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Synthesis and Characterization of SnO_2 Nanostructures Prepared by a Facile Precipitation Method

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Abstract

In this paper, tin dioxide nanoparticles were synthesized by a fast and simple co-precipitation method. For SnO_2 preparation, we used ammonia as precipitation agent and bis (acetylacetone) ethylene diamineas as capping agent. By changing in $SnCl_4$, acacen mole-ratio different morphologies were obtained. This semiconductor nanostructure has photo-catalyst activities and can degrade organic dyes as water pollution. The synthesized materials were characterized by X-ray diffraction (XRD) pattern, scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy. In situ poly vinyl alcohol-tin dioxide nanocomposite was prepared and results show that the SnO_2 nanostructure can improve flame retardant property of the PVA matrix.

1. Introduction

SnO_2 as a n-type semiconductor because of wide-energy-gap (3.6 eV) has attracted many considerations, therefore this product was used in many fields such as transparent conducting films, catalytic materials, environmental monitoring, biochemical sensor, lithium rechargeable batteries, dye-sensitized solar cells and ultra-sensitive gas sensors [1-4]. In addition SnO_2 as an alcohol sensor has great application in food industry and breath analysis that are important for human healthy [5]. This semiconductor has high sensitivity, short response–recovery time and good selectivity that is demanded for ethanol detecting [6]. There are many chemical and physical methods to preparation this kind of semiconductor such as hydrothermal, solvothermal, homogeneous precipitation, sol–gel, Pechini route, microwave method, carbothermal reduction, chemical vapor deposition and thermal evaporation [7-11].

Nowadays a lot of works have been done for synthesis different morphologies including hollow-spheres, core–shell, micro-spheres, nanospheres, nanowires, nanotubes, mesoporous and etc. Whereas one-dimensional nano architectures have attracted attention in the materials research community like nanowires, nanorods and nano needles [12-14]. For example Vuong et al. synthesised SnO_2 micro-spheres, nano-rods and nano-flowers via simple hydrothermal route [15]. Zhang et al. studied mesoporous tin dioxide nanopowders based sensors to selectively detect ethanol vapor [16]. Sahay et. al. prepared mono crystalline SnO_2 materials and studied AC transport properties [17]. Guo et al. were surveyed SnO_2 crystals with controllable morphology [18].

In this study we synthesized tin dioxide by simple and low-cost co-precipitation method by using $SnCl_4$ as precursor. Tin dioxide nanoparticles has rutile structure. We used different kinds of ammonia as precipitation agent and acacen as capping agent and also effect of $SnCl_4$: acacen mole ratio on the size and morphology was considered.

2. Experimental

2.1. Materials and characterization

All chemicals material were of analytical grade and were used without further purification. $SnCl_4$, ammonia and Bis (acetylacetone) ethylene diamine were purchased from Merck Company, XRD patterns were recorded by a Philips, X-ray diffractometer using Ni-filtered Cu Kα radiation. FT-IR spectra were recorded on Galaxy series FTIR5000 spectrophotometer. Room temperature photoluminescence was studied by a Perkin Elmer fluorescence instrument. SEM images were obtained using a LEO instrument model 1455VP. Prior to taking images, the samples were coated with a very thin layer of Pt to make the sample surface conductor and prevent charge accumulation, and obtaining a better contrast. Thermal gravimetric analysis (TGA) was carried out using a Shimadzu TGA-50 H instrument with a flow rate of 20.0 mL min^{-1} and a heating rate of 10 °C min^{-1} . The effect of nanostructure on the flame retardant properties has been measured using UL-94 test. In UL-94 a bar shape specimen of plastic 130 × 13 × 1.6 mm is positioned vertically and held from the top. A Bunsen burner flame is applied to the specimen twice (10 s each). A V-0 classification is given to material that is extinguished in less than 10 s after any flame application, drips of particles are allowed as long as they are not inflamed. A V-1 classification is received by a sample with maximum combustion time <30 s, drips of particles are allowed as long as they are not inflamed. The sample is classified V-2 if it satisfies the combustion time criteria of V-1, but flaming drips are allowed. Materials are ranked as N.C. in UL-94 tests when the maximum total flaming time is above 50 s. The sample is classified HB when it shows slow burning on a horizontal specimen; burning rate < 76 mm/min [19-23].

