STRUCTURAL AND OPTICAL PROPERTIES OF ZINC TITANATE ELECTROSPUN ONE DIMENSIONAL NANOSTRUCTURES

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ABSTRACT

This paper reports the synthesis and the characterization of 1D Zinc titanate nanobelts of different molar ratios Zn/Ti = 0.26-0.40-0.80 (Zn(CH3COO)2/TTIP) prepared by electrospinning. The samples were annealed at 600°C and 900°C temperatures in air for 5 hr. The as-spun and annealed (Zn(CH3COO)2/TTIP)/PVP composite nanobelts were characterized by scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy analysis (EDX), X-ray diffraction (XRD), Raman spectroscopy and photoluminescence (PL). The results in this paper demonstrate that heat treatment has an influence on the process of crystallization. According to the X-ray diffraction, the formation of ZnTiO3 rhombohedral phase. Raman spectroscopy results confirm the formation of ZnTiO3 phase. They are in good agreement with the X-ray diffraction. Photoluminescence reveals that high quantity of Titanium makes shift from emitted bands to greater wavelengths (visible region). However, high temperature causes a shift from emission bands to greater wavelengths and regeneration of other bands.

Key words: Titanium oxide, Zinc oxide, Electrospinning, 1D, Nanobelts, Photoluminescence.

INTRODUCTION

Transparent conductive oxides (TCO) such as Zinc oxide (ZnO) and titanium oxide (TiO2) have attracted considerable attention in different fields such as photovoltaic1,2 optoelectronics3, touch screens4, electrochromic devices5 and flat panel displays6-8 and due
to their transparency to visible light and good conductivity. The elaboration of such materials at nanoscale such as one-dimensional nanostructures have attracted many researchers because of their outstanding physical and chemical properties.

Different synthetic strategies have been elaborated to design these 1D nanostructures like high temperature physical evaporation, template-directed methods, electrospinning, solvothermal synthesis and self-assembly methods. These materials were obtained in different shapes like nanotubes, nanofibers, nanowires and anocables. Among these synthesis techniques, the electrospinning is a simple and low cost method that allows manufacturing 1D nanomaterials with an easy control of the chemical and physical properties.

Since 1960s many researchers have been interested in Zinc titanate (ZnTiO₃) materials and its characterizations. It has three crystalline phases: ZnTiO₄ (CFC), ZnTiO₃ (hexagonal) and Zn₂Ti₃O₈ (cubic), and undergoes many transformations at different temperatures. At a temperature, superior than about 800°C, ZnTi₃O₈ is decomposed into ZnTiO₃ and rutile TiO₂ phase. At about 945°C, ZnTiO₃ is decomposed into Zn₂TiO₄ while TiO₂ rutile is a stable phase and an important photocatalytic material.

In this paper, we have fabricated ZnTiO₃ nanobelts by electrospinning method and detailed structural and optical characterization of the obtained nanostructures. The structural and optical changes induced by high temperature annealing will be discussed here. The photoluminescence properties of these nanomaterials will be also highlighted.

**EXPERIMENTAL**

Titanium tetra-isopropoxide TTIP (Ti{OCH(CH₃)₂}₄; 97%), zinc acetate (Zn(CH₃COO)₂ 99.99%), polyvinyl pyrrolidone PVP (Mw = 1300000), ethanol (98%) and dimethyl-formamide (DMF, 99.8%) were purchased from Sigma–Aldrich.

