

Synthesis and Characterization of ZnO doped by Al via sol-gel method

تحضير وتشخيص اوكسيد الزنك المدعم بالالمنيوم بطريقة sol-gel

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Abstract

Preparation of ZnO doped with Al using ethylene glycol as a media at room temperature, nano crystals was obtained stable up to 700 °C highly crystalals with 17A° and 12A° in length TEM(transmitted microscope) ,the prolongation of absorption band is between (367-800)nm with energy gap =4.448 EV.The Characterization with Uv(Ultra violet),TEM(Transmission Electron Microscope), SEM(Scanning Electrons Microscope) and XRD(X-Ray Difractions) were showed a good uniform crystals.

الخلاصة

تم في هذا البحث تحضير اوكسيد الزنك المدعم بالالمنيوم بواسطة استخدام اثلين كلايكول كوسط بدرجة حرارة الغرفة وتكوين مركب نانوي ثابت في درجات حرارة تسخين تصل الى 700 مئوي. ومن خلال التشخيص بواسطة اشعة اكس والمكروسكوب الالكتروني النافذ تبين ان المركب يمتلك بلورية عالية ويحتوي على نوعين من البلورات ذات اطوال 17 اكليستروم و12 اكليستروم وامتلاك استطالة لامتصاص ضوئي تمتد من 268-800 نانومترو ذو ارتفاع طاقي مقداره 4.448 فولت.

Introduction

ZnO has been attracted more attentions and become a chief material for the applications in the blue to ultraviolet (UV) light emitting devices [1], light detecting devices [2], piezoeletronic devices and high power electronics, due to its numerous excellent material performances. Therefore, the synthesis of high-quality ZnO material with controlled micro structure for optoelectronic and electronic de- vices is a very important topic. Presently, various techniques for high-quality ZnO film growth have been studied [3–6]. In most studies. Indeed, good quality ZnO films have also been grown on ZnO substrate [7–9]. However, In addition, up to now, various methods have been used to synthesize the ZnO nanostructured materials (such as laser deposition and thermal evaporation) which are generally treated at high temperature[10,11].However, it still remains great challenge to develop .New approach for fabricating ZnO nanomaterials, particularly for preparing aluminum -doped ZnO nanorods by simple process with low cost, easy operation, etc. Soft chemistry route is an effective and promising approach to synthesize ultrafine ZnO nanorods and nanowires at low temperature [12,13]. In the present work, Al-doped ZnO nanorods are synthesized by simple soft chemistry method at low temperature and principally investigated the influences of Al-doping on light absorbance property and in ZnO nanomaterials at room temperature.

2. Experimental details

All chemical reagents were analytical grade without further purification. The synthesis process of Al-doped ZnO nanorods was briefly, 2M NaOH solution was slowly dropped into the stirring mixture containing 0.75M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.25M and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with Zn/Al ratio=3, at 29°C. The resulted solution stirred with 50ml of ethylene glycol for 2 hours, 20ml of 2M NaOH was added, immediately viscose Gel of Zinc oxides crystals was occurred, which is forced the stirring to stopping, aging the gel at room temperature for 18 hours. Then the precipitates was collected and washed four times with deionized water. Finally the Al-doped ZnO nanorods were obtained after drying at 70 °C for 6 h. were heated at 700 °C. For 2hrs.

