Indium Tin Oxide Nanoparticles Formation for Organic Electronics
INDIUM TIN OXIDE NANOPARTICLES FORMATION FOR
ORGANIC ELECTRONICS

BY
HYEONGHWA YU, B.Sc.

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AUTHOR: Hyeonghwa Yu
B.Sc., (Opto-electric Display Engineering)
Hoseo University, Asan, South Korea

SUPERVISOR: Dr. Ayse Turak

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Abstract

Indium tin oxide is a transparent conductive oxide electrode which is widely used for organic electronics. Morphology of ITO plays an important role in the performance of organic electronics. To understand the influence of the substrate morphology in device performance, a controllable route for producing periodic and aperiodic roughness of ITO surfaces are necessary. In this thesis, this was attempted by using various approaches to forming ITO nanostructures. Initially, ITO was deposited by a traditional sputtering procedure. However, the roughness distribution of the sputtered ITO resulted in a Gaussian distribution, unsuitable to further studies of roughness. ITO nanostructures can also be formed by depositing ITO nanoparticles on an ITO substrates. Using acetate and chloride precursors, ITO films were produced from solution and formed into nanoparticles using the reverse micelles deposition approach. The acetate route (InAc+SnCl₂+ethanol), was the most successful prior to the nanoparticle formation, showing high quality ITO with bixbyte crystal structure and Sn percentages of 20%, low enough to form a conductive film. Nanoparticles were fabricated with diblock copolymer reverse micelles(PS-b-P2VP). Reverse micelles were found to act as a nano reactor, restricting the size of nanoparticles by having hydrophilic reactants undergo chemical reactions inside the micelles. However, nanoparticles from the reverse micelles revealed Sn percentages much above 20%. This was attributed to
the solubility difference of the precursors leading to displacing or preventing of precursor loading into the reverse micelles. The change of the stirring time, the micelles concentration, the sequence of precursors loading, and the weight of precursors were not found to affect the Sn concentration; moreover, large variations in Sn concentrations were observed. From quantitative nano mechanical testing of the micelles, a maximum load amount for the precursors was observed, confirming that the high concentration of Sn was likely due to the solubility differences between the precursors and their ability to penetrate the micelle. By manipulating the nanoparticles distribution through spin coating speeds, micelles concentration, and deposited volume, several degrees of order were obtained, though hexagonal packing was not observed. In general, even though Sn concentration were found to be above 20%, nanoparticles were successfully fabricated with reverse micelles, confirming that the reverse micelle technique is a good strategy for future studies of roughness.
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Organic electronics have emerged as a thin film device technology for next generation displays, solid state lighting, and photovoltaics. Organic light emitting diodes (OLEDs) are already used commercially in displays and significant development has been made in organic photovoltaics (OPVs). One of the advantages of organic devices is the low-cost mass production of large-area devices[1–4].

Using simple printing processes, current state-of-the-art organic devices are based on fully solution-processed polymer blends, using reel-to-reel(R2R) or ink-jet approaches for up-scaling to production-scale manufacturing lines[2–5]. Indium tin oxide (ITO) is widely used as the transparent conductive oxide electrode in most organic technologies. ITO films are mostly prepared by chemical vapor deposition[6]; thermal evaporation[7]; and direct current (DC) and radio frequency magnetron sputtering[8] which require expensive vacuum systems and high temperatures that are not compatible with reel-to-reel processes[3]. To effectively take advantage of ambient processing, non-vacuum approaches for electrode fabrication are highly desirable[3, 5]. Much progress has been achieved in recent years on producing ITO electrodes from
solution[9, 10]. These films, however, often result in higher resistivities and lower performances[11]. A simple approach to overcome these limitations is to use ITO nanoparticles[11]. However, the synthesis of colloidal ITO nanoparticles in solution is complicated. Research has focussed on controlling the size of nanoparticles by hydrothermal processes[12–14] mineralizers,[15], and stabilizers[16–18], but that they result in high polydispersity and broad size distributions[15]. In this thesis, we introduce a nano-sized ITO deposition method using diblock copolymers to control the size of the particles.