Zinc titanate 1D nanostructures were synthesized by electrospinning technique using titanium tetra-isopropoxide (TTIP) and zinc acetate Zn(CH₃COO)₂ as precursors. In a typical experiment three solutions were prepared of three different ratio molar Zn/Ti= 0.26-0.40 and 0.80. 0.25 g of zinc acetate Zn(CH₃COO)₂ was dissolved in a mixture of 5 mL DMF, 2.5 mL ethanol and 5 g of PVP was added then to the solution. The ratio molar of the latter is Zn/Ti = 0.26. The Zn/Ti = 0.40 and 0.80 was prepared with the same method by changing the volume of TTIP and adding 1 and 1.5 mL, respectively. The precursor mixtures were
stirred for 15 min at room temperature to obtain sufficient viscosity required for electrospinning. The electrospinning solutions were placed into a 22 mL syringe with a 25 gauge stainless steel needle at the tip. The syringe pump was adjusted to 0.3 mL/hr of feeding rate. Then, the electric voltage of 30 kv was applied between the needle and the collector. The distance between the tip of the syringe needle and the collector (Al plate) was fixed to 17 cm. The samples were left overnight in air to fully hydrolyze. To remove the polymer and achieve crystallinity, the composite were then treated in air at different temperatures 600°C, and 900°C for 5 hr with a heating rate of 2°C/min. The microstructures, the phase and the crystal structure of the 1D nanostructures synthesized were analysed using scanning electron microscopy (SEM, Hitachi S-4800), X-ray diffraction (Panalyticalxpert-PRO diffractometer equipped with ax’celerator detector using Ni-filtered Cu-radiation), Raman (Jobin-Yvon S. A., Horiba, France) and Energy-dispersive X-ray spectroscopy analysis (Zeiss EVO ED15 microscope coupled with an Oxford X-maxn EDX detector). Photoluminescence of 1D nanostructures was measured at room temperature using the experimental setup, described elsewhere by Chaaya et al.23 The PL was excited by solid state laser (355 nm) and the emission spectra were recorded in the range 360-800 nm.

RESULTS AND DISCUSSION

The morphology of the obtained 1D nanostructures was examined by scanning electron microscopy (SEM). The composite obtained were treated in air at different temperatures: 600°C Fig. 1 (a-c) and 900°C Fig. 1 (d-f). As shown in Fig. 1 (a-c), the 1D NSs exhibit at 600°C a nanobelt like structures with an average thickness of 120 nm and width of 800 nm. After calcination at 900°C Fig. 1 (d-f), the average thickness and width decreases to 90 nm and 600 nm, respectively. This can be explained by the process of crystallization. The loss of ethanol and DMF, the degradation of PVP and the decomposition of TTIP24.
EDS analysis shown in Table 1 reveals the presence of Ti, Zn and O. No other elements are present in the sample. This confirms that heat treatment at 600°C and 900°C removes PVP, DMF and ethanol completely from the nanobeltls. The X-ray diffraction indicates the formation of zinc titanate oxide ZnTiO$_3$ rhombohedral for different ratio molars at 600°C and 900°C. At 600°C Fig. 2(a) and for different ratio molars, there is a formation of ZnTiO$_3$ phase; i.e. the variation of ratio molar does not influence on the formation of ZnTiO$_3$ phase. Group space is G.S: R3 (148), lattice parameters a = b = c = 5.07 and angle $\alpha = \beta = \gamma \neq 90^\circ$. It is justified by the presence of the most intense peaks (104) and (110) were observed at $2\theta = 32.84^\circ$ and $2\theta = 35.20^\circ$, respectively, while the weak peaks at $23.82^\circ$, $40.29^\circ$, $41.14^\circ$, $48.76^\circ$, $53.34^\circ$, $56.69^\circ$, $61.73^\circ$, $63.25^\circ$ and $68.89^\circ$ correspond to (012), (113), (021), (024), (116), (018), (214), (300) and (112), respectively. This results are in good agreement with what is reported in the map data JCPDS [26-1500]. This formation is due to the reaction between zinc oxide and titanium oxide obtained by the decomposition of organometallic precursors at 345°C$^{16}$. However, ZnTiO$_3$ starts to crystallize at 450°C$^{16}$. The appearance of pics ZnO hexagonal phase$^{25}$ and TiO$_2$ rutile-anatase phases$^{25}$ with different proportions is due to variation of molar ratio between the samples. Appearance of Zn$_2$TiO$_4$ cubic phase when Zn/Ti = 0.4 and in existence when Zn/Ti = 0.26 and 0.8, which is justified by the effect of the amount of Ti, which was different to Zangying et al. report. In the report of Zangying et al. is mentioned temperature less than 885°C. ZnTiO$_3$ exists and decomposes at temperature more than 900°C to Zn$_2$TiO$_4$ and TiO$_2$ rutile, which are different from our results is due to time of calcination chosen and the amount of Titanium because there is no formation of Zn$_2$TiO$_4$ at 600°C after 1.5 hr of calcinations$^{16}$. At 900°C Fig. 2(b), complete formation of ZnTiO$_3$ rhombohedral phase, transformation of TiO$_2$ anatase to TiO$_2$ rutile, there is a ZnO trace and TiO$_2$ anatase. In existence of Zn$_2$TiO$_4$ phase after calcination.
is different to Zanying report, which is different of our results. The absence \( \text{Zn}_2\text{Ti}_3\text{O}_8 \) phase is similar to Zanying et al.\(^{16} \) report and different to How\(^{26} \).
to demonstrate the formation of ZnTiO$_3$ Rhomboedral phase. Fig. 3(a-b) shows Raman spectra of the ZnTiO$_3$ nanobelt calcined at 600°C, and 900°C. At 600°C [Fig. 3(a)] when Zn/Ti = 0.26 ZnTiO$_3$ rhomboedral structure is identified by four Raman bands at (177-231-266-709) cm$^{-1}$. The position of bands of ZnTiO$_3$ as shown Fig. 3(a) are approximately in good agreement with the X-ray diffraction$^{28}$. 

