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The Comparison of Characteristics in Tin Doped Indium Oxide (ITO) Synthesized via Nonaqueous Sol-Gel and Solvothermal Process

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Abstract— *Tin doped indium oxide nanoparticles were synthesized by nonaqueous sol-gel method and solvothermal process from indium acetylacetonate ($In(acac)_3$) and tin bis(acetylacetonate)dichloride ($Sn(acac)_2Cl_2$) in oleyamine as the starting materials. The structure and morphology of ITO samples were analyzed by XRD and TEM. The electrical conductivy and specific surface area of both ITO samples were also determined and compared to each other. The ITO prepared via solvothermal method showed better results that prepared by nonaqueous sol-gel method.*

Keywords— ITO, Tin doped Indium Oxide, nanoparticles, nonaqueous sol-gel, solvothermal.

I. INTRODUCTION

There is continuing interest in Tin-doped Indium oxide (ITO) for a variety of applications including liquid crystal displays, optoelectronic devices, heat reflecting mirrors, and sensors. [1-7] More recently, nanoparticles (NPs) made of ITO have been investigated as emerging materials for catalyst support in fuel cell applications due to high conductivity of indium oxide as well as its stable durability in acid at oxygen reduction reaction (ORR) relevant potentials. [8] In addition, the serious problems involved in reducing the Pt utilization such as carbon corrosion of the support substrate, [9] Pt sintering, [10] Pt dissolution [11] are also overcome by reason of combining Pt nanoparticles with the SnO_2. [12,13]

It is evident that for nanoparticle synthesis, in which size and shape have a crucial influence on the properties of the materials. Therefore, preparation of ITO powder with nano size, excellent dispersibility, high crystalline and homogenous shape is the key requirement to bring about the good characteristic of ITO materials include electrical conductivity and specific surface area. Metal oxides NPs can be synthesized by a variety of solution-based techniques such as coprecipitation, sol–gel chemistry, microemulsion, hydrothermal/solvothermal processing and template syntheses. Among them, the nonaqueous sol-gel method and the solvothermal method are particularly attractive routes which enables the formation of metal oxides at low temperatures and overcomes the aggregation of particles. [14]

In this manuscript, we report the solvothermal and sol-gel synthesis of ITO NPs from indium acetylacetonate ($In(acac)_3$) and tin bis(acetylacetonate)dichloride ($Sn(acac)_2Cl_2$) in oleyamine. The comparison of the structure and morphology of the materials in two methods is described. The conductivity and surface area of ITO Nps prepared by these methods are compared to each other.

II. MATERIALS AND METHOD

2.1. Materials

All reagents and solvents are commercially available and used without further purification . Indium(III) acetylacetonate (In(acac)3, 99,99%), oleyamine (70%) were purchased from Acros – Belgium. Tin(IV) bis(acetylacetonate)dichloride (98%) were purchased from Sigma – Aldrich. Ethanol (99,7%) were obtained from Xilong – China.

2.2. Preparation

2.2.1. Nonaqueous sol-gel synthesis process of ITO NPs

A total of 0.2699 g of $In(acac)_3$ and 0.026 g of ($Sn(acac)_2Cl_2$) were combined with 4 ml of oleyamine in a three-neck flask connected with a condenser. This solution was continuously stirred and heated at 235^oC for 3h in air. After the dark yellow suspension was produced, grey crystals were collected by centrifugation, washed many times with ethanol and dried at 80^oC for 24 h in air.

2.2.2. Solvothermal synthesis process of ITO NPs

The starting materials, 0.2699 g of $In(acac)_3$ and 0.026 g of ($Sn(acac)_2Cl_2$) were first dissolved in 4 ml of oleyamine under constantly magnetic stirring at 500 rpm for 1 hour. The mixtures were added to Teflon-lined stainless autoclave of 100 mL capacity, which was heated and maintained at 220^oC for 24 h, and then gradually cooled to room temperature. The resultant precipitate was collected by centrifugation, washed with ethanol for

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several times and dried at 80 °C for 12 h in air. The final ITO powders were blue.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns of ITO nanosupport-catalysts were obtained with XRD – D8 Advance – Bruker AXS (Germany) measurements using CuKa X-ray tube emitting at 1.54 Å. The data were collected from 20° to 80° in 2θ scale in step size of 0.03° with a scan rate of 2°. min-1.

Transmission electron microscopy (TEM) images were performed at 100 kV on a field-emission instrument of the type JEOL JEM-1010 with an ultrahigh resolution pole piece, providing a point resolution about 2 Å.

The specific surface area of the ITO nanoparticles was measured by multi-point Brunauer, Emmett and Teller adsorption (BET, Quantachrome Instruments Nova 2200e) with nitrogen gas at 77K.

Conductivity measurements were performed on ITO pellets (6 mm in diameter) prepared from about 120 mg of powder in an evacuated press under a pressure of 2 tons on Manual 12 Ton SpectroPress® instrument.

Resistance across the pellet was measured by a digital multimeter (manufactured by Faculty of Physics and Engineering Physics - University of Science HCM city) in a four-probe mode for eliminating the undesired resistance of the measuring circuit. The specific conductivity σ was calculated from the measured resistance R as $\sigma = \delta/RS$, where S is the electrode area and δ is the pellet thickness.