2.2. Synthesis of SnO_2 nanoparticles

The synthesis was performed in the solution of $SnCl_4$ in water. The pH value of the solution was controlled by 0.1 M ammonia. In the first reaction, stannic tetrachloride dehydrated ($SnCl_4$) was dissolved in distilled water to prepare 0.1 M aqueous solution, then ammonia was added to this solution under vigorous stirring to white slurry appear in pH of 11 (Fig. 1). In second part, Bis(acetylacetone) ethylenediamine (acacen) were used as capping agent in tow ratio: 1:2 and 2:1 for acac : $SnCl_4$. The slurry was filtered and washed thoroughly with distilled water and ethanol several times to remove the chloride ions and remained ammine completely from the precipitate. In final, the resulting precipitate was dried at 90 ºC.

For better crystallinity, the products were calcinated at 500 ºC.

Fig. 1. Schematic diagram of preparation of SnO_2 nanoparticles

2.3. Preparation of in situ nanocomposite

4.5 g of PVA was dissolved in 10 mL of water and $SnCl_4$ (2ml, 0.5 g) was dissolved in 5 mL of water. Ammonia and acacen were added to the solution. The solution was mixed under stirring for 6 h. For preparation of samples for UL-94 test after stirring, the product was casted on a template with dimension 130 × 13 mm and after about 48 h of solvent evaporation; the nanocomposite was placed in the vacuum oven for another 5 h for removal of residual traces of water. The final sheets for the test are 130 × 13 × 1.6 mm in dimension.

3. Results and discussion

XRD pattern of SnO_2 nanoparticles is shown in Fig. 2 which is indexed as a tetragonal phase (space group: P42/mnm). The experimental values are very close to the literature (JCPDS No. 88-0287).

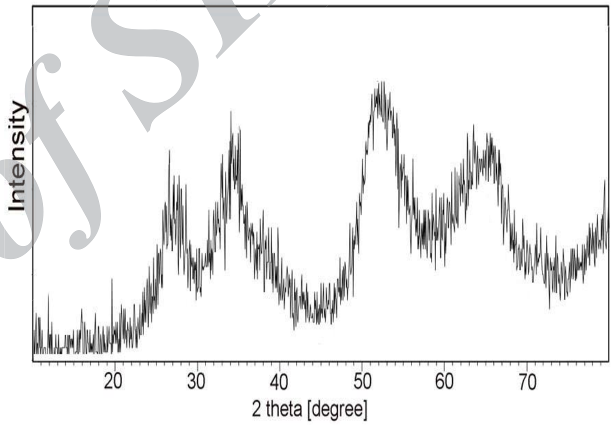

Fig. 2. XRD pattern of SnO_2 nanoparticles

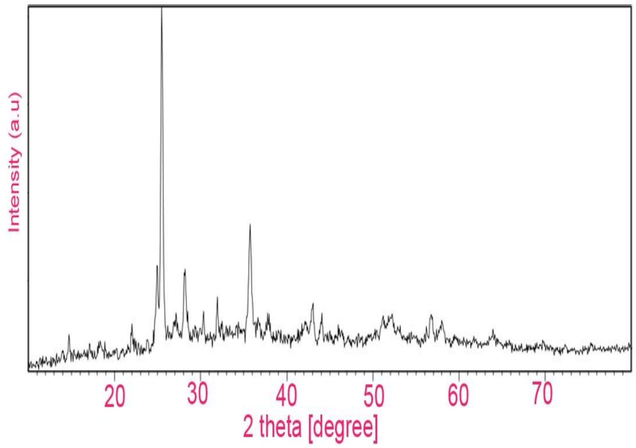

Fig. 3. XRD pattern of in situ PVA nanocomposite

XRD pattern of in situ PVA-SnO_2 nanocomposite is illustrated in Fig. 3 . Peaks of SnO_2 confirm presence of inorganic phase in the amorph poly vinyl alcohol matrix.

