A STUDY OF THE EFFECT OF CITRIC ACID
ON THE CRYSTALLINITY OF ZnO/TiO₂ NANOPowders

A. Shalaby¹,², A. Bachvarova-Nedelcheva³, R. Iordanova³, Y. Dimitriev²

¹ STCE – Science and Technology
Center of Excellence, Cairo-Egypt
E-mail: ashalaby@outlook.com
² University of Chemical Technology and Metallurgy
8 Kl. Ohridski, 1756 Sofia, Bulgaria
³ Institute of General and Inorganic Chemistry,
Bulgarian Academy of Sciences,
G. Bonchev str., bld. 11, 1113 Sofia, Bulgaria

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ABSTRACT

It is well known that the citric acid is used as a chelating agent which forms poly (basic acid) chelates with the metal cations in a nano-powder synthesis route. The aim of this investigation is to study the influence of the citric acid on the crystallization process in obtaining ZnO/TiO₂ nano-composites. Samples have been synthesized by the aqueous sol-gel method applying two different schemes with and without citric acid, respectively. Several compositions containing different TiO₂ (10, 90 mol %) and ZnO (10, 90 mol %) amounts were investigated. The as-prepared powders were calcinated from 100 to 500°C. The phase formation and structural transformation at every step of the synthesis route were followed by X-ray phase analysis and IR spectroscopy and the obtained results were compared.

Keywords: sol-gel, X-ray diffraction, TiO₂, ZnO, citric acid.

INTRODUCTION

The interest in studies of zinc oxide (ZnO) and titanium oxide (TiO₂) strongly increased during the past years due to their electric, optic, catalytic, magnetic and biochemical properties as well as to their relatively good chemical and thermal stability. A detailed survey concerning the photoinduced reactivity of titanium dioxide (TiO₂), as well as the description of the attempts and possibilities to improve its reactivity is also provided by Carp et al. [1]. On the other hand, a comprehensive review of properties, preparation, processing, and device applications of ZnO are summarized in Ozgur’s monograph [2]. In the past years, special attention has been paid to the synthesis of different binary ZnO/TiO₂ compositions with good photocatalytic properties, prepared by various methods: sol-gel [3 - 8], solid state reactions [9], different chemical routes [10 - 14] and mechanochemical synthesis [15]. Several authors established that the method of synthesis and the morphology of the nanoparticles have an essential impact on the photocatalytic processes [3, 16]. The preparation of nanosized active particles of TiO₂ and ZnO, especially by wet methods, is still a challenge to scientists with respect to both obtaining reproducible structures and constant physicochemical parameters. Our team has some experience in sol – gel synthesis of submicron ZnO powders, as well as powders in the ZnO – Mₐ₀ₘ₋ₓ (Mₓ = TiO₂, V²O₅) systems [17]. Comparative analysis of different schemes for synthesis of these powders for photocatalytic applications has been made. Moreover, in our previous investigations we established that the type and order of adding the precursor solutions influences the synthesis of the final products [18]. Recently, we have also obtained submicron ZnO/TiO₂ powders from different precursors and applying various sol – gel meth-
ods: aqueous, non-aqueous and a combustion one [17-21]. Nanopowders (50 - 100 nm) were obtained in the ZnO - TiO$_2$ system applying a modified aqueous sol-gel method [18]. The structure and photocatalytic properties of the prepared powders were studied as well. Additionally, TiO$_2$/ZnO nanocomposites were synthesized via a nonaqueous sol – gel method and their antibacterial activity against E. Coli was verified [19 - 21]. By the combustion gel method nanosized ZnO particles (2 - 8 nm) in the ZnO-TiO$_2$ system were prepared and their photocatalytic properties were investigated [22]. It was established that the citric acid is a good chelating agent and a suitable precursor that ensures high specific surface area, nanometric particle size and mesoporosity, which can activate photocatalysis of the obtained products [23, 24]. Recently, Ribeiro et al. evaluated the catalytic activity of TiO$_2$, synthesized by Pechini’s method, with varying molar ratios of 2:1, 3:1 and 4:1 of citric acid/metallic cations, in the photocatalytic degradation of the methyl red dye in aqueous solutions [23]. They observed higher photocatalytic efficiency of the 2:1 sample. Single SrTiO$_3$ phase was prepared using citric acid [24]. The authors established higher absorbance in the visible light range, which is of importance for the application of this phase. These results, concerning synthesis of nanoparticles and monophase products with citric acid, motivate us to continue investigations in sol - gel obtaining of ZnO/TiO$_2$ nanopowders with citric acid as a precursor. Comparison of the results for the products prepared with and without citric acid were also a subject of this study.

The aim of the present study was to verify the influence of citric acid on the crystallization process during the heating of the gels.

**EXPERIMENTAL**

**Samples preparation**

The main stages for sol-gel synthesis of the powders are shown in Fig. 1. A detailed scheme for synthesis of ZnO/TiO$_2$ nanopowders was presented in our previous

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**Fig. 1.** Scheme of the sol-gel synthesis of samples 1b (90TiO$_2$.10ZnO) and 2b (10TiO$_2$.90ZnO) obtained with addition of citric acid.
studies [17, 18]. For the composite nanopowders production, several analytically pure precursors were used: titanium ethoxide \([\text{Ti(OCH}_2\text{CH}_3)]\) (Fluka AG), zinc acetate, \(\text{Zn(CH}_3\text{COO)}_2\cdot 2\text{H}_2\text{O}\) (Merck), ethylene glycol \((\text{C}_2\text{H}_4\text{O})\) (Merck), absolute alcohol \((\text{C}_2\text{H}_5\text{OH})\) (Merck) and citric acid monohydrate \((\text{C}_6\text{H}_8\text{O}_7\cdot \text{H}_2\text{O})\) (Merck).

