

Effect of Shells ZnO; SiO₂ on SnO₂ Hybrid Core-Shell Nanospheres and their Structural, Morphological and Magnetic Properties

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Abstract: Nanocrystalline SnO₂ core and ZnO as well as SiO₂ shells coated core shell nanoparticles have been successfully synthesized by co-precipitation method. The as prepared samples were characterized by X-ray diffraction, FTIR, UV-Visible absorption, PL, FESEM, HRTEM with EDX measurements. The X-ray analysis showed that the obtained SnO₂ core with tetragonal rutile crystalline structure and the shell ZnO with hexagonal structure. FTIR result shows the functional groups present in the samples. The spherical morphology and the formation of the core-shell structures have been confirmed by FESEM and HRTEM measurements. The tunable optical features of core/shell nanoparticles were investigated with UV-Vis spectra and Photoluminescence (PL) studies. The observed PL spectra indicates the strong interfacial coupling between metal-oxides lead to the defects related emission bands with different intensity. From this investigation it can be concluded that the surface modification with different metal and insulating oxides strongly influences the optical properties of the semiconductor which enhance their potential applications towards optical devices fabrication.

Keywords: rutile tetragonal, Core-shell, Ferromagnetism, Interfacial effect, hydrophilic PEG.

1. Introduction

Over a past decade to up to date, nanometer-sized materials have received very much attention due to their unique physical, electrical, chemical and magnetic properties. The research in the area of nanoscale materials is motivated by the possibility of processing and designing nanostructure materials with unique properties thereby offering new and important technological applications. Due to their finite small size and high surface-to-volume ratio, nanostructure materials often exhibit novel, and sometimes unusual properties²². These materials behave differently from their bulk materials. Among oxide semiconductors, Tin oxide (SnO₂) is one of the most promising materials to be investigated today. This is because tin dioxide is a well-known n-type wide band gap (3.6eV) semiconductor²³, and for its potential application in transparent conducting electrodes, photochemical and photoconductive devices in liquid crystal display, gas discharge display, lithium-ion batteries²⁴. Lot of studies has been developed to the synthesis of SnO₂ nanostructures, e.g., spray pyrolysis, hydrothermal methods, chemical vapor deposition, thermal evaporation of oxide powders and sol-gel method^{25, 26} so far. Besides these studies, we adopted co precipitation technique for our investigations because it is very cheap and simple preparation method to synthesize nanomaterials.

In this study we report the fabrication and characterization of SnO₂ based hybrid core-shell nanoparticles at room temperature. Recently materials with multicomponent functional materials have been the subject of extensive research in material science. These hetero-structures were most widely investigated for technological applications²⁷. To tune their functionality it is important to choose the suitable shell material with compatible physical and chemical properties with the core material. Here we have chosen ZnO and SiO₂ as shell materials deposited on SnO₂ nanoparticles and investigate the structural and magnetic interfacial effect

between the core and the shell materials. Based on this concept typical double shell core-shell nanostructures ($\text{SnO}_2@ZnO@SiO_2$) have been synthesized and their structural and magnetic characteristics have been investigated through analytical techniques.

2. Experimental Details

2.1 Materials and methods

The chemicals Tin(II)chloride dehydrate $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, Zinc Acetate dehydrate $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Poly Ethylene Glycol (PEG) (~1000 MW), 1-Hexadecyltrimethyl ammonium chloride (TMAC) were purchased from Merck (Germany 99.9%) and used as without further purification. All the chemicals were of analytical grade. For all washing and cleaning purpose, double distilled water was used.

2.1.1 Synthesis procedure of Core/Shell/Shell nanostructures

2.1.2 Preparation of core SnO_2

The simple and common co precipitation method was employed to prepare core SnO_2 and ZnO as well as SiO_2 coated SnO_2 nanoparticles. To prepare pure SnO_2 , 1M of Tin(II)chloride dehydrate i.e. (11.28 gm) is dissolved in 50ml of distilled water and ethanol by (30:20) volume ratio under constant stirring. After 30min 0.1M of Poly Ethylene Glycol (PEG) (~1000 MW) has been added and drop by drop addition of 1M of NH_4OH until reached the pH level upto 10-11 to form the complete precipitation¹. The stirring was continued for further 5h at ambient temperature and followed by the ageing process for 12hs. Finally the end product was separated by centrifugation and washed several times with ethanol, acetone and distilled water consecutively. Obtained white color SnO_2 nanopowder was dried at 60°C under vacuum for 12hrs and crushed into fine powder using mortar and pestle.

