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Synthesis and Characterization of Undoped and Fe–doped SnO_2Nanoparticles

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Tin oxide (SnO_2) nanoparticles have been successfully prepared using co-precipitation route using of tin chloride and sodium hydroxide as tin source and precipitating agent, respectively. Fourier transform infrared spectrum, x-ray powder diffraction, scanning electron microscope, energy dispersive x-ray spectroscopy and transmission electron microscope were used to characterize as-prepared and heated samples. The broad XRD peaks were corresponding to small crystallitenanoparticles. Grain size of particles has been obtained around 6 nanometers using XRD patterns and Scherer's formula. SEM images were shown as rod morphology of nanoparticles and also a good monodispirsity of rods could be seen. The particle size was obtained less than 20 nm using TEM images. Nice superparamagneticproperty was obtained when the samples were calcinated at 200 °C. The particle size decreased as doping amount increased.

1. Introduction

Tin dioxide (SnO_2) nanoparticles are a wide band gap semiconductors that make them a proper combination of chemical, electronic and optical properties for technological device application [1-6]. Physical properties of tin oxide, such as transparency and semiconductivity make it an interesting oxide material from the technological point of view for gas sensors [6, 7].

Diluted magnetic semiconductor materials (DMSM) could be very important from the application point of view. In this field the most important materials are also oxide diluted magnetic semiconductor with room temperature ferromagnetism. Among these materials, wide band gap oxides are more interesting, such as SnO_2, TiO_2, ZnO [8].

Nanoparticles of tin dioxide and Fe-doped tin dioxide have been synthesized through various methods, such as hydrothermal, sol–gel, hydrolytic, carbothermal reduction, mechanochemical and co-precipitation methods [9-16]. The synthesizing methods are very important because of shape and morphology depending, they play an important role in applications. Generally, SnO_2 powders with high surface area are in favor of the applications of gas sensors [6, 15-17]. Therefore, more and more efforts have been focused on the preparation of SnO_2 with high surface area [17].

Not only in chemical applications oxide nanoparticles are used as support materials for dispersed metal catalysts but also they often exhibit

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catalytical activity by themselves. Furthermore, it becomes increasingly apparent that the active phase of some metal oxidation catalysts is in fact their oxides rather than the pure metal. Since these materials have a high surface to volume ratio they may be ideal for gas sensing applications. Tin dioxide nano-powder has been widely used as gas sensors, electrode materials, catalyst supports and solar cells [13, 17].

Especially, SnO_2 nanoparticles have been intensively studied for gas sensing applications not only because of their relatively low operating temperature, but also because of the fact that they can be used to detect both reducing and oxidizing gases by adding various doping elements [18,19].

In this study, the synthesis of pure and Fe-doped SnO_2 nanoparticles by co-precipitation proceeding for getting small size of particle and size distribution are reported. XRD patterns illustrate how structure of nanoparticles can differ from the corresponding bulk material. Here we present a study of $Sn_{1-x}Fe_xO_2$ doped with 4 and 7.93 at wt% of Fe characterized by atomic absorption spectroscopy and energy dispersive X-ray spectroscopy, respectively.

Finally, doping of tin dioxide nanoparticles with iron ions and their magnetic properties is described.

In this study we have got superparamagnetic materials using iron doping SnO_2 nanoparticles and the particle size has decreased as doping amount has increased.

2. Experimental Procedure

Undoped and doped of tin dioxide nanoparticles were prepared using chemical co-precipitation method, using analytical grade chemicals SnCl2 .9H2O4 and FeCl2 .4H2O(Merck Company) as source of tin and iron, respectively. Sodium hydroxide was used as a precipitating agent.

The salts were dissolved in double distilled water separately. 1M solutions of tin and iron chloride were prepared separately and then the solutions were added to each other. Sodium hydroxide solution (1 M) was added to the mixture drop by drop, till pH of the solution was close to 4 at room temperature. Final solution was stirred vigorously for one hour. Then the solution was centrifuged and precipitation was washed several times with double distilled water. The precipitation was dried at room temperature and calcined at 200 ^oC in furnace for several hours. Titration was done using $AgNO_3$ to ensure removing of ions.

