RESEARCH ARTICLE

Synthesis Characterization and Electrochemical Performance of Chromium Doped Tin Oxide

David Bahati¹*, Mukka Prasanna², Pulapa Venkata Kanaka Rao¹

¹University of Dodoma, Tanzania
²Centre for nano science and technology, India

*Corresponding author: Davic Bahati: david.bahati@udom.ac.tz

Abstract:

Chromium doped Tin oxide nanoparticles with chromium concentrations ranging from 1 to 5 wt% were synthesized by microwave irradiation technique. Standard characterization techniques were used to understand the characteristics of the nanoparticles obtained. X-Ray Diffraction (XRD) pattern depicted the tetragonal crystal structure for Cr doped SnO₂ nanoparticles. From the results of crystallite sizes for various doping concentrations, it was observed that doping inhibits the growth of crystalline grains of SnO₂. Scanning Electron Microscope (SEM) images confirmed the surface morphology modifications due to varying doping concentration of Cr, nanocrystallite showed extra agglomerated status with mesoporous structures. Energy dispersive spectrometer (EDAX) observations confirmed the doping of chromium ions in SnO₂ lattice. Other standard characterization techniques such as FESEM, TEM, HRTEM, FTIR, UV-Vis spectroscopic analysis were also carried out for the samples prepared. The electrochemical behavior of the sample was determined using Cyclic Voltammetry (CV) by scanning the potential at a rate of 50 mV s⁻¹ and for a maximum current of 600 mA carried out on undoped SnO₂ and Cr doped SnO₂. It was observed that as the wt% of Cr in Cr doped SnO₂ increases, the electrochemical performance increases as compared to undoped SnO₂. A fairly larger peak current of 15 μA and a larger oxidation peak potential of 0.76 V were observed for 5 wt% Cr doped SnO₂.
Introduction

Nanostructured metal-oxide semiconductor based sensors have wide applications in biological, environmental and analytical chemistry (1–5). Among the oxide semiconductors, tin oxide (SnO₂) is one of the promising candidates as a host material that has been used in gas sensors, dye-sensitized solar cells, electrochromic windows, transparent conducting electrodes, transistors, catalysts and supercapacitors (6–10). SnO₂ is a versatile material with a wide band gap (3.6 eV at 300 K) in its stoichiometric form, but due to lattice imperfections and oxygen vacancies arising during its production, it becomes n-type and conductive (9,11–13). SnO₂ material research has been of considerable interest because of its combined properties of plentiful oxygen vacancies, high optical transparency, chemical and electrochemical stability, good electrocatalytic activity, nontoxicity, good biocompatibility, and high electron communication features when doped (14). Chemical doping with appropriate elements (Fe, Cr, Co, Mn, Ni, etc.) is widely used as an effective method to tune surface states, energy levels of semiconductors and transport performance of carriers which enhances the electrical, electrochemical and magnetic properties of materials (12,14). The ionic radius of Cr³⁺ is close to that of Sn⁴⁺ (15,16), which means that Cr³⁺ can easily penetrate into the SnO₂ crystal lattice or substitute the Sn⁴⁺ position in the crystal. Various methods have been used to synthesize the SnO₂ nanostructures; Autoclave method, co-precipitation, pulsed laser deposition, spray pyrolysis, solid state reaction method, polymeric precursor's route, hydrothermal method etc. (17–21). However, it still remains a great challenge to develop a simple method for fabricating nano-SnO₂, particularly metal ion doped SnO₂ nanostructures with controlled morphology. Herein we report the synthesis of Cr doped SnO₂ nanoparticles by a simple microwave irradiation method that takes only a few minutes to complete the reaction with prevented agglomeration.

Experimental details

Materials

Chromium (III) nitrate nonahydrate [Cr(NO₃)₃9H₂O] and Stannous (II) Chloride dihydrate [SnCl₂2H₂O] from Fischer Scientific, were the starting materials used without further purification. Phosphate Buffer solution (PBS), Ammonium Hydroxide (NH₄OH) and ultrapure deionized water was used as solvent.
**Nanoparticle synthesis**

The growth solution of SnO$_2$ is prepared by dissolving 0.1M Stannous (II) Chloride dihydrate [SnCl$_2$·2H$_2$O] in deionized water. Ammonium hydroxide (NH$_4$OH) was added drop wise (about 1 drop per 3–4 s) to the above solution until the pH reached 10. This solution was again stirred for 30 minutes to form a greenish colloidal gel. Further, the hydroxide product was washed several times with deionised water and ethanol in order to remove the excess Cl$^-$ and NH$_4^+$ ions. Then the precipitate containing beaker was transferred into a microwave oven (600 W) and kept for 20 minutes. The product obtained is tin hydroxide which is calcinated at 800 °C for 4 hour to get the tin oxide nanoparticles. For doping approximate amounts of [Cr(NO$_3$)$_3$·9H$_2$O] with different Cr (1%, 3% and 5% by wt) content were mixed with Stannous (II) Chloride dihydrate [SnCl$_2$·2H$_2$O] in deionized water, Ammonium hydroxide (NH$_4$OH) was added drop wise until the pH reached 8 for all doping concentrations. Then the precipitate was washed with ethanol to remove excess Cl$^-$ and NH$_4^+$ ions and the beakers were transferred into microwave oven (600 W) and kept for 20 minutes. Finally, the Cr doped SnO$_2$ nanopowders were obtained after annealing the precipitates at 600 °C for 5 hours in an ambient atmosphere.