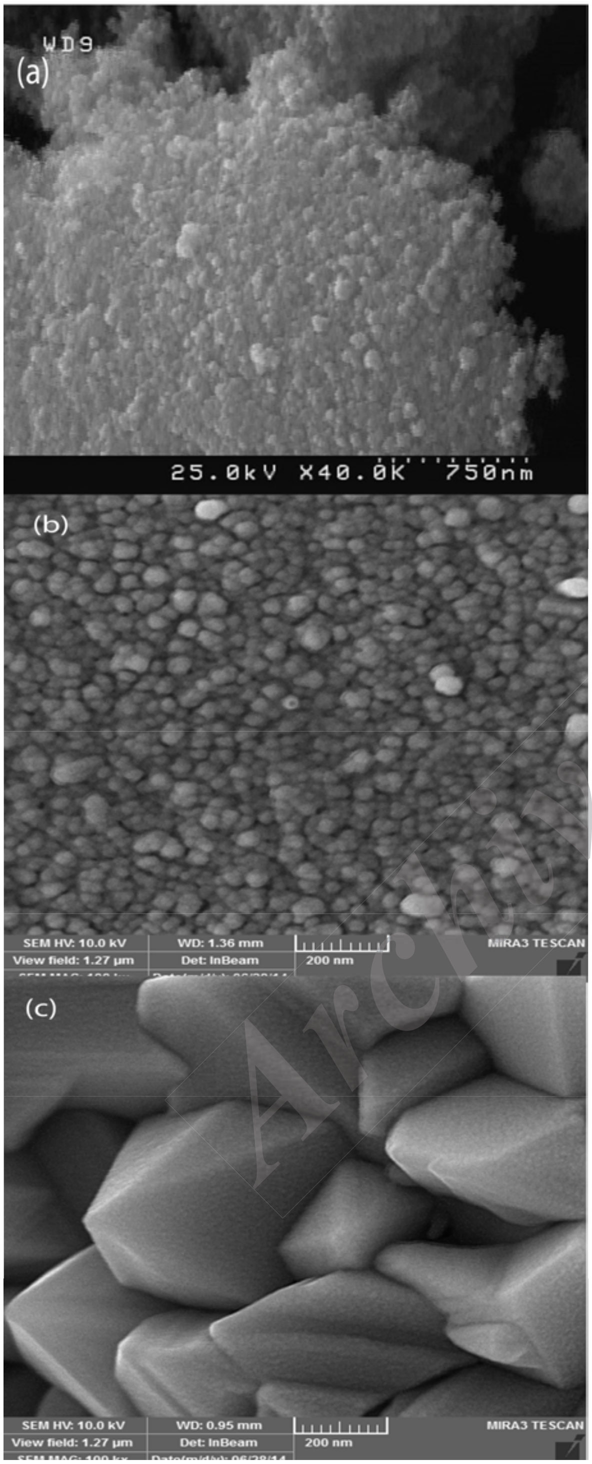

Fig. 4. SEM images of SnO_2 obtained by (a) NH_3 (b) acac:Sn 2:1 (c) acac:Sn 1:2

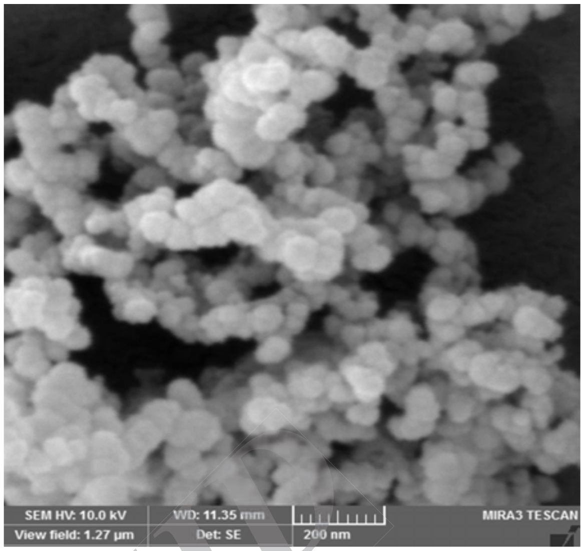

Fig. 5. SEM image of SnO_2 obtained at 1:1

The crystallite size measurements were carried out using the Scherrer equation,

$$Dc=0.9\lambda/\beta\cos\theta$$

where β is the width at half maximum intensity of the observed diffraction peak, and λ is the X-ray wavelength (CuK_α radiation, 0.154 nm). The estimated crystallite size is about 23 nm.