Results and discussions

. Fig. 1 shows the XRD patterns of pure ZnO nanorods for Al-doped ZnO nanorods the crystallinity and phase purity of the Al-doped ZnO nanorods and Fig.2 for the commercial ZnO. The morphology and microstructure of the as-prepared ZnO nanorods were studied by TEM. In order to confirm the incorporation of Al element into the structure, XRD was performed. All diffraction peaks can be indexed to hexagonal phase of ZnO (wurtzite structure, space group $P6_3mc$). The strong diffraction peak of (0 0 2) position at $d=2.47 \text{ \AA}$ crystal plane indicates the preferential growth of [0001] orientation for pure ZnO nanorods and Al-doped ZnO. The Al-doping does not alter the crystal structure and growth orientation, while it causes the lattice constant to change slightly as evidenced by shift in (0 0 2) peak position. As well known, the ionic radii of Al^{3+} is smaller than that of Zn^{2+} [14], therefore, it is within the expectation due to the substitution incorporation of Al dopant resulting a shift in the peak position, which is also consistent with the successful substitution of Zn position by the dopant [15]. By comparison, it can be found that the full width at half maximum (FWHM) of diffraction peaks from Al-doped ZnO nanorods slightly broaden (Fig.1) than that of pure ZnO nanomaterials fig.2, which illustrates that Al-doping can appreciably influence the ZnO crystallinity. The growth process of ZnO nanocrystal follows nucleation- absorption- orientation-coalescence a mechanism. In the growth process of pure ZnO nanocrystal, the positively charged Zn-(0001) plane of one growth unit coalesces with the negatively charged O-(0001) plane of another growth unit, the surface charges are compensated [18], furthermore, the growth process is easily terminated and as a result ZnO nanorods are formed. While the Al^{3+} substitutes the Zn^{2+} position on the positive surface, which leads to increasing the polarity of Zn-(0001) plane in one growth unit and enhances the coalescence tendency with negative O-(0001) plane of another growth unit. Therefore, the capability of oriented growth increases and the Al-doped ZnO nanorods are eventually formed. In addition, it can be clearly observed that the lattice spacing of (0 0 2) plane at $d= 0.164\text{nm}$ and (004) at $d=0.47\text{nm}$ from the XRD figures of both pure ZnO nanorods, which demonstrate that the obtained ZnO nanomaterials are single crystal structure nature. The growth direction is along c-axis, which are consistent with the former characterization result.

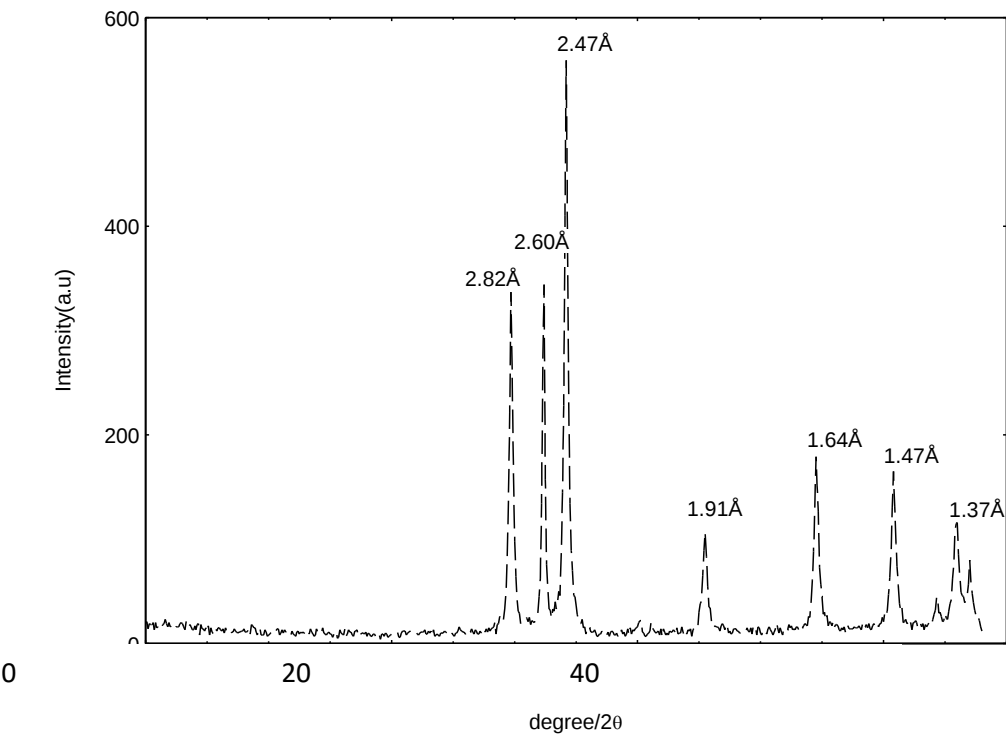


Fig 1. XRD pattern of–ZnO doped with Al- nanorods.