In organic devices, some challenges in stability and efficiency of organic devices remain. Many parameters can influence the performance of organic devices including the device architectures and choice of organic materials[19, 20]. Electrode morphology is a significant factor because the organic layers that act as injection and transportation layers are grown directly on the electrodes. This interface is modeled as being ideally flat; however, real electrodes always have non-homogeneous roughnesses. The surface morphology of the electrode is directly transferred to the organic layers; therefore, it is important to understand the correlation between the electrode morphology and the electrical and optical properties. Some researchers believe that the highly rough surface deteriorates device efficiency[21], whereas, others claim that the rough surface improves efficiency in some organic devices[22]. The main motivation for this project is to take advantage of the solution approaches to electrode formation and manipulate it in order to clarify the effects of electrode roughness on the performance of organic electronics.

In order to accomplish this goal, various approaches to producing ITO with controllable roughness were examined in this thesis. As a first step in examining such
effects, we introduce a nano-sized ITO deposition method using diblock copolymers to control the size of the particles, as referenced above. First, the fundamental principles of ITO, fabrication methods of ITO and possible significant benefits of rough ITO are demonstrated in Chapter 2. The experimental details and characterization are outlined in Chapter 3. In Chapter 4, sputtering, the most common approach to ITO, was examined, but found to result in Gaussian rough surfaces, with high sample to sample variability. To achieve controlled roughness, we then turned to solution approaches, covered in Chapter 5, and finally focussed on the technique of reverse micelle deposition to form 2D nanoparticle arrays, as described in Chapter 6. This technique, though promising, required in-depth examination of the stoichiometry of the resulting nanoparticles, detailed in Chapter 7. The novel approach of nanomechanical testing (Chapter 8), showed that the precursors are limited in their ability to load the micelles, yielding nanoparticles with higher than desired concentrations of Sn. However, the nanoparticles, independent of the stoichiometry, can be tuned to form various dispersions, as described in Chapter 9. In the conclusions and future work, in Chapter 10, the potential for the use of the ITO nanoparticles to further our understanding of roughness effects are examined.
Chapter 2

Background

2.1 ITO properties

In this study, we choose indium tin oxide (ITO) as a transparent conductive oxide (TCO) electrode. ITO is an n-type, wide band gap semiconductor with high free carrier density. It is widely used in most organic devices due to its high transparency in the visible range and high conductivity. ITO is formed by substituting tin to the indium oxide crystal lattice, such that, Sn replaces In$^{3+}$ positions and bonds with oxygen, yielding free electrons[23, 24]. These free electrons play a significant role in the conductivity of ITO. The formula of the compound is represented as $\text{In}_{(1-x)}\text{Sn}_x\text{O}_3$. It is well known that the physical properties of ITO films critical for their use in an organic device such as resistivity, carrier density, crystallinity, transmittance, and work function depend on the Sn concentration[24]. For resistivity, a critical Sn concentration exists. Initially, the addition of Sn decreases resistivity, but above 20% the resistivity begins to increase[24]. 5-20% Sn doping is typically used to achieve a resistance of about $10^{-4} \Omega \text{cm}^{-1}$[24–26]. This resistivity change can likely be tied
directly to the crystallinity. Figure 2.1 shows the X-ray diffraction profiles of ITO with varied Sn percentage. When ITO of below 20wt.% Sn concentration is annealed after deposition, the bixbyte In₂O₃ polycrystalline structure(Figure 2.2) is observed[24]. Therefore, to satisfy the conditions of a good TCO, ITO must contain less than 20% Sn.

2.2 Approach for ITO with controlled roughness

2.2.1 Growth techniques

Nano-structured surfaces can be produced by two approaches: “top-down” and “bottom-up”. A typical “top-down” approach is lithography, which has limited
resolution[28]. In comparison, the “bottom-up” approaches rely on self-organization to produce nano-scale patterns which can involve sputtering and chemical reactions.

ITO films can be prepared by chemical vapor deposition (CVD)[6], thermal evaporation[7], physical vapor deposition (PVD)[29], and sol-gel processes[9]. The choice of deposition methods result in films with different characteristics through the inherent controlling parameters.