**Results and discussions**

**XRD Analysis**

Figure 1 shows the results of XRD analysis of the undoped SnO$_2$ and Cr doped SnO$_2$ Nanoparticles obtained using Microwave Method.

![XRD patterns](image)

Figure 1: XRD patterns of (a) undoped SnO$_2$, (b) 1 wt%, (c) 3 wt%, and (d) 5 wt% Cr doped SnO$_2$ nanoparticles

The XRD patterns of undoped SnO$_2$ exhibit diffraction planes along (110), (101), (200), (211), (220), (310), (112), (301) and (321), which is consistent with rutile-type phase and tetragonal unit cell of SnO$_2$ (ICDD-PDF card no.46-0255). From figure 1 it is observed that there is increase in the peak intensities for Cr doped SnO$_2$ with no extra phase as the Cr concentration increases and is depicted that chromium ions substitute tin ions in tin oxide lattice. The observed
shrinkage of the unit cell volume is consistent with the fact that the ionic radius and valence of Cr\(^{3+}\) (63 °A) is smaller than that of Sn\(^{4+}\) (74 °A). The XRD results showed that the Cr\(^{3+}\) ions incorporate into SnO\(_2\) lattice or replace Sn\(^{4+}\) sites without changing the rutile structure. The average crystallite size (D) was determined using the diffraction peaks of (110) and (101) from Scherer's formula

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

(22,23). Where K is the shape factor whose value is taken as 0.89, \(\lambda\) is the wavelength of Cu Ka radiation, and \(\beta\) is the corrected full width at half maximum (FWHM) of the diffraction peak and \(\theta\) is the diffracting angle. The average crystallite sizes of the synthesized nanoparticles were 17.88 nm (undoped), 26.41 nm (1% by wt), 28.50 nm (3% by wt) and 49.46 nm (5% by wt) respectively. These results indicate that the crystallite size of the Cr doped SnO\(_2\) nanoparticles increase as the doping concentration increases.

Scanning electron microscopy (SEM) analysis

Figure 2 shows the SEM images of undoped and Chromium doped SnO\(_2\). It is observed that the prepared SnO\(_2\) particles are nanorods with some agglomeration, which may be due to annealing of SnO\(_2\) nanoparticles (NPs). However there is some non-uniformity in the shape and the existence of porosity. The measured mean particle size of the tin dioxide particles from the SEM image is 47.8 nm, which is comparable to XRD values determined for the particle size. A relatively uniform mixture of tetragonal like structures could be observed and the nanocrystallite showed extra agglomerated status with mesoporous structures.

Elemental analysis of NPs was done by using energy dispersive spectrometer (EDS) the plot of spectrum is shown in Figure 4. Emission peaks such as O and Sn observed in the EDS spectrum shows the presence of tin and oxygen elements and confirmed the stoichiometry of NPs.

![Figure 2: SEM images for undoped and Cr-doped Tin Oxide](image)
Field emission scanning electron microscopy (FESEM) analysis

Field Emission Scanning Electron Microscope (FESEM) was used to observe the morphology and structure changes. Figure 3 show that doping significantly alters the morphology of the nanorods. The surface of the SnO₂ particles with 1% Cr doping are nano rods as shown in Figure 3(a), the grain size formed and surface modifications by increasing the concentration to 3 wt% is shown in Figure 3(b), modification of surface are also evident on increasing the Cr dopant level to 5 wt%, it is observed that the grain size formed on the surface of SnO₂ film decreases on increase of Cr dopant (Figure 3(c)). Further large regular rectangular and triangular shaped grains are formed on the surface of SnO₂ and the size of grains decrease with increasing dopant concentration.

![Figure 3: FESEM Images of (a) 1wt% (b) 3 wt% and (c) 5 Wt% Cr doped SnO₂](image)

Energy dispersive analysis of X-Ray (EDAX)

Figure 4 shows the compositional analyses of the Cr doped samples as depicted in the EDX spectra. The spectra show chromium peaks implying incorporation of Cr ions into SnO₂ lattice. Furthermore, Hume-Rothery rules of substitutional solid solution suggest that substitutional incorporation of dopant is possible if the ionic radii of the host atom and the dopant must not differ by more than 5% (24–26). In this investigation, the ionic radii of Sn⁴⁺ and Cr³⁺ are 0.069 and 0.063 nm, respectively, which are well within 5% difference. This shows that Cr ions substitutionally replace Sn ions in the SnO₂ lattice.