SEM images of SnO_2 obtained by ammonia, acacen : Sn at mole ratio 2:1 and 1:2 are illustrated in Fig. 4a-c respectively. By using ammonia agglomerated nanoparticles were synthesized. At mole ratio 2:1 nanoparticles with average diameter less than 40 nanometer were obtained while at ratio 1:2 polyhedral micro-structures were achieved. Fig. 5 shows synthesized product at mole ratio 1:1 and confirms mono-dispersed nanoparticles with mediocre size less than 50nm were obtained.

Schematic of capping agent effect on the morphology and particle size is shown in Fig. 6. FT-IR absorption spectrum of nanoparticles is depicted in Fig. 7. Absorptions around 400-600 are related to Sn-O bonds and broad peak at 3300-3500 is responsible for hydroxyl adsorbed on the surface of nanoparticles. FT-IR spectrum of in situ PVA-SnO_2 nanocomposite is shown in Fig. 8. Because of in situ preparation absorption related to acacen also are observed beside peaks of polyvinyl alcohol and tin dioxide, presence of capping agent on the nanocomposite is suitable for flame retardancy property,

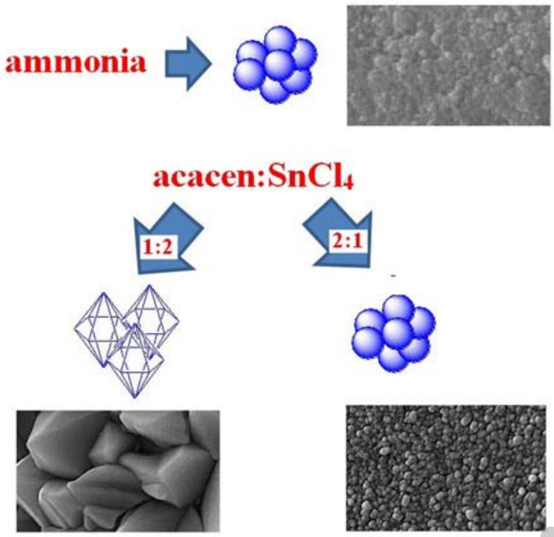

Fig. 6. Schematic diagram of preparation of SnO_2 nanoparticles

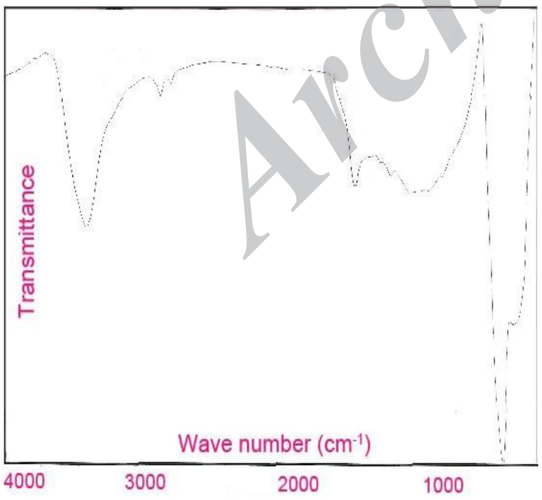

Fig. 7. FT-IR spectrum of tin dioxide

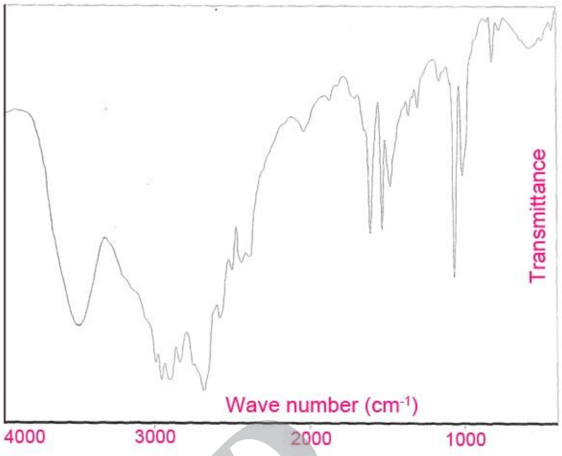

Fig. 8. FT-IR spectrum of PVA-SnO_2 nanocomposite

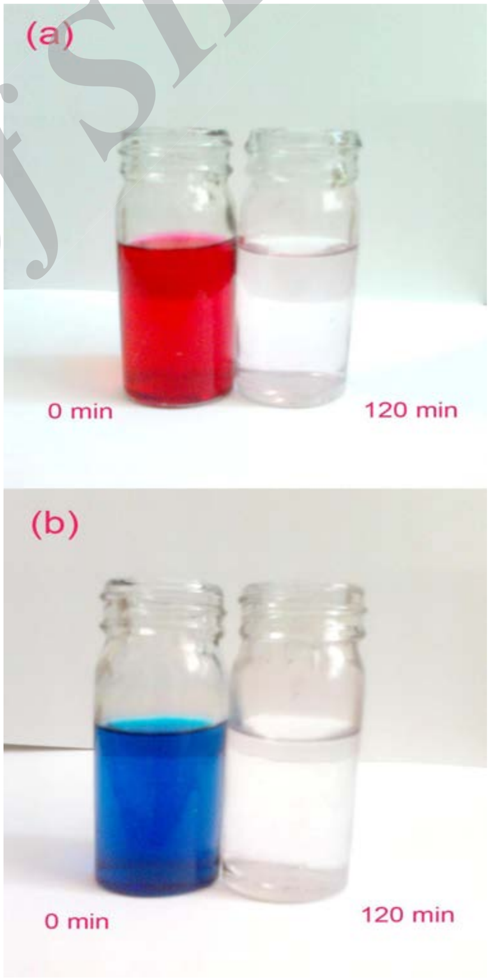

Fig. 9. Degradation of dye under UV irradiation (a) Methyl-orange (b) Eriochromschwarz-T

Methyl-orange and Eriochromschwarz-T as typical organic pollutants were employed as targets because of the relative stability of their molecular structure. The as-prepared nanoparticles have the potential to be applied to improve environmental problems associated with organic and toxic water pollutants. The photo-catalytic activity of the tin oxide nanoparticles (synthesized at mole ratio 1:1) was evaluated by monitoring the degradation of organic dyes in an aqueous solution, under irradiation with UV light.