X-ray diffraction patterns of calcined samples were taken in a diffractometer (Rigaku-Miniflex model). Source of X-ray was $Cu_{k\alpha}$ with a wavelength of 1.5406 Å.

FT-IR transmission spectra were taken on JASCO 640 plus infrared spectrometer with the range of 4000-400 cm^{-1}. Samples were prepared by mixing samples powder with KBr, which were ground and pressed into a transparent pellet with a diameter of 1 cm. The Transmission Electron Microscopy (TEM) is taken in the JEOL JEM-2100 FTEM model which operates in voltage range of 160 to 200 kV.

Weight percentage of iron (4wt %) was obtained using atomic absorption spectroscopy (Spectr. AA220: Version 4.10).

Magnetization measurement was performed at room temperature using a Vibrating Sample Magnetometer (VSM) device, in the Development Center of University of Kashan (Kashan, Iran).

The Scanning Electron Microscopy (SEM) was taken in the Philips XL10 model and the applying voltage was 17 kV.

The EDAX pattern was taken using the Philips XL10 model and the working voltage was 17 kV.

3. Results and Discussion

Figure 1 shows XRD patterns of three samples calcined at temperature 200 ^oC.All diffraction peaks are well assigned to tetragonal crystalline phase of tin oxide (with the reference pattern JCPDS 880287). As it can be seen, the peaks are so broad; this is because of nanosize particles. It is obvious that the width of peaks has increased with increasing iron percentage which we have found in Ni-doped SnO_2 in previous published study [20].

This indicates that particles size decreases with the increase of iron percentage. By using Scherer's formula (1), grain size of particles is obtained 6.0, 3.6 and 3.5 nm for pure samples and doped samples with 4.00 and 7.97 Wt% iron percentages respectively.

$$D=K\lambda/\beta Cos\theta(1) \qquad (1)$$

Where K is a parameter that related to shape of particles, if particles are spherical K will be 0.9, λ is wavelength of CuKα radiation and β is the full

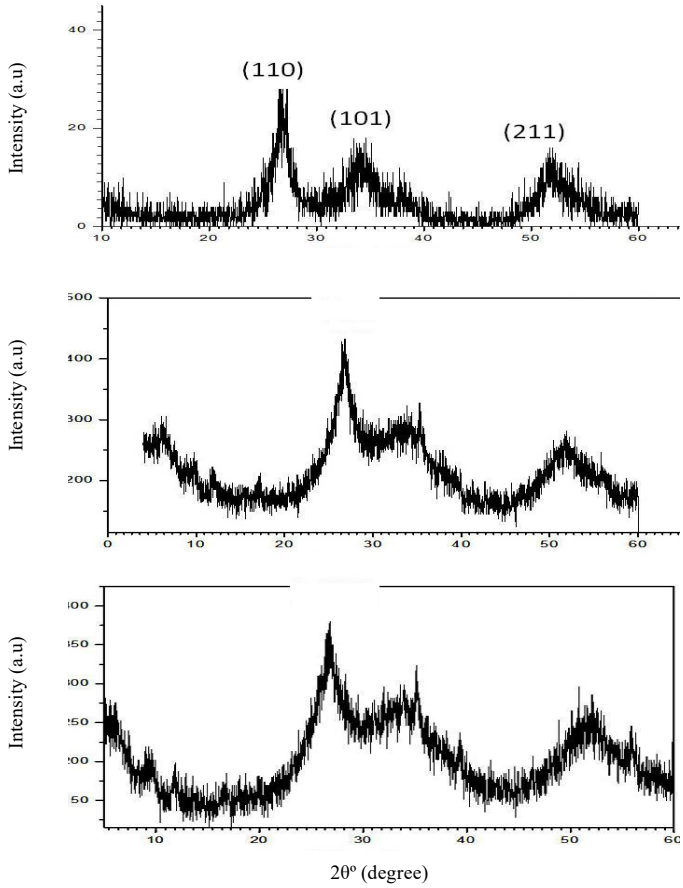


Fig. 1 XRD patterns of (a) undoped and Fe doped SnO_2 samples with (b) 4% and (c) 7.93% doping

width at half maximum (FWHM) of the (hkl) peak at the diffracting angle of 2θ [7].