![Figure 4: EDAX spectra of (a) 1 wt% (b) 3 wt% and (c) 5 Wt% Cr doped SnO₂](image)
**Fourier transform infrared (FTIR) spectroscopy**

FTIR analysis is carried out in the wavenumber range from 450 cm\(^{-1}\) to 4000 cm\(^{-1}\). The samples are with KBr, thoroughly mixed and pelletized by pressing under sufficient pressure, before FTIR analysis. FTIR spectra of SnO\(_2\) nanoparticles prepared at 600 °C are shown in Figure 5. The broad peak centered at 619 cm\(^{-1}\) is observed. The broad band between 800 and 500 cm\(^{-1}\) was due to the vibrations of Sn-O. To obtain more details of defects in SnO\(_2\):Cr films FTIR is employed. The main IR features of SnO\(_2\) at 468 and 619 cm\(^{-1}\) are assigned to O–Sn–O and Sn–O stretching vibrations, respectively. Two interesting features are observed: One is the weak feature of O–Sn–O vibration in the undoped SnO\(_2\) film, which goes with the presence of vibration at 644 cm\(^{-1}\). This vibration becomes weakened and disappears as the Chromium (Cr) concentration increases; the other characteristic is the presence of Sn–Cr feature at high doping levels, which causes the splitting of O–Sn–O feature. A band corresponding to the presence of adsorbed water (H\(_2\)O) 1630~1640 cm\(^{-1}\) and hydroxide absorption (OH) bands in the range of 2500~3500 cm\(^{-1}\) were observed.

![Figure 5: FTIR spectra of undoped SnO\(_2\) and Cr doped SnO\(_2\)](image)

**Transmission electron microscope (TEM) analysis**

Typical TEM and high-resolution transmission electron microscope (HRTEM) images of undoped and 5 wt% Cr doped SnO\(_2\) samples are shown in Figure 6 (a & c) a spherical morphology with average size of 21nm and 16 nm respectively is observed the results are in good agreement with the estimated average crystallites size from the XRD pattern. The HRTEM image for undoped and 5 wt% Cr doped SnO\(_2\) nanoparticles are shown in Figure 6 (b & d). Undoped SnO\(_2\) nanocrystallites exhibited highly symmetrical and sharp lattice lines which confirm their single crystalline and defect free nature. However, Cr-doping seems to introduce twin-like defects in the crystallites as shown in Figure 6(d). Further,
presence of any secondary phase or trace elements in the samples is not identified using HRTEM.

Figure 6: TEM image of (a) undoped SnO$_2$, (c) 5 wt% Cr doped SnO$_2$ nanoparticles & HRTEM images of (b) undoped SnO$_2$, (d) 5 wt% Cr doped SnO$_2$ nanoparticles

**Optical band-gap using UV-Visible spectrophotometer**

From the transmittance spectra shown in Figure 7 the Optical band gap values were obtained using the Tauc’s formula (27). For undoped SnO$_2$ band gap is 3.58 eV which is in good agreement with the reported values of Arun kumar sinha (11) it is observed that Cr doping has a positive influence on the temperature dependent of resistance.
Cyclic voltammetry analysis

The electrochemical behaviour of the sample is determined using Cyclic Voltammetry (CV) by scanning the potential at a rate of 50 mV s⁻¹ and for a maximum current of 600 mA carried out on undoped SnO₂ and Cr doped SnO₂. From figure 8 it is observed that for undoped SnO₂ (Figure 8(a)) the peak current is 11 μA for doping concentration of 1 wt % the peak current is 12 μA for doping concentration of 3 wt % the peak current is 13 μA, as the wt % of Cr in Cr doped SnO₂ increases, the electrochemical performance increases as compared to undoped SnO₂, a fairly larger peak current of 15 μA and a larger oxidation peak potential of 0.76 V were observed for 5 wt % Cr doped SnO₂.
Figure 8: Cyclic Voltammetry of (a) undoped SnO$_2$, (b) 1 wt% doped (c) 3 wt% doped and (d) 5 wt% Cr-doped SnO$_2$ nanoparticles

Conclusion

Undoped and Cr doped SnO$_2$ nanoparticles were synthesised using microwave irradiation method. The influence of Cr doping concentration on the structure, morphology, optical and electrochemical properties are reported. XRD patterns of undoped sample revealed the pure tetragonal rutile structure of SnO$_2$. UV Spectroscopy shows decreasing band gap of SnO$_2$ by addition of Chromium. The cyclic voltammetric (CV) studied confirmed that Cr doped sample have good electrochemical behaviour when compare to pure SnO$_2$ sample.

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