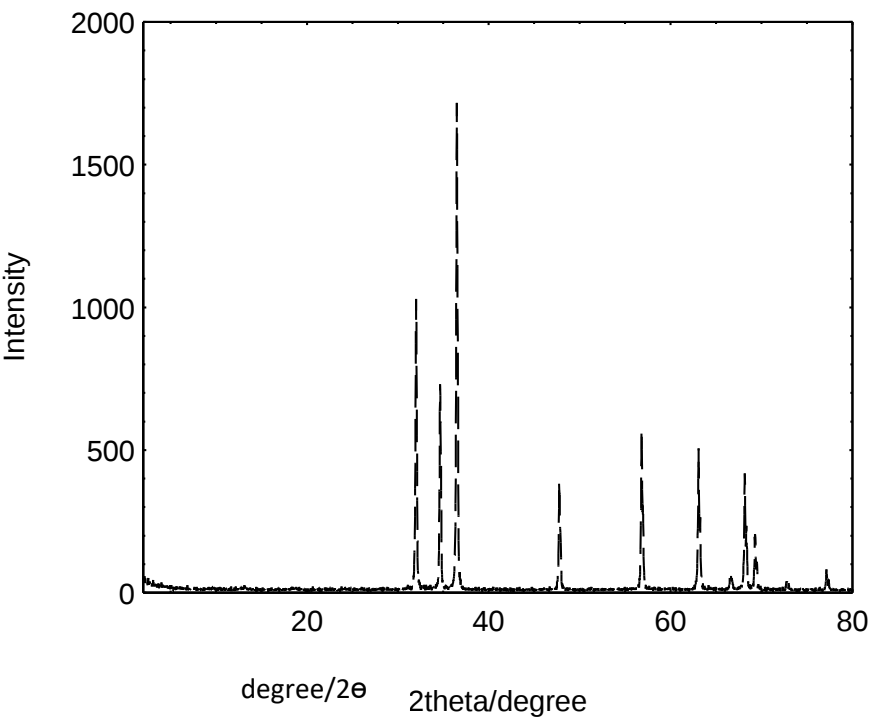


Fig.2 XRD pattern of commercial ZnO

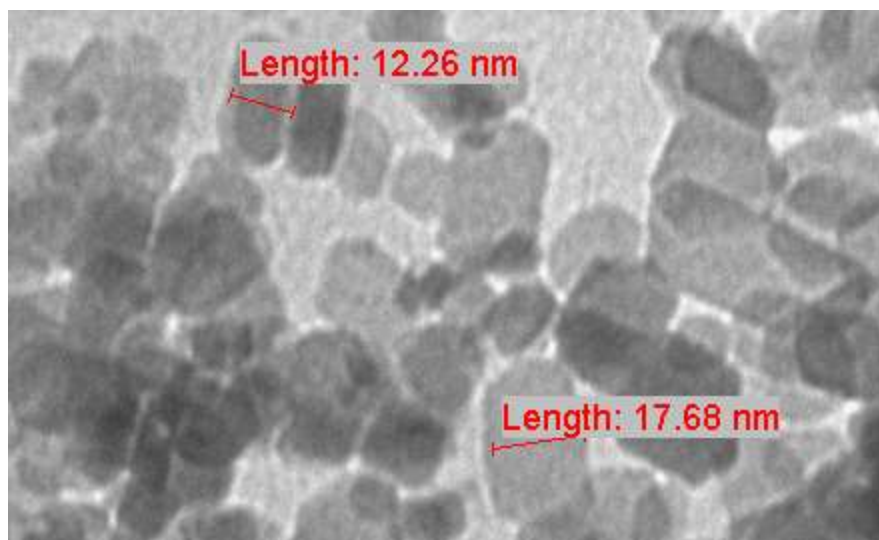


Fig 3a. TEM image measurements show the crystal length and the width of the Al-doped ZnO nanorods.

