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Influence of s, p, d Block Dopant on PEG Mediated SnO_2 Nanoparticles and Nanorods

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ABSTRACT

K, Al, Ni doped PEG mediated SnO_2 has been successfully synthesized by using hydrothermal method. The as synthesized product was characterized with X-Ray powder diffratometer (XRD), UV-Vis absorption spectrophotometer (UV-Vis), Photoluminescence spectroscopy (PL), Transmission Electron Microscopy (TEM). The results show the particle size of Al doped PEG mediated SnO_2 is below 10 nm, while that of K and Ni doped SnO_2 samples is over 15 and 22nm indicating that the introduction of Al can effectively prevent SnO_2 from further growing up in the process of calcinations. The UV absorption edges exhibit a blue shift, which can be attributed to the quantum confinement effect in the prepared samples. The emission spectra exhibit two sharp peaks at around 400 and 430 nm. Significant morphological changes were observed from TEM analysis.

Key words: Semiconductors, dopants, hydrothermal,

INTRODUCTION

Nanomaterials have attracted a great interest due to their intriguing properties different from those corresponding to bulk state. The fabrication of nanostructured materials has been an active and challenging subject in material science and other fields [1]. Semiconductor nanoparticles have been extensively studied from both experimental and theoretical viewpoints, owing to their potential application in solar energy conservation, Photocatalysis and in the field of optoelectronics [2-5]. SnO_2 nanoparticles as an n-type semiconductor with a wide band gap (E_g=3.6 eV) have been attracting much attention due to wide range of applications in gas sensors optoelectronics, dye based solar cells, secondary lithium batteries, electrode material and

catalysts. SnO_2 has been used as the predominant sensing materials in the field of solid-state sensors for environmental monitoring such as CO, NO, and C_2H_5OH etc. One of the most common methods to modify the properties of SnO_2 is by introducing dopants. Many results have showed that several additives (Fe, Cu, Co, Cr, Al, Mg and Mn) could lead to increase of surface areas of SnO_2 based powder [6]. The added active element could stabilize the SnO_2 surface and decrease its grain size spontaneously. Doped SnO_2 nanopowders acts as an important base material for variety of gas sensors. At low temperatures (≤500 $^{\circ}$C) different cation (Ni, Mn, Fe, Mg) were observed to modify the surface chemistry of SnO_2 particles, influencing selectivity of gases. Particle behavior in suspension and markedly decreasing the grain size as a function of dopants concentration [7,8]. Al doped SnO_2 composites act as a active anode material in lithium ion batteries, the best electrochemical performance is achieved for 10% Al containing SnO_2 prepared from citrate precursors, and the electrochemical performance of this material is strongly influenced by the precursor and the thermal treatment [9]. Several physical and chemical synthetic methods are available for the preparation of SnO_2 material including solgel [10] Chemical vapor deposition [11], annealing precursor powder [12], thermal evaporation and microwave heating [13]. Generally these preparation mentioned above usually involves high temperature, complex procedures, sophisticated equipment or rigorous experimental conditions. Micelle technique, electrical deposition and hydrothermal method focus on a simpler route [14]. Among these, hydrothermal method proves to be simple, cost effective, powerful, nonpolluting and energy economical in the preparation of doped SnO_2 nanoparticles.

In this paper, K, Ni, Al doped SnO_2 nanoparticles and nanorods using PEG as a non-ionic surfactant was synthesized using simple and efficient hydrothermal method and the influence of temperature on the optical properties and morphologies were also discussed.

MATERIALS AND METHODS

Experimental Procedure

Pure and K, Al, Ni doped SnO_2 nanopowders were prepared by dissolving 0.02 mol of $SnCl_2.2H_2O$, 0.02mol of PEG and 3 mol % corresponding nitrate salts (K, Al, Ni) were added in 50ml of water containing appropriate amount of NaOH and stirred vigorously for 2 h. The reactants were put into Teflon-lined stainless steel autoclave of 100ml capacity. The sealed autoclave was maintained at 170°C for 24h, and then cooled to room temperature naturally. Finally, the collected yellow precipitate was washed with deionized water and absolute alcohol several times. The samples were dried at 60°C and calcinated at 400, 600 and 800°C for 2h in order to eliminate the organics and to study the influence of temperature..