Figure 2 shows the FT-IR spectrums of the pure and doped samples calcined at 200 ºC. In tin dioxide sample two peaks at 465 cm^{-1} and 650 cm^{-1} are attributed to Sn-O-Sn vibration bond as reported in literatures [9]. The band at 3419.17 cm^{-1} is corresponding to O-H bond which is previously reported [10].The FT-IR spectrum confirms formation of tin oxide and presence of water in the sample. Doped sample with 4.00 wt% iron shows formation of oxide bond that corresponds to Sn-O (425 cm^{-1}, 471 cm^{-1}) [9], Sn=O (1072 cm^{-1}) and Sn-O-Sn (634 cm^{-1}) these vibrating bonds show formation of Fe - O and Sn - O bonds in doped sample. The bond at 1072.23 and 969.055 cm^{-1} belongs to Sn - O and Sn = O modes of surface cation–oxygen bonds respectively [9]. The above discussion confirmes vibration bond between iron and oxygen, which can not be observed in pure SnO_2 sample. This can confirm Fe-doped SnO_2 nanoparticles.

Figure 3(a) and 3(b) show SEM images of the doped nanoparticles calcined at 200 ºC. A good monodispersity with rod and spherical nanoparticle shapes is obtained. The nanoparticles size of SnO_2 and Fe-doped SnO_2 is obtained 38 and 48 nm respectively.

Figure 4 shows (EDAX patterns) of sample A which are doped with 7.93 wt% iron.

Figure 5 shows TEM images of SnO_2 nanoparticles the shape is spherical and the particle size is less than 20 nm.

Figure 6 shows magnetization versus applied magnetic field at room temperature for doped samples. The hysteresis loops show a low magnetization. The low value of M_S suggests that only a small fraction of atoms are contributing to ferromagnetism of the sample, this is because of homogeneous distribution of Fe atoms in tin dioxide lattice [8].

The magnetization for both the samples (4 % and 7.93 %) is small and does not saturate at this range of applied field. The Magnetization increases as doping amount increases to 7.93%wt. It can indicate the presence of a magnetic relaxation and the presence of a large fraction of superparamagnetic particles in the samples [8, 21]. The reason for not getting a saturated value of magnetization is the fact that very fine particles in the samples undergo superparamagnetic relaxation at room temperature. Coercivity force (H_c) and magnetic

