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CHARACTERIZATION OF TIN OXIDE AND TIN OXIDE-GOLD COMPOSITE PREPARED VIA SOL-GEL TECHNIQUE

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Abstract

Tin oxide particles were synthesized with the use of sol-gel technique. The gel obtained was treated with heat at 400 °C to obtain the tin oxide particles. The properties of both the tin oxide and the functionalized tin oxide nanoparticles were examined. The FTIR result for the two samples confirms the realization of tin oxide with the O-Sn-O vibration localized at 596.00 cm⁻¹ and 657.77 cm⁻¹ for tin oxide (TO) and tin oxide-Gold nanoparticles composite (GTO) respectively. The response of the material to light was studied and the transmittance observed to be high and the absorption was low within the region of visible light (400 nm – 800 nm) of the electromagnetic radiation. The composite was observed to have a higher absorption of visible light compared with the one not functionalized. The energy band gaps of the tin oxide only and the tin oxide-Gold composite were around 3.6 eV and 3.75 eV respectively. The average grain sizes of the TO and GTO obtained from the XRD pattern are 3.66 nm and 3.89 nm respectively. The surface morphology studied by the use of scanning electron microscopy of the samples show homogeneous and smooth nanoparticles. The optical characterization done shows that the particles prepared has a high transparency in the visible region and also of wide band gap which made it suitable for use as transparent front contact in the production of photovoltaic devices and a potential photocatalyst.

Keywords: Tin oxide, Sol-gel, Photovoltaic, Nanoparticles.

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Introduction

In this twenty-first century, nanotechnology is really revolutionizing several areas like electronics, optoelectronics, sensing etc.(Gul, 2012).Metal oxides which are semiconductor in nature, especially in form of particles in Nano scale, have provoked quest of scientists due to their fascinating features, which are not the same from those of their bulk state. (Ashok *et al.*, 2015). Tin oxide (SnO_2) that is not functionalized, is a wide band-gap semiconductor (with energy gap greater than 3 eV) which shows a very high transparency to visible light (%T greater than or equal to 85%) and conductivity which is n-type as a result of oxygen vacancies (Ziad *et al.*, 2014).The two principal oxides of tin are;(SnO_2) and (SnO). The reality of the oxides reveals the duality of the tin valences; +2 and +4 oxidation states (Alaf, *et al.*, 2013). According to Nagirnyak, *et al.*, (2016), oxides of metal are the pillars of recent various smart materials and devices due to their physical and chemical properties which can be tuned.A study carried out by Ashok *et al.*, 2015 reveals that a few reliable methods have been used in the preparation of SnO_2 nanostructures with a good control over its particle size and some other physical properties.

These techniques include hydrothermal, organo-metallic synthesis, sonication methods, etc. However, these techniques are cumbersome, expensive or energy/time-consuming. On the contrary, sol-gel technique is a simple process to

synthesize homogeneous nanoparticles which is of high purity and crystallinity at a low temperature. In this method, the solution from precursor is transformed into solid which is inorganic by: the dispersion of colloids in a liquid (sol) and then conversion of the sol formed into another phase known as gel; by condensation and hydrolysis. It was made clear that this process leads to preparation of amorphous precipitates and appropriate calcination is essential to induce particle growth by re-crystallization and to produce an effect on the particle morphology. Lan (2005) presented the advantages Sol-gel technique offers in contrast with others: synthesis of materials with wet chemical is involved, so the make-up of the materials can be tailored at molecular level. Hence, stoichiometric homogeneous control of the functionalization achieved almost effortlessly. Since liquid precursors are used, it is possible to cast in a particular range of shapes the glass and ceramics, like thin film, fibers, and monoliths, etc, without the need of machining or melting. Finally, it is cost effective because the temperature required in the process is low, close to room temperature, and no delicate vacuum system is needed.

In this work, the optical and structural characteristics of tin oxide and its gold composite synthesized by the Sol-gel technique were investigated and also the relevance of the synthesized material in production of photovoltaic devices and photocatalysis mechanism.

Methods

The method used for synthesis of tin oxide Nano-powder in this work is termed Sol-gel technique. 0.1 M of $\text{SnCl}_4.5\text{H}_2\text{O}$ (3.51 g of $\text{SnCl}_4.5\text{H}_2\text{O}$) dissolved in 50 ml of distilled water in a beaker together with 50 ml of ethylene glycol to make a 100 ml precursor mixture. The mixture obtained was stirred on amagnetic stirrer at 300 rpm and while stirring, 0.1M aqueous ammonia solution added in drops for about an hour. The composite of tin-oxide with gold nanoparticles was obtained by about 5 drops of the prepared Gold (III) Chloride trihydrate (HAuCl_4) solution to the mixture during stirring. The gel resulted was filtered by

