



Synthesis and characterization of iron tin oxide thin films from single source bimetallic precursors



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ABSTRACT

Two new bimetallic precursors, [(C₅H₅)Fe(C₅H₄)COOSn(C₄H₉)₃] (**A**₁) and [(C₅H₅)Fe(C₅H₄)COOSn(C₆H₅)₃] (**A**₂), were synthesized by reacting 4-ferrocenylbenzoic acid with tributyltin chloride and triphenyltin chloride in refluxing toluene. Single crystal analysis showed the molecules to adopt the usual trigonal bipyramidal geometry, the ferrocene ligand being perpendicular to the phenyl ring and tin carboxylate cycle. Thermogravimetric studies revealed the decomposition of both synthesized compounds in the range 450–500 °C, leaving a residue corresponding to the mass of SnO₂·1/2Fe₂O₃ for **A**₁ and SnO₂·Fe₂O₃ for **A**₂. The synthesized compounds were used as precursors for depositing FeSnO_x thin films by aerosol assisted chemical vapor deposition (AACVD) on a glass substrate (at 400 and 450 °C). Scanning electron microscopy (SEM) of the thin films showed the formation of spherical globules at 450 °C for both precursors, with the average roughness of the thin films being 2.48 and 3.41 nm for **A**₁ and **A**₂, respectively. The XRD pattern for **A**₁ at 450 °C shows the incorporation of the iron in a substitutional position in the tin oxide lattice due to the small difference in their atomic radii. In the case of **A**₂, only spinel iron oxide (magnetite and maghemite) with the dominance of maghemite is found.

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1. Introduction

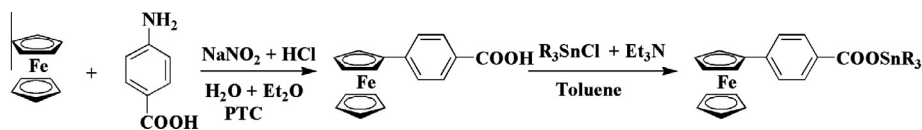
Ceramic oxides are fascinating materials with a wide range of functional properties due to their modified surface morphologies [1,2]. SnO₂ is an n-type semiconductor with a band gap, *E_g*, of 3.6 eV at 300 K [3]. It has found numerous applications in thermo-electric energy conversion [4], transistors [5], solar cells [6] and as a gas sensor [7–9] by virtue of its thermal stability, chemical durability, enhanced ability to adsorb oxygen and non-stoichiometric stable phases [10]. However, certain limitations have been observed for tin oxide gas sensors, e.g. cross sensitivity [11], reduced selectivity for reducing gases and high operation temperature for gas sensing [12]. These demerits may be fixed by modifying the adsorption surface sites of these sensors [13]. A superior gas sensing performance can be achieved by designing a sensitive layer with a complex composition [14,15] where the function of the receptors and the transducer are divided [16]. Metals having an electronegativity lower than Sn(IV) guarantee outstanding sensitivity when doped into tin oxide [9]. In recent years, tin oxide

doping with noble metals (Pd, Pt, Au) and other metals [8] (Fe, Co, Ni, Mn, Sb, Zn) has been extensively studied [17]. Iron oxides are found to be more appropriate for doping as they increase the adsorption site by reducing crystallite growth and also due to their solid solubility and stability [18]. Moreover, their valance band is also suitable for oxygen evolution. Thus the incorporation of Fe into SnO₂ reduces the amount of oxygen bonded to Sn, which in turn enhances the sensing ability of Sn [19]. These exceptional properties of iron oxides, coupled with a large surface to volume ratio of tin oxide, results in high selectivity and sensitivity in these composite materials [3]. In recent years, tin oxide doping with magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃) and hematite (α-Fe₂O₃) have been reported to manifest efficient gas sensing properties [20–23]. Gas sensors made from these composites have a lower operating temperature and sensitivity due to an enhanced surface to volume ratio [20–23].

Structural changes associated with doping mainly depend on the method of synthesis of these composite materials [24]. Therefore, iron doped tin oxides have been reported using different techniques, viz. pulsed laser pyrolysis deposition [25], the sol-gel technique [26,27], co-precipitation [25], ball milling [28], combustion [29], solvothermal reduction [30], atomic layer deposition [31] and R_f magnetron co-sputtering [32]. Aerosol-assisted chemical

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Scheme 1. Synthesis of organotin(IV)ferrocenylbenzoates, where PTC is Phase Transfer Catalyst, R is *n*-butyl for **A**₁ and phenyl for **A**₂.

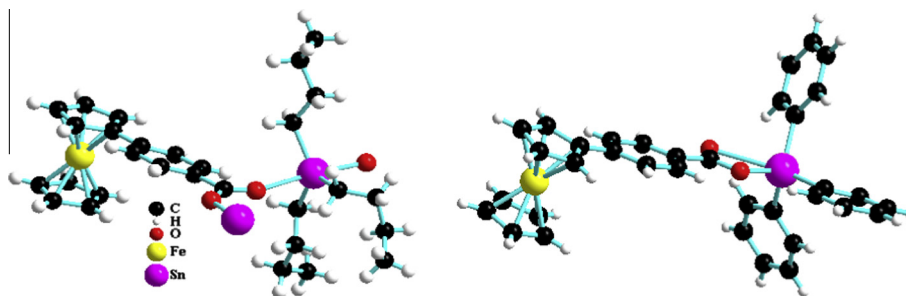


Fig. 1. molecular structure of **A**₁ (right) and the repeating unit structure of **A**₂ (left) with the color coding scheme. (Color online)

Table 1

Crystallographic data for compounds **A**₁ and **A**₂.