**Sputtering method**

DC magnetron sputtering is the most extensively used method to fabricate ITO[8, 26]. During sputtering, a voltage is applied across argon (Ar) gas. Some electrons collide with the Ar to induce ionized gas ions, resulting in a glow discharge or plasma condition. When the glow discharge occurs, gas ions bombard the ITO target, scatter, and eject atoms from the ITO target material. Surface heating, atomic mixing and alternation of surface topography can occur[30]. The ejected ions travel through the vacuum to deposit on the glass substrate to grow a film. On the substrate, atoms
bind each other at the molecular level, and form layers. The gas ions have significant control over the properties of the deposited film. The kinetic energy of ions in particular is critical for the interaction with the substrate surface\[31\]. When the kinetic energy is less than $10^{-2}\text{eV}$, which is the thermal energy $K_B T$ at room temperature, condensation and chemisorption occurs\[31\]. In order to start the sputtering process, kinetic energy must be around at $10^4\text{eV}$, but thereafter, the ions are buried beneath the surface leading to low sputtering probability\[31\]. By tuning the gas pressure, it is possible to tune the atomic-scale roughness\[8\].

**Sol-gel process**

The fabrication methods of inorganic materials generally are high temperature/high vacuum procedures. An alternative approach for oxide materials is the sol-gel process, which is based on small molecule precursors and low temperature\[32\]. Sol-gel is a solution based chemical process forming a sol, or colloidal particles. This low cost process has high controllability. Moreover, the sol-gel process can produce particles of different sizes and morphology, such that the deposited film can have building units on the nano-scale. The precursors are usually metal alkoxides or metal chlorides, and the process involves two steps: hydrolysis reaction and condensation reaction. During the process, stabilizers, which are strong bases that reduce the metal cation, are used to control the size and shape of nanocrystals \[33\].

Nano-sized ITO has been synthesized using sol-gel processes; generally require heat treatment to promote crystallinity\[25, 29\]. The annealing temperature was found to be a key factor to adjust the size of the nanoparticles\[17, 34\]. Hong et al.\[34\] obtained ultra-fine sized particles with 5 nm diameter at low temperature annealing
of 300°C, and found increasing particle size with temperature, resulting in higher conductivity. Kim et al. [35] controlled the size by increasing from 3 to 21% Sn, leading to smaller particle size, but the lowest resistance was shown with 3-5% Sn. This suggests that the size of the crystallites is inversely proportional to the electrical property; therefore, the size of the particles crystalline should be optimized for better electrical property. Chen et al. [36] achieved sol-gel processed ITO film with a high transparency (90.2%), low resistivity ($7.2 \times 10^{-4} \Omega \text{cm}$), and low surface roughness (1.14 nm) which are comparable to that of ITO produced by sputtering.

### 2.2.2 ITO nanoparticles

One approach to produce roughness in a controlled way is by introducing nanoparticles on the electrode surface (Figure 2.3). The degree of roughness is described by two components: the height ($h$) of nanoparticles and the correlation length ($l$) between nanoparticles. The roughness is easily manipulated by the spacing ($l$) between ITO nanoparticles. If $h/l$ is around “1”, it denotes a very “rough” surface. By tuning the $h/l$, we can get the roughness of various degrees.

![Figure 2.3: Correlation between length and height of nanoparticle, a large rough surface $h/l_1$ and a small rough surface $h/l_2$](image-url)
Reverse micelles deposition

In order to use nanoparticles to control the roughness as described above, there needs to be a tunable method of achieving a 2D array of nanoparticles. One such method, relying on solution routes to producing compounds, is the reverse micelle deposition technique. Diblock copolymer reverse micelles have been widely used to synthesize nanosized metals and semiconductors\cite{37-45} since the first report on the reduction of platinum, palladium, rhodium, and indium metal salts\cite{46}. The inherent nature of diblock copolymer micelles is that they easily form self-assembled monolayers with 2-dimensional periodic arrays with a high degree of hexagonal order as shown in Figure 2.4\cite{42, 45}.