The crystalline structure of the material was analyzed by XRD using XPERT PRO with CuK_{α} radiation λ=1.5406Å at scanning speed of 2^{o}/min from 20^{o} to 80^{o}. The absorption spectra of the samples were measured in the range of 200 –2000 nm using UV-Vis spectrophotometer using SHIMDZU UV 310PC. The room temperature PL spectra of the samples was recorded with fluorescence spectrometer (FLS920) using Xe lamp as the excitation source at the excitation wavelength (λex =325 nm). The morphology of the samples were studied TEM Philips CM-200 working at 200KV.

RESULTS AND DISCUSSION

Fig 1 (a-g) shows the XRD pattern of pure and K, Al, Ni doped SnO_2 nanoparticles at different temperatures. All the diffraction peaks of XRD can be readily indexed to the tetragonal SnO_2 with rutile structure (JCPDS21-1250). No peaks of other types are observed and dopant exists in the SnO_2 .Samples indicating that dopants may enter crystal lattice of SnO_2 and does not cause transformation of lattice structure of SnO_2 . The XRD peaks of pure PEG mediated SnO_2 are obviously narrower and sharper, which reveals that the crystal size of pure PEG mediated SnO_2 are about twice larger as that of Al-SnO_2. Among the dopants K enhances the growth of the crystal while Al retards the growth process. It can be noticed from the figure the particles calcined at 400^{o}C are less crystalline than that of particles at 800^{o}C.With the increase in calcinations temperature, the diffraction peaks become narrower and stronger due to the fact that the particle size grows larger and crystallinity is improved. The particle sizes were calculated using Scherer's formula and are tabulated.[15]

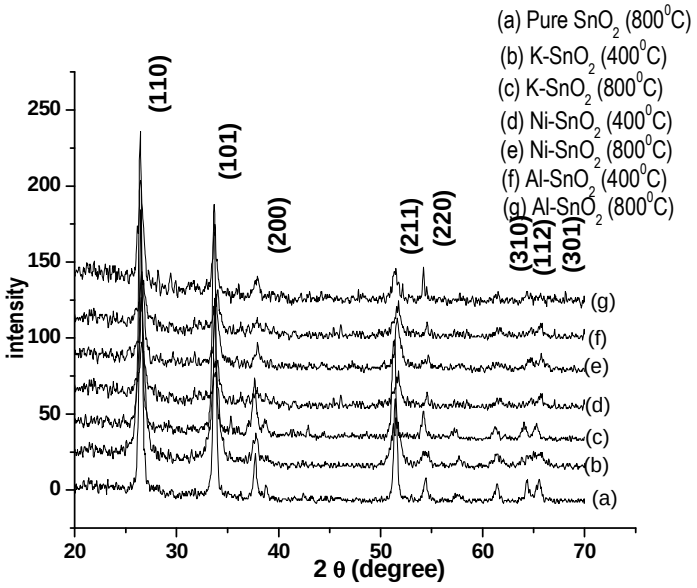

Figure1(a-g): XRD pattern of prepared SnO_2 pattern using different dopants at various temperature

Nanosized semiconductor particles generally exhibit threshold energy in optical absorption measurements, due to the size-specific band gap structures, which is reflected by blue shift of the absorption edge with decreasing particle size[16]. The optical absorption of the samples using various dopants calcinated at 800^{o}C are shown in the fig.2(a-d).The absorption edges were found at 300,312,317,321 nm respectively for Al, Ni, K doped and pure SnO_2 samples. Considering the blue shift of the absorption edge from the bulk SnO_2, the absorption onsets of the present samples can be assigned to the direct transition of electrons in SnO_2 nanocrystals.