2.1.3 Preparation of SnO_2/ZnO core-shell nanospheres

To modify the surface of SnO_2 with ZnO, dissolving 1g of stannous chloride dehydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and 1gm of TMAC in 100 ml distilled water. The resultant solution was kept under constant stirring for 30mins and then the transparent solution was taken for ultrasonication process. After 1h sonication process, 1g of Zinc (II) Acetate solution was added drop-wise to the SnO_2 dispersed solution over the period of 5-10 min under vigorous stirring. After complete dissolution, ammonia solution was added to the above solution by drop wise. The stirring was continued for another 8h at ambient room temperature and followed by 12h ageing process. The end product was washed several times with de-ionized water, acetone, and ethanol followed by the calcinations process at 120°C for 12 h under vacuum.

2.1.4 Preparation of $\text{SnO}_2/\text{ZnO}/\text{SiO}_2$ core-shell-shell nanospheres

SiO_2 covered SnO_2/ZnO nanospheres were prepared through a versatile Stöber method as follows². Simply, 0.1gm of SnO_2/ZnO nanostructures was dispersed in 50ml of ethanol under constant stirring and the solution was further processed to ultrasonication for complete dispersion of the particles. Required amount of Tetra Ethyl Ortho Silicate (TEOS) and NH_4OH was added in the ratio of 1:4 to the above solution. Initially TEOS was dropped in to the solution under stirring and followed by the drop wise addition of Ammonia solution was added. The second shell silica was grown on SnO_2/ZnO surface was carried out by continuous stirring for 24 h. The end product was separated by centrifugation and washed several times with deionized water, ethanol and acetone to remove the untreated secondary silica particles. Finally, it is dried at 80° C for 12 h at room temperature.

2.2 Characterization

The as synthesized product was characterized by X-ray diffraction (XRD) using a BRUKER D5 Phase model powder X-ray diffractometer (XRD) with Cu K α radiation ($\lambda=1.54 \text{ \AA}$) (40 kV, 350 mA) in the range of 20-80° (2θ) at a scanning rate of 6° min⁻¹. The morphologies of the energy dispersive X-ray (EDX) analysis were obtained by field emission scanning electron microscope (FESEM) and HRTEM images were recorded with a Tecnai G2 20S-Twin transmission electron microscope operating at an accelerating voltage of 120 and 200 kV, respectively. FTIR spectra of the samples were obtained from the Perkin FTIR spectrophotometer over range of 400-4000 cm^{-1} and UV-Vis spectrophotometer (Shimadzu UV-2450) was used to study the optical absorbance of the sample. Jobin Yvon Fluorescence spectrometer (PL) was used to analyze the luminescent

characteristics of the material. Magnetic features of the as synthesized samples were obtained from the Vibrating Sample Magnetometer (VSM; Lakeshore, Model 7407).

3. Results and discussion

3.1 Structural studies

3.1.1 XRD analysis

Figure.1 shows the X-ray diffraction pattern of as synthesized core SnO₂ and the shells ZnO and SiO₂ coated SnO₂ nanospheres. The crystallinity of the sample is clearly evident by the sharper diffraction peaks at respective diffraction angles which can be readily indexed for its rutile tetragonal structure of the as-prepared SnO₂ powder. The obtained rutile phase is comparable with the standard JCPDS data (Card No. 88-0287). The diffraction peaks at $2\theta = 26.63, 33.89, 37.97, 51.85, 54.95, 57.88, 61.98, 64.75, 66.01$ corresponds to (110), (101), (200), (211), (220), (310), (112) and (301) diffraction planes of SnO₂ core³. The average crystallite size of the as-prepared SnO₂ was calculated as 23nm from the most intense peak (110) plane of SnO₂ based on Debye Scherer equation. For ZnO coated SnO₂ shows the additional diffraction peaks which belongs to the hexagonal ZnO nanostructure and their corresponding (hkl) planes were indexed according to the standard JCPDS (# 36-1451) card number⁴. So the peaks of ZnO were found in the core-shell nanostructures indicating the presence of ZnO in the core-shell sample and the shell thickness was found to be ~3-5nm. After the second shell SiO₂ has coated, the XRD pattern drastically changes and exhibits tetragonal phase of SnO₂ with reduced intensity. Thus it confirms the dense SiO₂ has been covered on the surface of SnO₂ and completely suppresses the ZnO peaks. Further, no peaks due to any solid-solution between Sn and Zn or other related oxides have been observed in the XRD pattern thus it confirms the formation of pure core-shell nanostructures.