As time increased, more and more dye is adsorbed on the nanoparticles catalyst, until the absorption peaks (λmax) of Methyl orange and Eriochromschwarz T, that are 510 and 516 nm respectively, decrease and vanish around 120 min. Dyes were degraded at 120 min of irradiation. The dyes concentration decreased rapidly with increasing UV-irradiation time, and the absorption peaks almost disappeared after 120 min. Degradation of organic dyes with tin oxide nanoparticles are shown in Fig 9. Organic dyes decompose to carbon dioxide, water and less toxic or nontoxic residuals.

In the last two decades polymer matrix nanocomposites have also been extensively investigated, since just a small amount of nanoparticles as an additive leads to production of novel materials with excellent physicochemical properties [19-23]. In this research influence of tin chloride on the flame retardancy of PVA was examined.

The results of UL-94 tests for pure PVA and in situ PVA-SnO_2 nanocomposite are N.C and V-0 respectively. The results show that SnO_2 can enhance the flame retardant property of the PVA matrix. The enhancement of flame retardancy of nanocomposite is due to suitable interaction between polymer chains and tin oxide nano-additives [19-23].

4. Conclusion

Different structures of tin dioxide were synthesized via chemical reaction, the influence of various precursors on the particle sized of the products was investigated. Photo-catalytic property of tin oxide in degradation organic pollutants in water was investigated. Nanostructures were characterized by XRD, SEM, and FT-IR. In situ poly vinyl alcohol-tin dioxide was prepared and results show that the SnO_2 nanostructure can improve flame retardant property of the polymeric matrix.

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