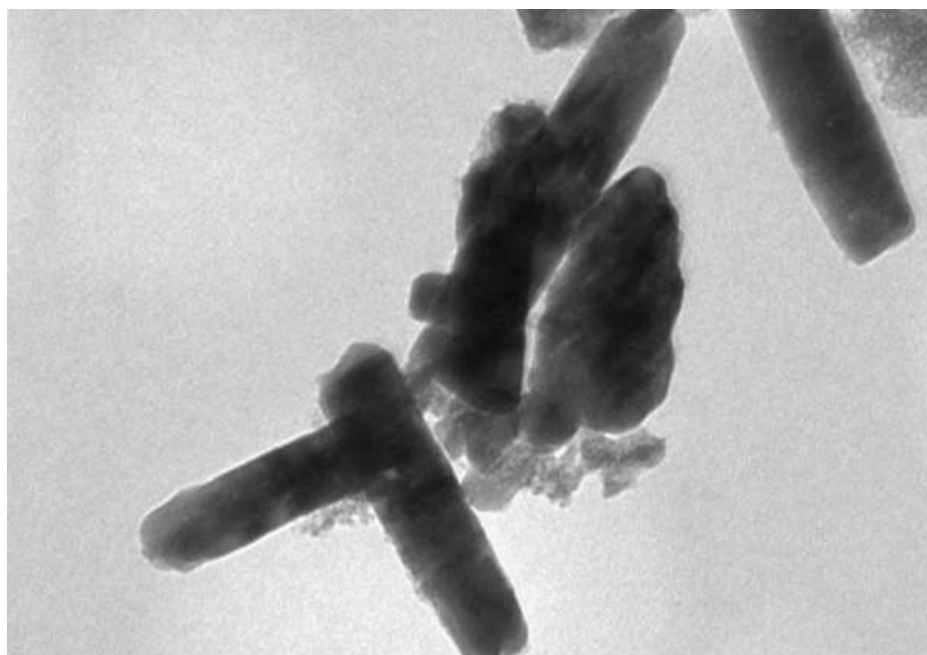


Fig 3b. TEM image ZnO doped with Al nanorods

The morphology and further structure characterizations were investigated by TEM. The images of ZnO doped with Al sample are shown in Fig. 3c. From the images, it is clear from the image that the interactions are very important, which is face-face interactions observed. ZnO nanomaterials are flower-like structure.

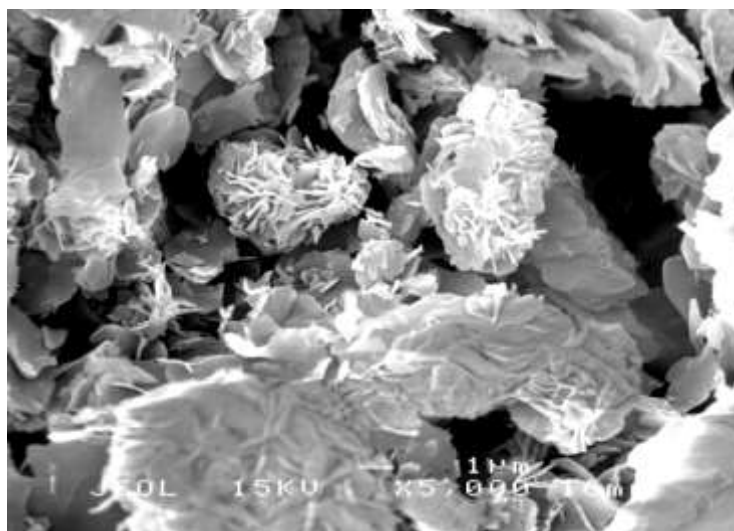


Fig.3c morphology of nano ZnO prepared by the Al doping Sol-Gel method by scanning microscope (SEM).