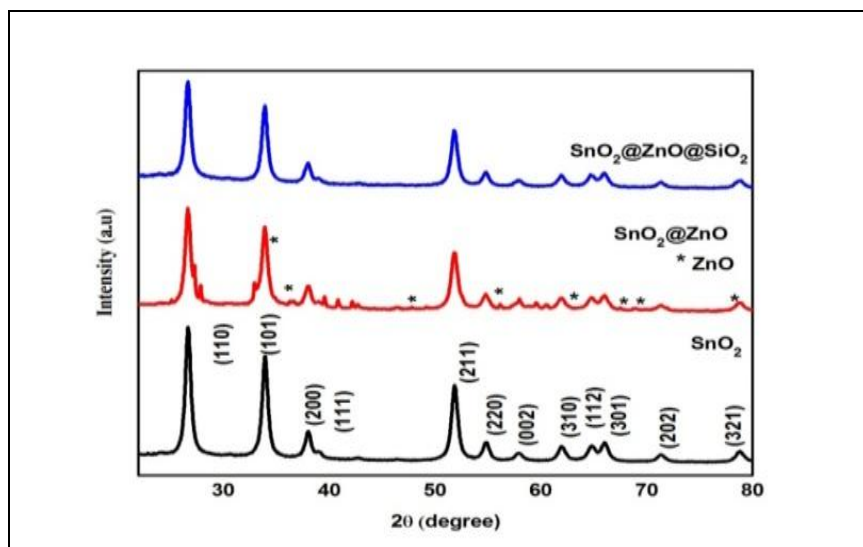


Figure 1. XRD Pattern of pure SnO₂, SnO₂@ZnO and SnO₂@ZnO@SiO₂

3.1.2 FTIR Studies

Figure. 2 shows the room temperature FTIR spectra of core SnO₂, SnO₂/ZnO and SnO₂/ZnO/SiO₂ core/shell/shell nanoparticles. For pure SnO₂, one of the principal bands centered at 635cm⁻¹ is assigned to a fundamental vibration ν (Sn-O) of tin dioxide^{5,10}. The peak at 1129 cm⁻¹ is related to the vibration of hydroxyl-tin (Sn-OH) bond [11]. The band at 1623cm⁻¹ may be attributed to the bending mode of O-H bonds. The broad band appearing in the region 3000-3500 cm⁻¹ may be due to vibration of adsorbed water and ammonia. In the case of SnO₂/ZnO core-shell nanostructures the additional peaks positioned at lower wave number region corresponds to the Zn-O absorption bond⁶⁻⁸. Finally, the second shell SiO₂ coated SnO₂ sample exhibits the strong bonds at 1071cm⁻¹ and 1346cm⁻¹ are the characteristic absorption peaks due to the Si-O-Si bond is similar to the earlier reports^{9,12}. From this FTIR data base analysis both ZnO and SiO₂ were successfully coated on the surface of the SnO₂ nanoparticles.