III. RESULTS AND DISCUSSION

The measured X-ray powder diffraction spectrum in the range of angles (2□) between 20° and 80° for the Tin doped indium oxides nanoparticles is presented in **Figure 1**. All diffraction peaks match the JCPDS 06-0416 database for the cubic bixbyite In_2O_3. No diffraction due to SnO_2 phases are observed, suggesting that Sn is incorporated into the In_2O_3 nanoparticles. The peaks of ITO2 NPs prepared via solvothermal method are stronger and narrower than that of ITO1 NPs prepared by sol-gel synthesis, indicating that the solvothermal method produces high crystalline materials. It has been found that Sn^{4+} doping induces the shifted peaks of ITO to the higher 2θ values comparing to pure In_2O_3 due to a smaller ionic radius of Sn^{4+}. The ITO2 NPs prepared via solvothermal method show this clearly than ITO1 NPs prepared by sol-gel route. The result suggests that the doping level of ITO2 NPs synthesized via solvothermal is better. In addition, the color of ITO products (Figure 2) have the following change: white as In_2O_3 NPs, gray as ITO1_solgel and blue as ITO2_solvothermal. This observation can be explained that the doping level of Sn into the structure of In_2O_3 NPs is higher, the free-electron concentrations are more, which influences the UV vis transmission spectra of ITO NPs. [15,16]

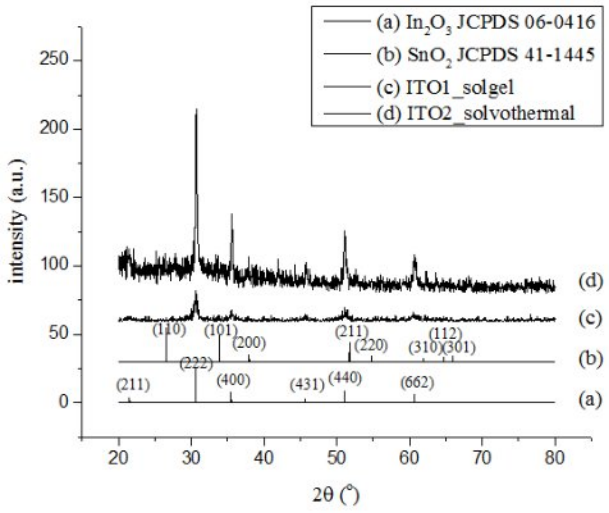

Fig.1: XRD patterns of tin-doped indium oxide (ITO) NPs with the different synthesis methods.

Fig. 2: The color of In_2O_3 sample (a), ITO1_solgel (b) and ITO_2_solvothermal (c).

TEM micrographs of ITO1 sample without using calcination process are presented in **Figure 3** shows the TEM images of ITO1_solgel and ITO2_solvothermal. Surprisingly, ITO1_solgel NPs are isolated as flowerlike clusters with size distribution in the range of 7 to 14 nm while ITO1_solvothermal NPs shows the spherical shapes and the high crystallinity of the particles with relatively uniform sizes of ca. 50 nm, in good agreement with XRD results determined by the Scherrer's formula. The morphology of ITO1 and ITO2 are completely different because the surface of ITO1_solgel is covered by organic ligand whereas the organic coverage is broken by solvothermal process. [17]

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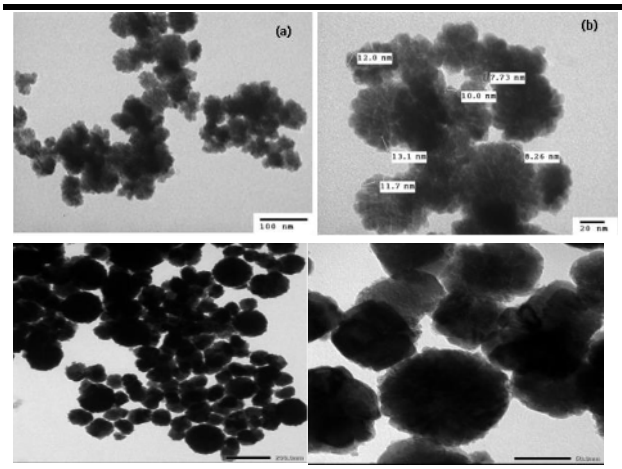

Fig.3: TEM micrographs of ITO samples: the overview of ITO1_solgel (a) and ITO2_solvothermal (c); the high resolution of ITO1_solgel (b) and ITO2_solvothermal (d).

Sample	EC (S/cm)	BET (m^2/g)
ITO1_solgel	0.089	63.568
ITO2_solvothermal	1.25	17.369

There were nearly four times as much the surface area value of ITO1_solgel (63.568 m^2/g) as that of ITO2_solvothermal (17.369 m^2/g). On the other hand, ITO2_solvothermal shows the higher electrical conductivity value than the other sample, respectively 1.25 S/cm and 0,089 S/cm. The results are consistent with good crystalline structure and high doping level of ITO2 prepared via solvothermal method. However, its surface area value is quite small because the particles size is relatively large.

IV. CONCLUSIONS

In summary, the ITO NPs have been successfully synthesized by both methods include sol-gel and solvothermal process. The solvothermal route show the properties such structure, shape, and electrical conductivity of ITO materials are superior to the sol-gel synthesis. However, the particles size is the major drawback of ITO NPs prepared via solvothermal method. The as-prepared ITO samples can be further investigated for noncarbon support of Pt in PEMFC.

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