b) sample 7B; c) sample 10.

Fig. 14. Photocatalytic activities of: a) sample 3A; b) sample 4A; c) sample 4B; d) sample 11.
CONCLUSIONS

Comparative analysis of different schemes of preparation of ZnO and binary mixtures with its participation shows that the production of powders for photocatalytic applications depends on many factors. Of importance are: the main precursor, the concentration and type of the solvents, the time of thermal treatment. All these factors are to be taken into account in each separate case. The experiments performed showed that an important problem with sol-gel methods is the trend to aggregation of the particles. It has been shown that the introduction of small amounts of TiO₂ in presence of ethylene glycol leads to better results as compared to pure ZnO and a combination of ZnO and V₂O₅.

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REFERENCES