Fig.4 shows the ultra violet-Visible light absorptions of Al-doped ZnO nanorods (upper line) consisted of two parts: one narrow peak in the ultraviolet (UV) region, and another broad emission band in visible light (VL) region. In UV region, the emission peak of pure ZnO nanorods is at about 376 nm (lower line) the peak of ZnO doped with Al nanorods is at about 378 nm, which are generally originated from the near-band-edge (NBE) exciton transition in wide band gap of ZnO, namely the recombination of free excitons through exciton-exciton collision process [20]. The shift in peak position illustrates that the Al-doping can slightly tune the structure of energy level and band gap of ZnO nanomaterials. In VL region, both pure and doped ZnO nanomaterials exhibit broad absorbance band from about 420 to 800 nm, which is usually related to defects or oxygen vacancies in ZnO, in which the emission results from the radiative recombination of photogenerated hole with an electron occupying the defect or oxygen vacancy [27,28]. By comparison, it can be found that the luminescence band of ZnO doped with Al nanorods is wider than that of pure ZnO nanorods, illustrating that Al-doping can increase the defects and oxygen vacancies in ZnO nanomaterials. Up to now, many researchers have demonstrated that the defects or oxygen vacancies have significant influence on the magnetic property of materials [21]. As well known, the pure ZnO nanorods are paramagnetic material. Two key factors probably lead to ferromagnetism appearance in ZnO nanomaterials: one is increase in number of defects and oxygen vacancies; another is exchange interactions between Al (3d) and O (2p) spin moments. These are well agreement with hypothesis based on the uv experiments and the theoretical calculations in literature [29,30]. Furthermore, Al-doping can adjust the energy level structure of ZnO nanocrystal and increase the number of defects and oxygen vacancies, which lead to enhance ultraviolet absorbance properties of ZnO nanomaterials. The stable room-temperature Uv-Vis and ferromagnetism properties of this material may be help for the future spintronics and transparent nano devices. Fig 4 show the UV-Visible spectrum on solid sample for the ZnO commercial and the resulted ZnO clearly indicate the prolongation of the light absorbance band and there are an energy gap which is different from the commercial sample $E_{gap}=3.100\text{ V}$ and the resulted ZnO with $E_{gap}=4.844\text{ V}$, short band at $\lambda=256\text{ nm}$.

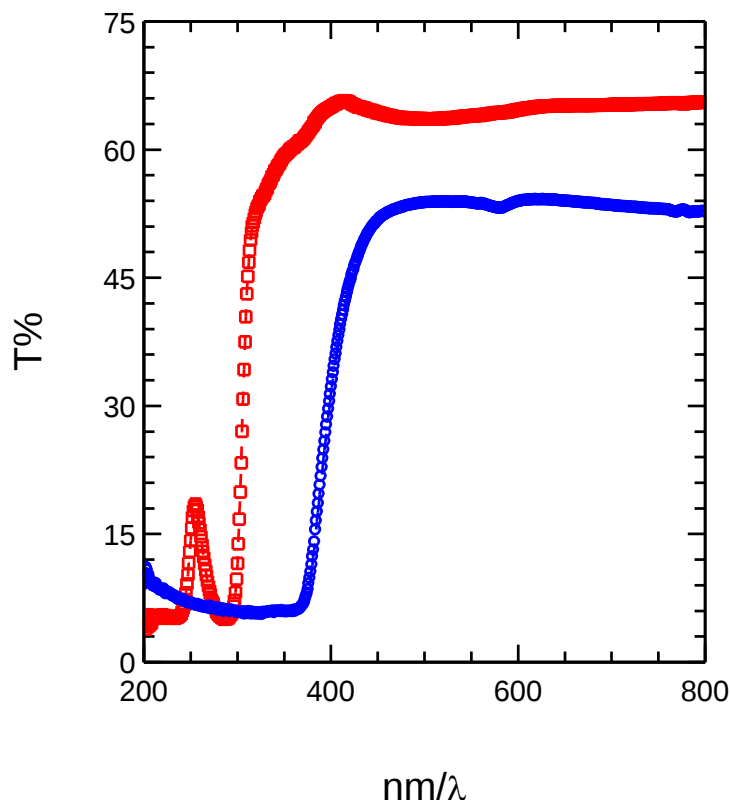


Fig 4. Solid UV-Visible spectrum of commercial ZnO(lower) and of the resulted synthesis ZnO(upper).

Conclusions

That preparations of pure ZnO nanorode is possible by economic method at room temperature, the resulting nanomaterials have improved optical properties more than the commercial ZnO furniture by the US company Across may be that cause to the Al doping by ZnO vai the sol-gel method. A good crystallization in nanorod shap was obtain.

Acknowledgment

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