The micelles are synthesized from an amphiphilic diblock copolymer consisting of a hydrophilic and a hydrophobic block and form core-corona micelles spontaneously in selective solvents\cite{38, 42}. When the diblock copolymers are dissolved in a nonpolar solvent such as toluene, the hydrophobic tails form the outer block to shield the inner core hydrophilic heads; hence, spherical core-corona reverse micelles are formed (Figure 2.4). A commonly used diblock copolymer is polystyrene-b-poly(2-vinylpyridine) (PS-b-P2VP). In the reverse micelles system, PS forms the shell, and P2VP the core due to their relative polarity. As the hydrophilic P2VP block typically has high affinity for water, polar reagents can segregate inside the micelle and coordinate with the pyridine via metal-ligand with nitrogen or via ion exchange\cite{48}. These processes allow the control of the nano-scale chemical reaction and nanoparticle growth. The metal reagents chelation with the pyridine is verified with Fourier transform infrared spectroscopy or nuclear magnetic resonance by showing the changing of the pyridine peak\cite{49, 50}. Due to the addition of reagents, the micelles are swollen which can
Figure 2.4: Schematic of nanoparticles formation using reverse micelles (modified from [47]).
be measured by dynamic light scattering[41, 50]. The reagents inside of micelles will increase the stiffness of the micelles core, and the change of mechanical properties can be measured by atomic force spectroscopy[51]. The key advantages of this approach are that the reverse micelles strongly stabilize the nanoparticles in solution, without the use of conventional stabilizers[38] and, as the synthesis of nanoparticles is limited by the size of micelle, better control of the size distribution can be achieved. The nanoparticle loaded reverse micelles can be spin coated onto any substrate. Nanoparticle arrays are then formed after plasma etching with oxygen to remove the polymeric micelles by destroying the C-C bond[40, 43]. A simple schematic of nanoparticle formation inside the reverse micelles is illustrated in Figure 2.4. PS(x)-b-P2VP(y) is the typical nomenclature describing the diblock copolymer where x monomer units of PS are linked to y monomer units of P2VP. Although the diblock copolymer can form micelles or reverse micelles depending on the solvent, the PS block, x, must be larger than the P2VP block, y, to result in stable spherical micelles(x≥2y)[45].

One of the major benefits of the reverse micelle deposition approach is the high degree of control over the size and dispersion of the nanoparticles. There are many factors that control both the size and the spacing of the particles. As the micelles form a monolayer upon spin-coating, the dispersion of the nanoparticles is related to the diameter of the micelles. The diameters can be modified by changing the polymer properties[52] such as block ratio and polar weight, and by changing the solvent [53]. Stubenrauch et al.[52] proposed that the micelles size decreases with decreasing molar weight of the polymer by keeping the block ratio between the x and y. Krishnamoorthy et al.[53] showed that using the same polymer dissolved in different solvents such as toluene and xylenes, different size and periodicity were
obtained. In that study, micelles formed by dissolving polymer in toluene show hexagonal closely packed array with nanoparticles of 11 nm diameter and 72 nm spacing. On the other hand, the nanoparticles obtained from xylenes are bigger, with 18 nm to 40 nm diameter and 90 nm to 140 nm spacing[53]. The size of micelle can generally also be adjusted during the experimental process as size gas been found to be proportional to stirring times[41, 54], the amount of metal loading[41], and micelle concentration[54]. The size of the nanoparticles themselves can also be changed by controlling the amount of precursor loading into the micelles[42, 55], and by changing the diblock copolymer[42, 52, 55, 56]. The particle size has been seen to increase by increasing the amount of metal salt added to the solution[42, 55]. In addition, Bennett et al.[55] showed a saturation of nanoparticle size of after a critical amount of metal salts loading. Stubenrauch et al.[52] shows the influence of block ratio, when the molecular weight(Mw) was kept, on the size of micelle and core. The overall micelles size stays constant, whereas the core size decreases with increasing the block ratio of outer blocks (x) to inner blocks (y). As the core size can be reflected the nanoparticles size, the change of block ratio will influence the particle size. In a similar way described by Stubenrauch et al.[52], Cho et al.[56] showed that the nanoparticles diameter is proportionally decreased with decreasing the Mw of the copolymer while fixing the molar fraction of P2VP(\( f_{P2VP} \)). Changing of the different diblock copolymer influences on not only the size of particles but also the periodicity. The size and periodicity are related. Krishnamoorthy et al.[53] demonstrated a variation of the periodicity by changing polymer concentrations, and spin-coating rates. Increasing the polymer concentrations through dilution decreases the inter-particle distance; however, over-diluted leads to patchy coverage, and a non-homogeneous
distribution[53]. The periodicity also can be increased by increasing the spin coating rates[53]. Another way of changing the inter-particle distance is by simply adding the homopolymer that formed the outer shell in the reverse micelles[55]. By addition of homopolymer into the micelles solution, the area density was significantly decreased, though this leads to loss of packing regularity[55]. Generally, there are a variety of variables that can be modified to control the size and dispersion of nanoparticles using the reverse micelles approach.