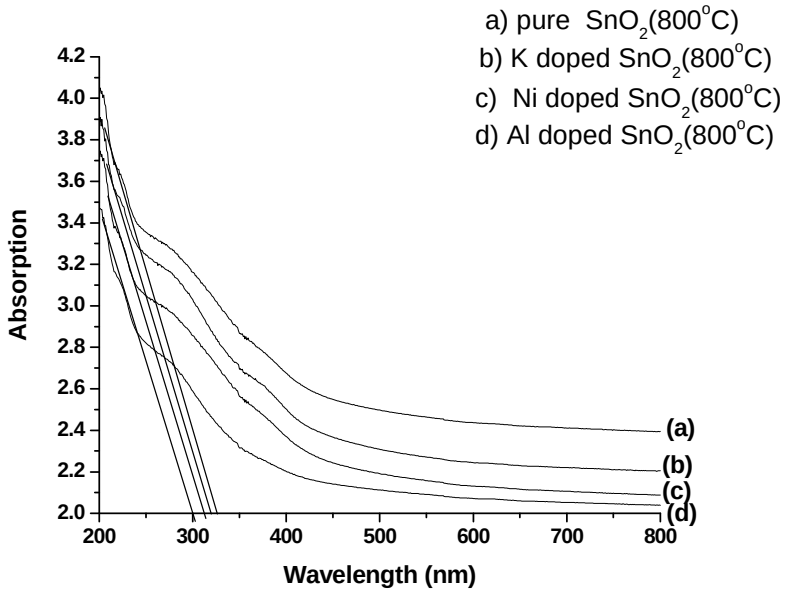

Figure 2(a-d):Absorption spectra of doped and undoped SnO_2

One of the main objectives of the present investigation is to clarify the effect of dopants on the luminescence property. Fig 3(a-d) shows the emission spectra of pure and doped SnO_2 samples calcinated at 800^oC . From the fig 3, it can be observed that for pure and K, Ni doped SnO_2 the emission spectra exhibits a peak at 400nm which attributes to electron transition, mediated by defects levels in the band gap, such as oxygen vacancies, and so forth. It can be observed that the addition of K^+ to SnO_2 host lattice can result in the increment of PL intensity of SnO_2 host, while the characteristic peaks of K^+ ions could not be collected. In the case of Al doped SnO_2 the spectra exhibits an additional peak at 430 nm, which might originate from the luminescence centers formed by tin interstitials. Probably after introducing the dopants the defect still play a dominant role a propos the luminescence process.

Generally, oxygen vacancies are known to be the most common defect and usually act as radiative centers in luminescence processes. The oxygen vacancies present in three different charge states: V_o^0, V_o^+, V_o^{2+} in the oxides [17]. The oxygen vacancy is an intrinsic donor in SnO_2. Because V_o^0 is a very shallow donor, it is expected that most oxygen vacancies will be in their paramagnetic V_o^+ state under flat band conditions [17].