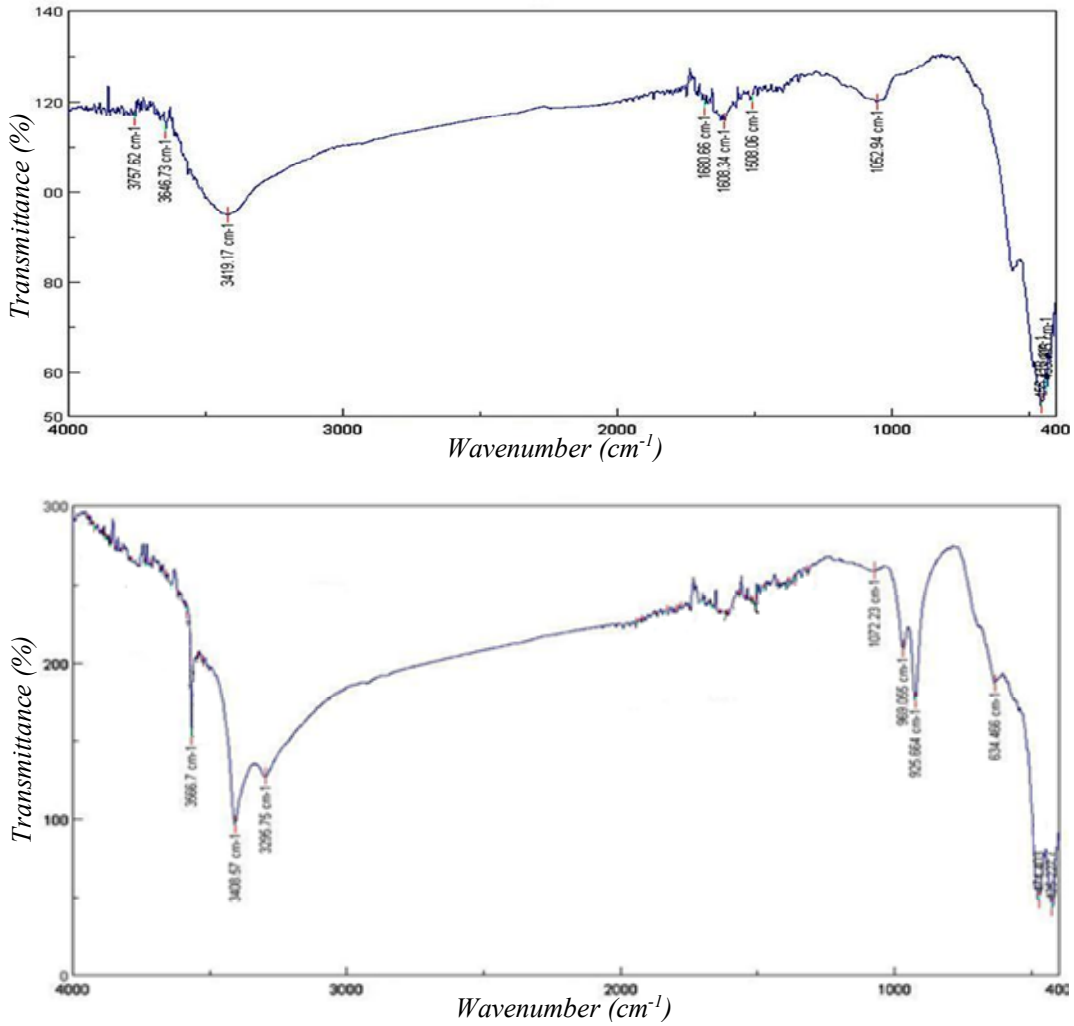


Fig. 2 FTIR spectra of (a) undoped and (b) Fe doped SnO_2 samples

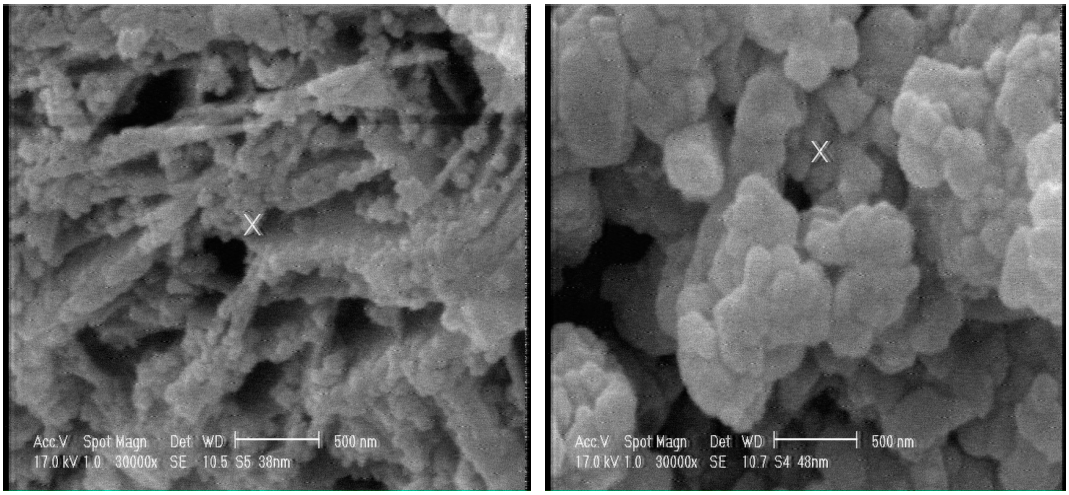


Fig. 3 SEM images of (a) undoped and (b) Fe-doped (7.93 wt%) SnO_2