### 2.3 Organic Electronics

The basic organic light emitting diodes (OLEDs) structure consists of a glass substrate, ITO as a transparent electrode, organic layers for light generation and transfer layers, and a metal as an electrode. In a similar manner, organic photovoltaics (OPVs) consists of a glass substrates, ITO as a transparent electrode, organic layers for light absorption and charge transport to produce electricity, and a metal as an electrode. OLEDs are characterized by current density-voltage-luminance (J-V-L), internal and external quantum efficiency, and luminescence measurements. OPVs are characterized by current-voltage (I-V), power efficiency, and external quantum efficiency.

The external quantum efficiency (EQE, $\eta_{ext}$) for OLEDs can be calculated by multiplying internal quantum efficiency (IQE, $\eta_{int}$) and out-coupling efficiency ($\eta_{out}$)

$$\eta_{ext} = \gamma \chi \eta_{r} \eta_{out} = \eta_{int} \eta_{out}$$

(2.1)

where $\gamma$ is the charge carrier balance factor, $\chi$ is exciton spin factor, and $\eta_{r}$ is
the efficiency of radiative decay. The charge balance factor, the exciton factor, and
the efficiency of radiative decay can be summarized as the IQE $\eta_{int}$. Specifically,
the charge balance factor, $\gamma$, is the fraction of the injected charge carriers that form
excitons. Under ideal conditions, all the holes and electrons will form excitons and $\gamma$
=1 under a uniform electric field. The exciton spin factor, $\chi$, explains the spin statistic
of the formed exciton. During electron-hole pair recombination, singlet and triplet
excitons are formed. The probability of forming a triplet exciton is statistically three
times higher than the probability of a singlet exciton. Thus, for fluorescence, the
maximum values is 0.25 due to singlet excitons, while a value of 1 is possible for
phosphorescence where both singlet and triplets contribute to emission. Another
factor influencing the emission is the efficiency of radiative decay, $\eta_r$, given by

$$\eta_r = \frac{\Gamma_r}{\Gamma_r + \Gamma_{nr}} = \frac{\text{number of emitted photons}}{\text{number of generated excitons}} \quad (2.2)$$

where $\Gamma_r$ and $\Gamma_{nr}$ define the radiative rate and non-radiative decay rate of excitons
respectively which can be raised from exciton energy transfer into quenching (thermal
energy). Theoretically, IQE can reach 100% under the assumption of balanced charge
injection and recombination, using a phosphorescent material for the emitter, and
suppressed non-radiation. However, there are limitations to achieving 100% out-
coupling efficiency[57–61].

Many organic molecules have a planar shape, which leads to an anisotropic elec-
tron density distribution. The anisotropic molecules consist of delocalized $\pi$ orbitals
perpendicular to the molecular plane. The orientation of anisotropic molecules re-
results from the strength of the interaction between the molecules and the electrode
surface[62, 63]. Organic molecules are held together by weak van der Waals forces
(\(\pi - \pi\) overlap). When the interaction is larger than the van der Waals force, the \(\pi\) orbital of the organic molecule couples with the \(d\) orbital in the electrode surface, causing a face-on orientation with their \(\pi\) plane stacking direction, perpendicular to the electrode surface (Figure 2.5(a)). In the other case, when the interaction is smaller than the van der Waals force, an edge-on orientation (\(\pi\) plane stacking direction parallel to the electrode surface) will be formed (Figure 2.5(b)). In organic electronics, ITO is widely used as a transparent electrode. When organic molecules are deposited on ITO, due to the oxide termination, organic molecules mostly have edge on orientation\[64, 65\].