Materials and Methods

Materials

Tin tetrachloride penta-hydrate ($\text{SnCl}_4.5\text{H}_2\text{O}$), ethylene glycol and ammonia were used for tin oxide nanoparticles synthesis. Gold (III) Chloridetrihydrate (HAuCl_4) was used in addition to other materials for the composite. The deionized water was used in the synthesis as a solvent for precursors such as $\text{SnCl}_4.5\text{H}_2\text{O}$, ethylene glycol and liquid ammonia.

the use of filter paper and afterward washed three times by de-ionized water to remove excess ammonia. The precipitate in the filter paper put in the crucible was heated at a temperature of 150 °C for 2 hours to remove water molecules. Finally, whitish particles were obtained after drying, and then the dried sample was further annealed at 400 °C for 2 hrs. The tin oxide (not functionalized) gives lustrous yellowish colour while the tin oxide-gold nanoparticles composite gives a brownish colour.

Characterization

The spectral for the transmittance and absorbance of the synthesized material were plotted via the measurement of its response to electromagnetic radiation using UV-VIS spectrophotometer (Model 6800 JENWAY) in the range of 350 nm to 800 nm. The hf (eV) value obtained from the graph of $(\alpha hf)^2$ versus photon energy (hf) is the band gap of the material. A Spectroscopy applying Fourier Transform Infrared, which is tagged FTIR, was done to obtain the Spectra for the confirmation of formation of O-Sn-O bond. The properties related to structure and size of SnO₂ nanoparticles were studied by X-ray diffraction measurements (BRUKER ECO D8 ADVANCE diffractometer) using the Cu K α ($\lambda = 1.5406 \text{ \AA}$) as a radiation source, operated at 40 kV and 25

mA with a scan rate of 0.02 °/s over the range of 10°-100° together with the Scanning Electron Microscopy.

Results and Discussions

Fourier Transform Infra-red Spectroscopy (FTIR)

Shown in Figures 1 and 2 are the FTIR spectra of tin oxide only and functionalized tin oxide particles. A typical band at 3403.00 cm⁻¹ and 3393.00 cm⁻¹ indicates that a strong hydrogen bond formed in the tin oxide only and functionalized particles respectively, between hydroxyl groups from ethylene glycol. This result agrees closely with that reported by Zhang and Liu (1999) as 3400 cm⁻¹. Some tin oxide O-Sn-O vibrations observed from the spectra as depicted by the small peak localized at 596.00 cm⁻¹ and 657.77 cm⁻¹ confirms the formation of the SnO₂ and the tin oxide –gold composite respectively. A strong band at 2354.28 cm⁻¹ was observed to be common to both samples and according to Marikkannan *et al.*, (2015) these were absorbed for SnO and correspond to an anti-symmetric CO₂ stretching Vibration

Fig. 1: FTIR of the tin oxide only

Fig. 2: FTIR of the tin oxide-Gold nanoparticles composite

Optical Properties

The UV-VIS absorbance spectra of SnO₂ nanoparticles and the functionalized tin oxide are given by figures 4 and 5. The characteristic absorption peak was found about a wavelength 270 nm in the region ($275 \text{ nm} \leq \lambda \leq 350 \text{ nm}$). It was observed that the tin oxide gold composite has absorption of visible light higher in contrast to that of tin oxide. This property can make the material suitable for application in degradation of harmful substances through photocatalysis. Also, the particles functionalized with gold nanoparticles have a band gap higher than the tin oxide only. This

shows prolonged recombination of the hole and electron according to Alabi and Babalola, (2013) due to electron sink in gold nanoparticles. This feature also emphasized the fact that the functionalized tin oxide can be a good photocatalyst as rate of recombination of electron-hole pair is minimized. The transmission of the electromagnetic radiation in the visible region is high as shown in Fig 3. As the material can transmit visible light very well, it is confirming the existing works done on tin oxide as transparent conductive oxide (TCO) to be used as a photo anode in new generation solar cells.

Fig. 3. Transmission spectra of the tin oxide nanoparticles

Fig. 4. Absorption Spectra of the tin oxide nanoparticles

Fig.5. Comparison of the Absorption spectra of the Tin oxide only and the Tin oxide gold-nanoparticles composite. (KEY: The spectra with square shape is GTO, the one of circular shape is TO)

In the production of semiconducting materials, doping is the intentional introduction of impurities into a pure intrinsic semiconductor to achieve modulating its electrical properties. SnO has been reported as a remarkable n-type semiconductor by Bendjedidi *et al.*, (2015) among many researchers.