The selected precursors were mixed in the respective ratios, corresponding to compositions \(90\text{TiO}_2.10\text{ZnO}\) (samples 1a, b) and \(10\text{TiO}_2.90\text{ZnO}\) (samples 2a, b). They were dissolved in ethanol and ethylene glycol at room temperature under intense stirring to achieve complete dissolution and the occurrence of hydrolysis processes. The citric acid monohydrate was added to the Zn acetate solution during the preparation of samples 1(b) and 2(b). Samples: 1(a) and 2(a) were obtained without citric acid. White xerogel was obtained by drying at 110°C for 2 h. Subsequently, the as-obtained xerogel was subjected to evaporation, drying and calcinations from 200 to 500°C for 1 h exposure time in air.

**Samples characterization**

The phase formation processes were followed with a Bruker D8 Advance X-ray apparatus, Cu Kα radiation. The main short range orders of the nanopowders were determined by IR spectroscopy (Nicolet 320 FTIR spectrometer) with a resolution of \(\pm 1\text{ cm}^{-1}\), by collecting 64 scans in the range 2000 - 400 cm\(^{-1}\) at room temperature using a standard KBr pellet technique.

**RESULTS AND DISCUSSION**

**Phase transformation and structure analysis**

Fig. 2 shows the XRD patterns of the sample with nominal composition \(90\text{TiO}_2.10\text{ZnO}\): (a) without and (b) with citric acid. As it is seen from the figure, sample 1a is amorphous up to 400°C. The \(\text{TiO}_2\) (anatase) crystal phase (JCPDS 78-2486) appears at 500°C. In the other case, where citric acid is used (sample 1b) an earlier crystallization at 300°C is observed. The average crys-

![Fig. 2. XRD patterns of sample 90TiO₂.10ZnO (1): sample 1a without and sample 1b with citric acid.](image)

![Fig. 3. XRD patterns of sample 10TiO₂.90ZnO (2): sample 2a without and sample 2b with citric acid.](image)
tallite size of the obtained at 500°C powders calculated from the broadening of the diffraction line by Scherrer’s equation for sample 1a is about 16 nm, while for the one with citric acid (1b) it is around 13 nm.

Fig. 3 presents the XRD patterns of the sample with nominal composition 10TiO$_2$•90ZnO: (sample 2a) without and (sample 2b) with citric acid. The obtained results show that at 300°C the sample obtained without citric acid is not well crystallized, while in the other case at this temperature, ZnO (JCPDS 36-1451) is detected as a main crystalline phase. With the increasing of temperature, ZnO remained the main crystalline phase in the obtained samples. The average crystallite size of the prepared at 500°C powders calculated from the broadening of the diffraction line with Scherrer’s equation for sample 2a is about 5 nm, while for 2b with citric acid it is around 10 nm. Thus, more fine powders were obtained in this case. Looking at XRD patterns of samples 1b and 2b (Figs. 2, 3) it can be seen that citric acid enhances the crystallization process at lower temperatures (300°C). In comparison to other data for ZnO/TiO$_2$ nanocomposites obtained recently, we established that the particles size of our powders was considerable smaller [25]. On the other hand, a closer look at samples 1a and 2a, prepared without citric acid, showed that the sample with higher TiO$_2$ content, improved the thermal stability of the amorphous phase up to 400°C (Fig. 2, sample 1a). These results confirm our previous suggestions [18].

The IR spectra of investigated samples (1 and 2), calcinated at 400 and 500°C are presented in Figs. 4 and 5. Our attention was focused on the vibrations of the inorganic building units, which are only below 1000 cm$^{-1}$. The IR spectra of the compositions with high TiO$_2$ content (1a, 1b) showed a not well resolved area
between 400 and 800 cm$^{-1}$. According to R. Almeida [26] the presence of such an absorption area corresponds to the formation of Ti-O, Ti-O-Ti bonds between TiO$_6$ octahedra. This is in coincidence with our previous investigations [18 – 21], where bands in the absorption range 700 - 400 cm$^{-1}$ were related to the vibrations of TiO$_6$ units, typical for TiO$_2$ (anatase) [27, 28]. As is seen from Fig. 5, in the IR spectra of the compositions with high ZnO content (2a, b), a band at 420 cm$^{-1}$ with a shoulder 460 - 440 cm$^{-1}$ is well defined. They could be related to the vibrations of ZnO$_4$ polyhedra [17, 29, 30]. According to Verges [30] the single band centred at 460 cm$^{-1}$ must be assigned to spherical particles, but when splitting occurs, prolative or platelike shapes are present. Probably, the shape of our ZnO particles is platelike, having in mind the obtained IR spectra (samples 2a, 2b, Fig. 5). This will be a subject of our future investigations. The obtained IR results are in a good accordance to our previous results [17-21] as well as they prove the phase formation established by XRD analysis.

**CONCLUSIONS**

Depending on composition, nanosized TiO$_2$ (13-16 nm) or ZnO (5-10 nm) particles were obtained in the binary ZnO – TiO$_2$ system applying an aqueous sol-gel method. The addition of citric acid enhanced the crystallization process at lower temperatures (300°C) but did not influence essentially the particles size. By IR spectroscopy it was established that TiO$_6$ and ZnO$_4$ are the main structural units building up the network.

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