### 2.4 Roughness effects on organic devices

Roughness at the electrodes has a number of effects on devices. For OLEDs, out-coupling efficiency \[66, 67\] and charge injection and transport properties\[68\] have been improved. For OPVs, the charge collection\[69, 70\] and power conversion efficiency\[71–73\] have been improved. For ITO, generally it is difficult to enhance the optical and electrical properties simultaneously since they are generally inversely proportional to each other. Yang et al.\[74\] recently demonstrated that nano-patterned ITO maintains
its electrical performance while increasing the incoming light absorption for organic photovoltaics.

### 2.4.1 Roughness effects on optical properties

![Diagram of light out-coupling and in-coupling losses](image)

Figure 2.6: Schematic of (a) light out-coupling loss in OLED: substrate mode, and wave guide mode. (b) light in-coupling loss in OPV: wave guide mode

The out-coupling efficiency is generally much lower than 100% as OLEDs are of a multilayer structure with different refractive indices. The refractive indices of the organic layers, ITO, and glass are \( n_{\text{org}} = 1.7-2.0 \), \( n_{\text{ITO}} = 1.8 \), and \( n_{\text{sub}} = 1.5 \), respectively.

When excitons are generated in the organic layer, the light will be out-coupled via the organic layers, ITO, and the glass substrate. However, some of the light will not out-couple from the devices but rather couple into some optical modes in the layers, resulting in a decrease in efficiency (Figure 2.6). The optical modes are the waveguide modes (WGM) in the substrate and the organic layer, and the surface plasmon mode. The waveguide mode occurs due to the difference in refractive indices causing total internal refraction (TIR) at the interface, and results in the largest loss to the emission.
of light. According to ray theory, the out-coupling efficiency can be analyzed easily by assuming only isotropic emission occurs and ignoring the microcavity effects, and scattering. Snell’s law should be obeyed at the interface between two materials of refractive indices $n_1$ and $n_2$ when light passes between the two different materials.

$$\frac{\sin \theta_1}{\sin \theta_2} = \frac{n_2}{n_1}$$ (2.3)

Since the critical angle is the angle of incidence at which the TIR occurs, it occurs when the transmitted angle reaches $\theta_2 = 90^\circ$. The value of $\theta_1$ is equal to the critical angle($\theta_c$) which is given by Snell’s law,

$$\theta_c = \sin^{-1}\left(\frac{1}{n_s}\right) \approx \frac{1}{n_s}$$ (2.4)

when the generated light in the semiconductor reaches an air interface, and the refractive index of semiconductor is denoted by $n_s$. Using the spherical polar coordinate system, the area of the escape cone that is described by the portion of the area of sphere of radius $r$ and critical angle $\theta_c$ is

$$A = \int dA = \int_0^{\theta_c} \int_0^{2\pi} \sin \theta \ d\theta d\phi = 2\pi r^2 (1 - \cos \theta_c)$$ (2.5)

The out-coupling efficiency $\eta_{out}$ is the ratio of the fraction of the sphere that light can escape and the total area

$$\eta_{out} = 1 - \cos \theta_{c_1} \approx \frac{1}{2n_{org}^2}$$ (2.6)

The fraction of light trapped in the substrate and in the ITO layers is[75]
where $\theta_{c1}$ is the critical angle at the air-organic interface given by $\sin^{-1}(n_{\text{air}}/n_{\text{org}})$ and $\theta_{c2}$ is the critical angle at the substrate-organic interface given by $\sin^{-1}(n_{\text{sub}}/n_{\text{org}})$. Light emitted at angles less than $\theta_{c1}$ will escape from the devices. Light emitted at an angle between $\theta_{c1} < \theta < \theta_{c2}$ is trapped in the substrate (substrate mode). Finally, light emitted at angles larger than $\theta_{c2}$ is trapped in the ITO/organic layers (waveguide mode). If the refractive indices are substituted into the above equations, the calculated efficiency will be 18%, 34%, and 48% for the light out-coupling, the trapped light in the substrate, and the trapped light the ITO/organic layers in OLEDs (Figure 2.6). Although 100% IQE is obtained, the maximum EQE can only be theoretically 18%. For a fluorescent emitter, it can be as low as 4.5% due to the reduced exciton spin factor ($\chi=0.25$)[61].