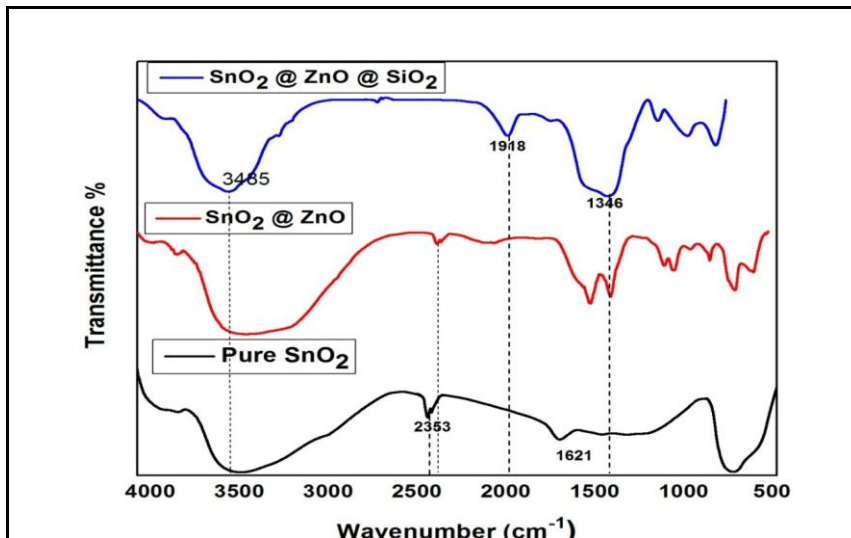


Figure 2. FTIR of pure SnO₂, SnO₂@ZnO and SnO₂@ZnO@SiO₂

3.2 Morphological studies

In order to identify the morphology and typical core-shell nanostructure of tin oxide coated with ZnO and SiO₂ shells bright-field HRTEM images were taken with corresponding SAED patterns are shown in Figures. 3(a, b, c, d, e, f). The HRTEM images of these nanostructures show almost uniform and spherical morphology. The formation of nanoparticles can be attributed to the following mechanism. For the tetragonal phase of SnO₂, several groups have indicated that the (110) and (001) surfaces have the lowest and the highest surface energies, respectively¹⁴. It means that SnO₂ prefer to grow along the [110] direction, forming the SnO₂ nanostructure. In aqueous solution, the concentration of the precursor is extremely low in order to obtain the nanostructure. From the figures it can be observed that the particles were agglomerated due to the high surface area of the nanoparticles. Pure SnO₂ sample exhibits spherical shape and having the average crystallite size of ~21nm is shown in fig 3(a) and (b) shows its corresponding SAED pattern as that of the earlier reports¹³. This agrees with the XRD results. For ZnO coated SnO₂ core-shell nanostructures also exhibits spherical shape particles¹⁵ should be observed were shown in 3 (c) and its SAED pattern in 3(d). This may be caused due the reaction temperature, precursor ratio taken and adding of surfactant. It is clearly seen in the figure for ZnO coated SnO₂, the dark region is the core and the surface around the core is the ZnO shell. Thus there is no doubt in the formation of SnO₂@ZnO core-shell nanostructure. In the case of SiO₂ encapsulated SnO₂/ZnO core-shell nanostructure the spherical shape remains same was observed in fig 3(e) and its corresponding pattern in 3(f). According to these TEM images, no doubt the core-shell nanostructure is certainly formed.

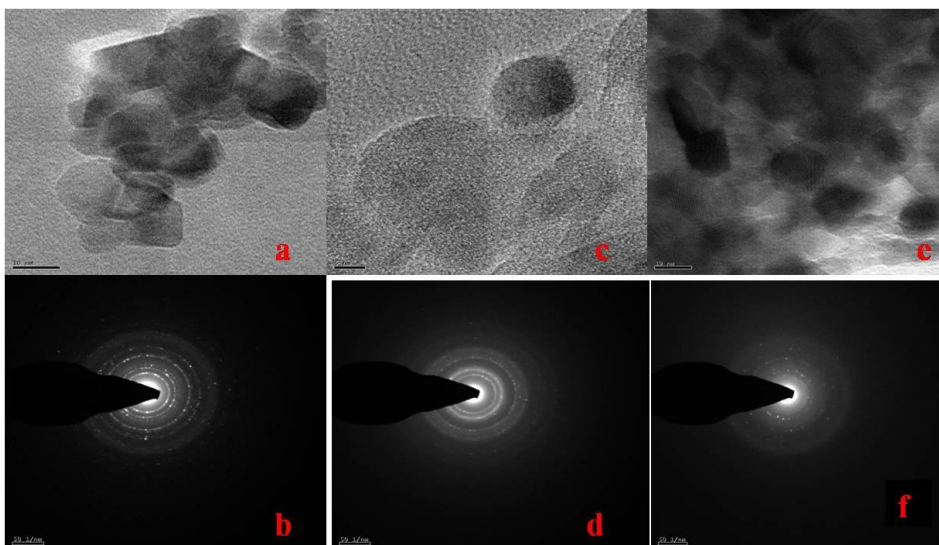


Figure. 3(a, c, e) HRTEM micrographs of pure SnO₂, SnO₂@ZnO and SnO₂@ZnO@SiO₂ and 3(b, d, f) their corresponding SAED pattern