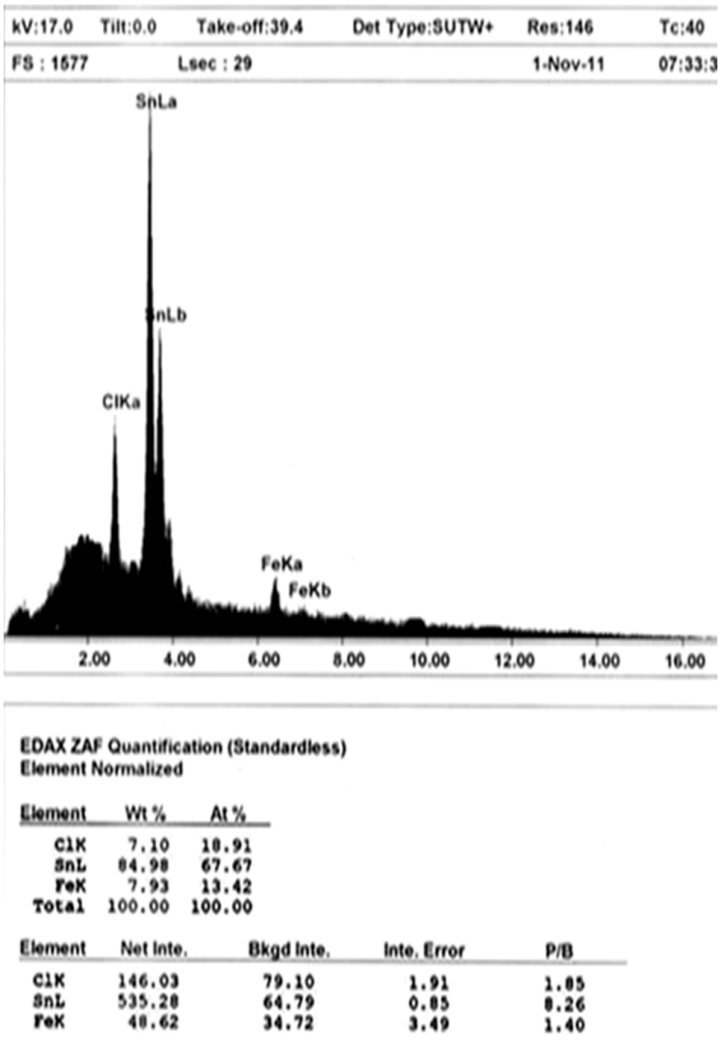


Fig. 4 EDX pattern for Fe-doped SnO_2 (7.93 wt %) nanoparticles

remanence (M_r) are zero. This can confirm that the samples are superparamagnetic and particle size is so small with a single domain [22].