Fig. 3: (a) Raman spectra of ZnTiO$_3$ nanobelts of different molar ratios annealed at 600°C in air for 5h. (b) Raman spectra of ZnTiO$_3$ nanobelts of different molar ratios annealed at 900°C in air for 5h
The bands (144 (E_g)-197(E_g)-399 (B_1g)-519 (B_1g)-639 (A_1 + B_1g) represent the vibrational modes, which are active in spectroscopy of anatase phase of TiO_2.28-32

Table 1: EDX data showing the weight percent of elements of ZnTiO_3 annealed at 600 and 900°C

<table>
<thead>
<tr>
<th></th>
<th>600°C</th>
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<th>600°C</th>
<th></th>
<th>600°C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R = 0.26</td>
<td>R = 0.40</td>
<td>R = 0.80</td>
<td>R = 0.26</td>
<td>R = 0.40</td>
<td>R = 0.80</td>
</tr>
<tr>
<td>Zn</td>
<td>07.22</td>
<td>10.29</td>
<td>14.40</td>
<td>06.86</td>
<td>09.13</td>
<td>13.46</td>
</tr>
<tr>
<td>Ti</td>
<td>27.15</td>
<td>25.33</td>
<td>18.22</td>
<td>28.43</td>
<td>26.74</td>
<td>19.16</td>
</tr>
<tr>
<td>o</td>
<td>65.63</td>
<td>66.02</td>
<td>68.38</td>
<td>64.71</td>
<td>64.10</td>
<td>67.38</td>
</tr>
</tbody>
</table>

The band at 144 cm\(^{-1}\) appear with a higher in intensity. The band at 345 cm\(^{-1}\) identify ZnO Wurtsite structure (multiple-phonon scattering processes)\(^{27}\). When Zn/Ti = 0.4 and 0.80 ZnTiO_3 rhomboedral structure is identified by four raman bands at (177-231-266-709) cm\(^{-1}\)

The position of bands of ZnTiO_3 as shown on Fig. 3(a) are approximately in good agreement with the X-ray diffraction\(^{28}\). ZnO Wurtsite structure structure is identified by one band at 345 cm\(^{-1}\).\(^{27}\) The bands (144 (E_g)-197(E_g) -399(B_1g)-519 (B_1g) represent the vibrational modes, which are active in spectroscopy of anatase phase of TiO_2.28-32 and rutile has two raman active modes detected at 447 cm\(^{-1}\) 612 cm\(^{-1}\) A_{1g}.\(^{27}\)