3.3 Magnetic studies

To investigate the magnetic properties of pure SnO₂, SnO₂@ZnO and SnO₂@ZnO@SiO₂ core-shell nanoparticles room temperature magnetization measurements were performed on the samples and are shown in Figure. 4. From the figure it is clear that Pure SnO₂ exhibits diamagnetic behavior as commonly reported¹⁷. This behavior arises due to the 4⁺ valence state of tin (Sn⁴⁺) which favors 4d¹⁰ electronic configuration of Sn in SnO₂ and hence there is no unpaired d electrons in the material for any kind of ferromagnetic ordering¹⁶. Weak Ferromagnetic hysteresis loops were observed in ZnO and SiO₂ incorporated SnO₂ nanoparticles. The saturation magnetization and magnetic moments of these core shell nanoparticles were found to decrease with the coating of shell materials. The saturation magnetization for the pure, ZnO coated SnO₂ and SiO₂ coated SnO₂@ZnO nanoparticles are 0.0016 emu/g, 0.0013 emu/g and 0.0011 emu/g respectively. This indicates the well crystalline SnO₂ formation and the shells ZnO and SiO₂ nanostructures have been successfully covered on the surface of SnO₂.

The coating of ZnO on SnO₂ matrix can transform its diamagnetic state to ferromagnetic state. Ferromagnetic hysteresis loops were observed in ZnO and SiO₂ coated SnO₂ core-shell nanostructures. Ferromagnetism arises because of increase in the charge carriers between the core and the shell particles. Previously several authors were discussed the room temperature ferromagnetism of transition metal doped SnO₂ nanoparticles¹⁸⁻²¹. The coercivity (H_{ci}) values of pure and ZnO as well as SiO₂ coated SnO₂ core-shell nanoparticles were observed as 506.96 G, 386.86 G and 353.78 G respectively. After the coating of ZnO and SiO₂ over SnO₂ nanoparticles the reduction in saturation magnetization was observed. It is mainly due to the interfacial effect of the typical core-shell nanostructures. It is probably due to the complete dissipation of ZnO crystals into the outer dense SiO₂ layer which is suppressing the activity of ZnO¹². This kind of tunable magnetic features of the core-shell nanostructures via the surface modification will be the potential candidate for future spintronics, magneto-optical sensors and magnetic related technological applications.

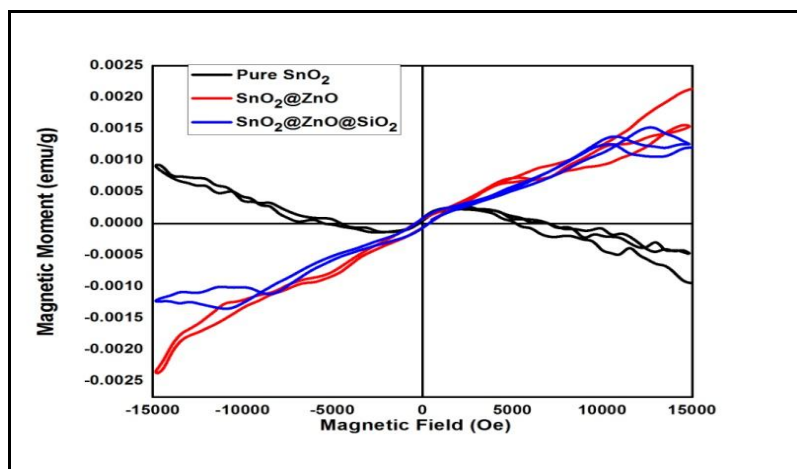


Figure. 4 VSM images of pure SnO₂, SnO₂@ZnO and SnO₂@ZnO@SiO₂

4. Conclusions

In summary, well crystalline SnO₂ and ZnO as well as SiO₂ coated SnO₂ core-shell nanoparticles have been successfully synthesized by chemical precipitation method. Polycrystalline nature with tetragonal shape of pure SnO₂ and hexagonal shape of ZnO had grown on core was confirmed by X-ray diffraction analysis. The morphology of these core-shell nanoparticles has been investigated by FESEM. Core-shell nanostructures of the samples were obtained from the HRTEM analysis. Pure SnO₂ shows diamagnetic feature at room temperature. After coating of ZnO and SiO₂ on SnO₂ nanoparticles shows weak ferromagnetism instead of diamagnetism was observed by VSM. This indicates the interfacial effect between the core and the shell materials. Thus by deposit the shell materials on the core material will enhance the desired property of the material. In this study concludes, the surface modification with insulating oxide layer coating can tune the magnetic features of SnO₂. Thus induces the multi-functionality of the magnetite nanostructures. However, it needs further investigations with the desired magnetic features could be the better choice of materials for Magneto-electronic devices.

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