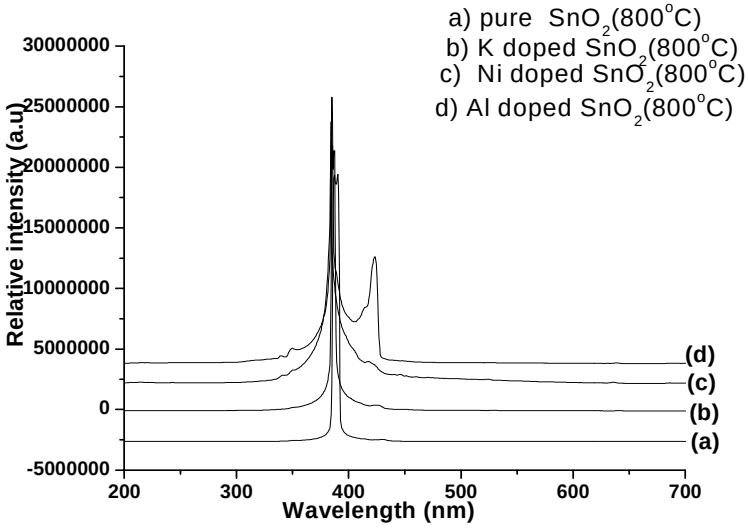

Figure 3(a-d): Luminescence spectra of SnO_2 using different dopants

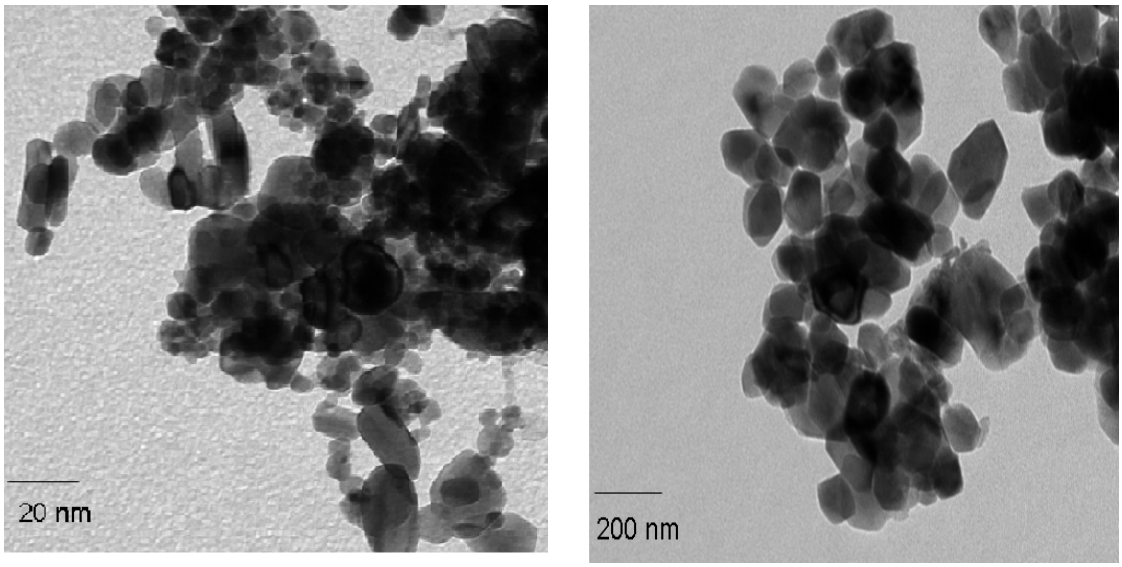

Figure 4a: TEM image of Al doped SnO_2 at 800°C, Figure 4b: TEM image of K doped SnO_2 at 800°C

The calcinations temperature has a strong influence on size and morphology of the samples. Fig.4 (a-c) shows a typical distribution in morphology observed in TEM bright field images for the samples calcined at 800°C. Particles of K and Ni doped SnO_2 samples are of almost spherical and agglomerated, while Al doped SnO_2 shows both nanoparticles and rods. The sizes estimated from TEM images are in good agreement with the sizes estimated by XRD and are tabulated in table.

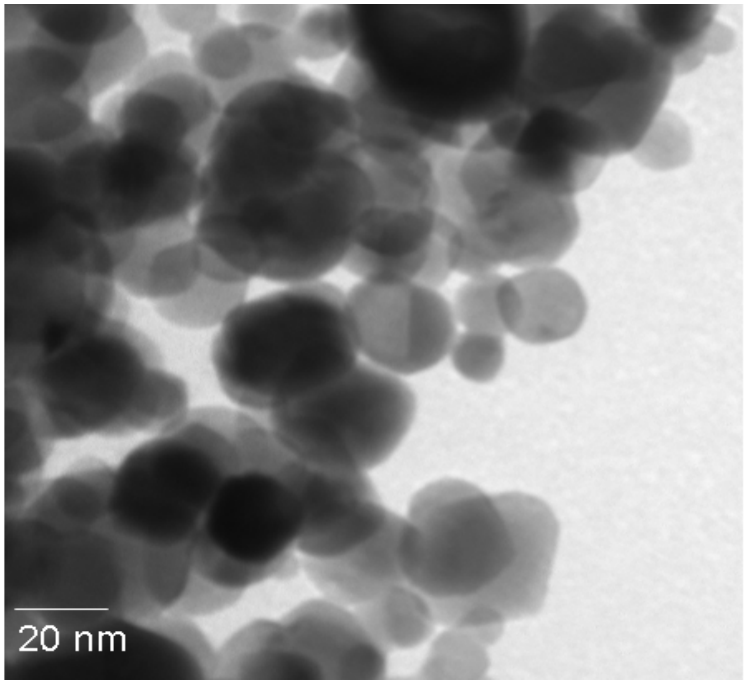

Figure 4C: TEM image of Ni doped SnO_2 at 800°C

***Table1*:Grain Size of doped and undoped SnO_2 nanoparticles at different temperature.**

Dopants	Temperature°C	Size from XRD nm
Undoped	400	32
	800	37
A: Doped	400	6
	600	9
	800	11
N: Doped	400	14
	600	15
	800	19
K Doped	400	18
	600	21
	800	26

CONCLUSION

In conclusion, SnO_2 nano particles have been successfully prepared by a simple solvothermal method. XRD measurements indicates that the diameter of the particles vary from 5-35 nm. The nature of the dopants and calcinations temperature has great influence in luminescence process. TEM exhibit distinct morphological changes with the variations in dopants.

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