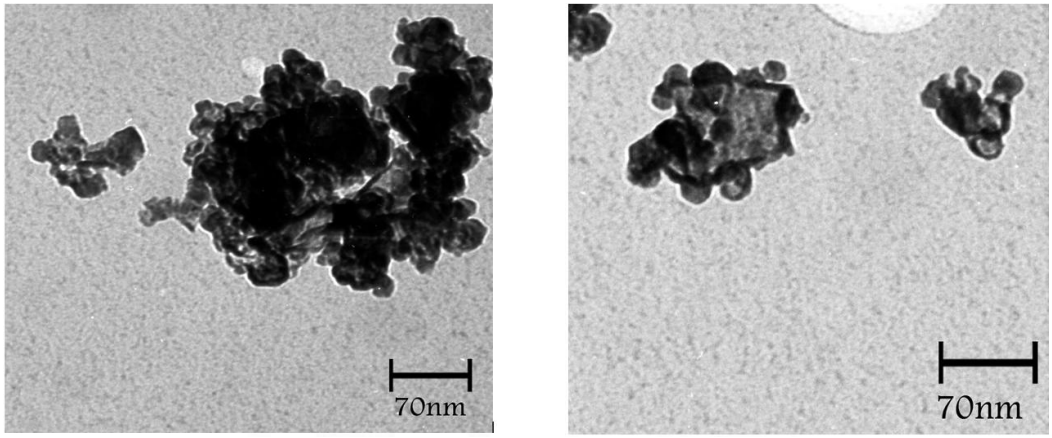
4. Conclusion

1- In the curent study, undoped and Fe-doped tin dioxide in nanoscale particles were successfully synthesized by co-precipitation. All samples were calcined at low temperature (200 ^oC). The XRD patterns show a broad peaks which point to nanograin size of particles. The Grain size of particles is obtained around 6 nm by using Sherere's formula.

2- The TEM and SEM images showed a narrow size distribution of nanoparticles for undoped and Fe-doped samples. We find out grain size decreases as the iron percentage of the doped sample increases.

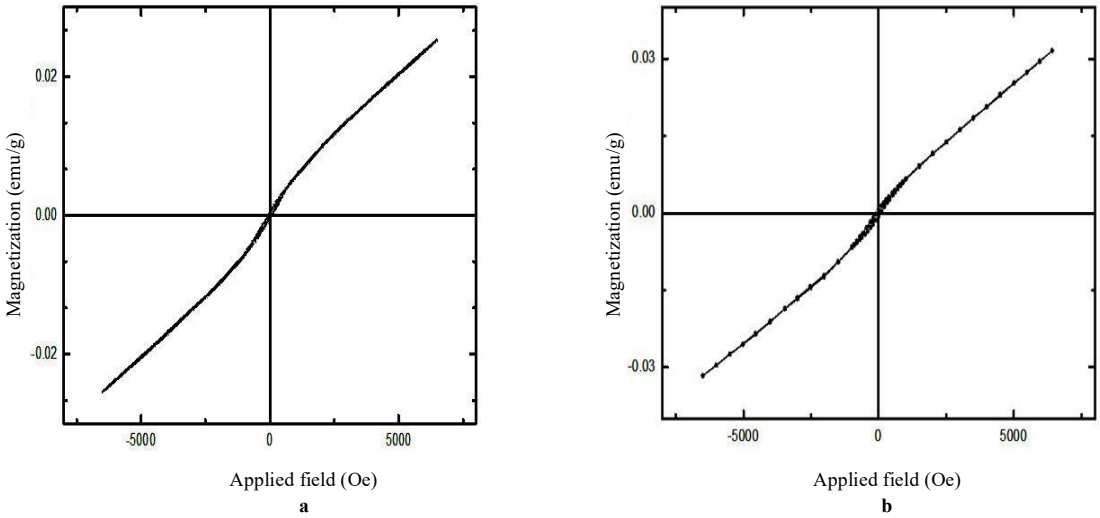
3- FT-IR Spectra of samples showed that SnO_2 and Fe doped SnO_2 nanoparticles were formed properly.

4- The VSM diagrams showed unsaturated magnetization of Fe-doped samples, wich can indicate presence a magnetic relaxation in the samples. The reason for not getting a saturated value of magnetization is the presence of very fine particles and magnetic relaxation in the nanoparticle samples. The hysteresis loops can confirm that the samples are superparamagnetic and particle size is so small



a b

Fig. 5 TEM images (a) and (b) of SnO_2nanoparticles (different regions)



a b

Fig. 6 magnetization of Fe-doped SnO_2 samples with (a) 4 wt% and (b) 7.93 wt%doping versus magnetic field

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