At 900°C [Fig. 3(b)] in three ratio molars ZnTiO_3 rhomboedral structure is identified by six raman bands at (177-231-266-344-468-709) cm\(^{-1}\).\(^{28}\) The position of bands of ZnTiO_3 as shown on Fig. 3(b) disappearance the peaks of TiO_2 anatase phase in three ratio molars and appearence one peak of rutile raman active mode at 612 cm\(^{-1}\) (A_{1g}) confirm the anatase to rutile transformation. A small peaks corresponding to (E_g) 144 cm\(^{-1}\) - (B_1g) 399 cm\(^{-1}\) mode indicating the presence of anatase phase. In our work, it was found that the formation of the rhombohedral phase of ZnTiO_3 was obtained at 600°C. However in other works, reaction between the oxides begins at 750°C whereas at 900°C the structure crystallization\(^{28}\).

The photoluminescence spectrum Fig. 4 (a-b) of two ratio molars Zn/Ti = 0.26 and Zn/Ti = 0.80 calcined at 600°C and 900°C were chosen to study the effect of the percentage of Ti and the increase of the calcination temperature on the optical properties of ZnTiO_3 nanobelts. At 600°C, when Zn/Ti = 0.26 [Fig. 4(a)], there is an appearance of one emission band at 526 nm green region. However when the percentage of Ti decreases Zn/Ti = 0.80, one emission band appears at 475 nm blue region. At 900°C [Fig. 4(b)], Zn/Ti = 0.26 three bands appear: 470 nm blue region, 560 nm green region and 800 IR region.
When Zn/Ti = 0.80, two emission bands appear: 480 nm blue region and 740 nm red region. Table 2 shows that the increase of Ti causes a shift from emitted band to greater wavelengths while the increase of temperature causes a shift from emission bands to greater wavelengths and regeneration of other bands. The emission bands: blue, green, red (visible region) and IR are related to the following structural defects: Oxygen vacancy Vo (hole trapes), Ti⁺³ Interstitials (electron trapes), Zinc vacancy (V_{Zn}) and Intertitial zinc (Zn_i)^{33,34}. 

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**Fig. 4:** (a) Photoluminescence of ZnTiO₃ of different molar ratios zinc titanate ZnTiO₃ nanobelts annealed at 600°C. (b) Photoluminescence of ZnTiO₃ of different ratio molar zinc titanate ZnTiO₃ nanobelts annealed at 900°C
Table 2: Pholuminescence data showing the wavelengths of emission bands of ZnTiO₃ of different molar ratios annealed at 600°C and 900°C

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Molar ratio Zn/Ti</th>
<th>λ (nm)</th>
<th>Color region</th>
</tr>
</thead>
<tbody>
<tr>
<td>600°C</td>
<td>0.26</td>
<td>526</td>
<td>Green</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>475</td>
<td>Blue</td>
</tr>
<tr>
<td>900°C</td>
<td>0.26</td>
<td>470</td>
<td>Blue</td>
</tr>
<tr>
<td></td>
<td></td>
<td>560</td>
<td>Green</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>480</td>
<td>Blue</td>
</tr>
<tr>
<td></td>
<td></td>
<td>740</td>
<td>Red</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>IR</td>
</tr>
</tbody>
</table>

CONCLUSION

In this paper, nanobelts of zinc titanate (ZnTiO₃) with three ratio molars were produced using electrospinning method. The structure of the pure phase obtained at 600°C is rhombohedral. It is determined by XRD and confirmed by Raman spectroscopy. The Zn₂TiO₄ structure appears at 600°C when Zn/Ti = 0.40 and disappears at 900°C, which was found different of literature. The increase of percentage of titanium in ZnTiO₃ favors a shift from emitted bands to greater wavelengths (visible region). However, high temperature causes a shift from emission bands to greater wavelengths and regeneration of other bands. In conclusion, that the increase of Ti rates and the calcination temperatures have useful effect on the optical features of zinc titanate 1D nanostructures.

REFERENCES