Crystal Parameters	A ₁	A ₂
Empirical formula	C ₂₉ H ₄₀ FeO ₂ Sn	C ₃₅ H ₂₈ FeO ₂ Sn
Formula weight	595.17	655.13
<i>T</i> (K)	100	100
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2(1)	<i>P</i> 2(1)
<i>a</i> (Å)	14.8099(10)	19.8715(17)
<i>b</i> (Å)	10.6510(7)	9.9001(8)
<i>c</i> (Å)	17.3791(12)	23.0622(19)
α (°)	90.00	90.00
β (°)	107.670(1)	112.522(2)
γ (°)	90.00	90.00
Cell volume	2612.1(3)	4191.0(6)
<i>D</i> _{calc} (g cm ⁻³)	1.513	1.558
Index ranges	-18 ≤ <i>h</i> ≤ 19 -14 ≤ <i>k</i> ≤ 13 -23 ≤ <i>l</i> ≤ 22	-23 ≤ <i>h</i> ≤ 23 -11 ≤ <i>k</i> ≤ 11 -27 ≤ <i>l</i> ≤ 27
<i>F</i> (000)	1224.0	1980.0
<i>Z</i>	4	6
<i>N</i> _{ref}	6832 [12978]	8184 [15405]
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0454, <i>wR</i> ₂ = 0.0853	<i>R</i> ₁ = 0.0750, <i>wR</i> ₂ = 0.1175
Goodness-of-fit	1.124	1.036
θ (°)	2.27–28.24	1.15–25.39

vapor deposition (AACVD), among different chemical vapor deposition techniques, is meticulous, effortless and quite flexible for the fabrication of multi-component oxides. It reduces the requirement for the precursor to be highly volatile. The usefulness of heterobimetallic coordination complexes as single source precursors for the formation of mixed-metal oxides thin films is relatively less explored [33–35].

Herein, we report the syntheses of two novel bimetallic precursor complexes, [(C₅H₅)₂Fe(C₅H₄)COOSn(C₄H₉)₃] (**A**₁) and [(C₅H₅)₂Fe(C₅H₄)COOSn(C₆H₅)₃] (**A**₂). These single source bimetallic complexes of organostannyl ferrocenyl benzoates were used in the fabrication of FeSnO_x composite thin films at different temperatures by using AACVD. Scanning electron microscopy (SEM) of the thin films showed spherical globules at both temperatures for both precursors, the average roughness of thin films being 2.48 and 3.41 nm, respectively.

2. Experimental

2.1. Materials and methods

All the operations were carried out under an inert atmosphere of nitrogen, unless otherwise stated. Tributyl tin chloride, triphenyl tin chloride, ferrocene, 4-aminobenzoic acid, sodium nitrite, triethylamine, hydrochloric acid and hexadecyltrimethylammonium chloride (CTAC) were purchased from Sigma Aldrich and were used without further purification. Organic solvents were purified prior to use by the literature method [36]. Elemental analysis was carried out with a CHNS/O Analyzer (Thermo Scientific Flash 2000 Organic elemental analyzer) and metal contents were determined by Fisons Horizon Inductively Coupled Plasma Optical emission spectroscopy (ICP-OES). IR spectra were recorded on an FT-IR Bio-RAD Merlin Varian Instrument (4000–200 cm⁻¹).

Single crystal X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer at 100(2) K using monochromatic Mo K α radiation. Data were reduced using SAINTPLUS28 and the structures were solved and refined with the SHELXTL29 suite. TGA was carried out using a Seiko SSC/S200 thermal analyzer at a heating rate of 10 °C /min under an N₂ gas flow. Powder X-ray diffraction (PXRD) measurements were carried out by means of a Bruker AXS D8 diffractometer using monochromatic Cu-K α radiation. The morphology of the films was determined with a FEG-SEM Philips XL30 electron microscope. The samples were carbon coated before observation of the surface morphology and the metallic ratio of the deposited films by EDAX-DX4. AFM analysis was performed using a Veeco CP2 instrument. A BRUKER AVANCE 400 MHz NMR spectrometer was used for recording multinuclear (¹H and ¹³C) NMR spectra.

2.2. Synthesis

2.2.1. 4-Ferrocenylbenzoic acid (**A**)

Compound (**A**) was synthesized using the reported method with some modifications [37]. 4-Aminobenzoic acid (14 g, 100 mmol), 160 mL of water and 24 mL of concentrated hydrochloric acid were mixed together and cooled to 0–5 °C using a salt water–ice bath. A solution of sodium nitrite (7 g, 100 mmol) in 50 mL of water was added dropwise under stirring. After complete addition, the solution was stirred for an additional 30 min and kept below 4 °C during this period. Ferrocene (9.5 g, 50 mmol) and 0.5 g CTAC were

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