Gold is a transition metal of variable number of valence electrons which depends on the formula it is involved in. Nevertheless, gold mostly has

one (1) valence electron, and occasionally three (3) valence electrons. The HAuCl_4 used to functionalized the tin oxide particles prepared has gold with three valence electrons. N-type extrinsic semiconductor is produced by adding pentavalent atoms to a pure semiconductor while a P-type semiconductor is obtained by the addition of trivalent atoms (with three valence electrons). In the n-type semiconductor there is the donor because of the excess electrons; the

‘impurities’ is the electron donor while that of a p-type is an electron acceptor. Tin can exhibit either 2 or 4 valence electrons and the addition of HAuCl_4 makes the functionalized tin oxide a p-type semiconductor because, gold in the nanoparticle solution serves as an electron acceptor. With this, a p-type extrinsic semiconductor is produced which shows a better absorption of photon energy than that of tin oxide only, even as observed from the absorption spectra compared (Fig.5)

The optical gap of the TO is about 3.6eV and that of GTO is 3.75eV. This is close to the bulk value of the band gap of SnO_2 . This wide energy gap makes the material a good potential semiconductor in dye sensitized solar cell. Also, the band gap being tunable (even by functionalizing) suggests a suitable candidate for fabricating optoelectronic Nano devices and also a good photocatalyst.

Fig.6. Tauc Plots $(\alpha hf)^2$ versus hf for (a) the Tin Oxide only and (b) Tin Oxide gold-nanoparticles composite

Structural Properties

The X-ray diffraction characterization of the SnO₂ samples was performed in order to identify the phase, crystal structure and to estimate average grain size. The recorded X-ray diffraction pattern of the Tin Oxide samples by sol-gel technique is presented in Fig. 7 and that of the tin oxide–gold nanoparticles composite in Fig. 8. The 2 θ peak values are as follows: 26.6⁰, 33.9⁰ and 51.8⁰ corresponding to diffraction from planes (110), (101) and (211) respectively for the Tin Oxide only while the peaks at 27.0, 34.5 and 51.8 respectively for the GTO from the same planes. The XRD patterns confirms the formation of SnO₂ nanoparticles with polycrystalline phase which demonstrates tetragonal rutile structure [JCPDS Card No: 41-1445, a = 4.743Å. c = 3.1859 Å]. The crystal planes (110), (101), (211) were prominently

Fig. 7. XRD pattern of the Tin Oxide nanoparticles (T.O) only

The increased grain size of GTO shows that impurities presence is confirmed when likened with the TO which has a particle size lower and indicates a material in a better Nano scale range.

The microscopy gives the surface morphology of the samples. Figures 7 and 8 reveal that the prepared tin oxide nanoparticles and the tin

seen in XRD indicating the polycrystalline nature of the nanoparticles. This is in agreement with the report of Zuoli and Jiaqi, 2013.

The average size of the Tin Oxide nanoparticles (TO) and Tin Oxide Gold-nanoparticles composite (GTO) were estimated to be 3.66 nm and 3.89 nm respectively using the **Scherrer's equation**:

$$g = \frac{K\lambda}{\beta \cos \theta} \quad \text{-----} \quad (1)$$

These really confirm the fact that the prepared particles is in Nano scale.

In the equation, K = 0.94 is the shape factor, λ = 1.5406 Angstrom is the wavelength of X-ray used, β = Full width at half Maximum (FWHM) in radians, θ = Bragg angle of the diffraction peak in radians and g = average grain size.

Fig. 8. XRD Pattern of the Tin Oxidegold-nanoparticles composite (GTO)

oxide gold-nanoparticles composite are aggregate of homogeneous particles. Although, the composite particle appears softer on the surface and together than the tin oxide. The rough appearance of the GTO is likely to be due to the presence of the gold nanoparticles as impurity in the nanomaterial.

(a)

(b)

Fig.9. SEM Images of Tin Oxide nanoparticles only

(a)

(b)

Fig.10. SEM Image of Tin Oxide gold-nanoparticles composite**Table 1: Summarized comparison of findings with other studies**

Findings as compared with other studies	Authors / year
Prolonged recombination of the hole and electron due to electron sink in gold nanoparticles	Alabi and Babalola / 2013
A strong band at 2354.28 cm^{-1} absorbed for SnO and suggest anti-symmetric CO_2 stretching vibration	Marikkaannan <i>et al</i> / 2015
Reported SnO as a remarkable n-type semiconductor, among many other researchers	Sagadevan / 2015
Hydroxyl groups confirmed from the FTIR spectra	Zhang and Liu / 1999
Confirmation of polycrystalline nature of the nanoparticles from the crystal planes prominently seen	Zuoli and Jiaqi / 2013

Conclusion

Tin oxide (SnO_2) Nano-crystallites were synthesized by Sol-Gel method. Here, we conclude from XRD analysis that particles are polycrystalline with tetragonal rutile structure. Morphological features of the material are obtained from SEM image and it shows homogeneous distribution of particles with particle size of about 3.7 nm. The absorbance and transmittance spectra shows that synthesized tin oxide Nano-crystallites were good materials for use as transparent conductive oxide and the effect of functionalizing with gold nanoparticles is studied on its properties. The energy band gap of SnO_2 nanoparticles only was measured from

the Tauc relation plot and obtained as 3.6 eV and 3.75 eV for tin oxide gold-nanoparticles composite.

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Conflict of Interest

We hereby declare that there is no conflict of interest as regards the content of this manuscript.

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