In a similar way to OLEDs, the in-coupling efficiency for OPVs can be calculated. There will be light loss due to the different refractive indices. Similarly, the refractive indices of glass and ITO are $n_{\text{sub}}=1.5$, $n_{\text{ITO}}=1.8$. For organic layers, the first organic layer grown on the ITO has a refractive index of $n_{\text{org}}=1.4$. Due to the organic layer, WGM appears in ITO later, leading to 63% light loss. Therefore, only 37% of light can reach the organic layer to form an electron-hole pair.

A periodically roughened electrode can eliminate TIR and allow more light to escape or enter the device (Figure 2.7 (b) and (d)). Due to the nanoparticles, although the critical angles at each layer are the same for flat and patterned samples, the
The molecular orientation also has an impact on the optical properties. Fluorescence anisotropy is polarized emission based on photoselective excitation[80].

When a photon(polarized light) is absorbed, the oscillating electric field of the incoming wave interacts with the transition dipole moment caused by the electronic
state of the molecules. For planar organic molecules with high aspect ratios (i.e. with one predominating long axis), the transition dipole moment tends to lie parallel along the long molecule axis. In such a case, the transition probability from a ground state to an excited state is $\cos^2(\theta)$, where $\theta$ is the angle between the direction of the absorption transition dipole moment and the electric vector of the excitation [79, 80]. Molecules preferentially absorb photons that have an electric vector parallel to the absorption transition dipole. Similarly, polarized emission occurs along an axis of the molecules (or direction of the emission transition moment).

Usually, when organic molecules are grown on the electrode with edge-on orientation ($\pi$ plane stacking direction parallel to the electrode surface), light is emitted toward the edge of the organic layers (Figure 2.8(a)). As described in Figure 2.9, roughness can be a route to changing molecular orientation during organic film growth. If face-on
orientation (π plane stacking direction normal to the electrode surface) is introduced, more light can be refracted toward the electrode or the glass substrate.

2.4.2 Roughness effects on electrical properties

![Electric field distribution](image)

Figure 2.10: Electric field distribution (a) on a smooth ITO surface and (b) on a rough ITO surface

Organic devices consist of organic semiconductor layers sandwiched between two electrodes. Ideally, surface charge accumulates as voltage is applied to the device, generating a uniform electric field in the organic layers as shown in Figure 2.10(a). The uniform electrostatic potential for the ideal flat interface is proportional to the distance from the electrode surface. However, if there is a rough surface, the electric field is concentrated on the points, which results in an additional electrostatic potential [22, 81]. Thus, electric potentials are heterogeneous, with a strong electric field at the summits, and a weak electric field at the valleys. This can lead to charge
separation of electron-hole pairs[22, 81] which has an impact on the charge balance. Additionally, this charge separation may be a benefit for OPVs[22, 69], which require free polarons separated from excitons to form a current, and destructive for OLEDs,[22] which rely on the radiative decay of excitons to emit light.

Another expected impact of anode roughness is the changing of organic molecular orientation[82]. If face-on orientation is introduced on ITO, it can improve the charge transport by easier charge movement through \(\pi - \pi\) overlap (Figure 2.5 (b))[65, 83, 84]. Figure 2.9 shows an example of how face on orientation can be achieved on edge of nanoparticles. Peisert et al.[62] illustrated that face on orientation of the molecules in organic devices decreases the energy barrier at the metal organic interface, leading to enhanced charge injection and charge transport [83, 85, 86]. This results in an increase of short circuit current and fill factor for OPVs[83, 84], and reduced driving voltage and improved operational stability for OLEDs[87, 88].
Chapter 3

Experiment

3.1 Materials

An indium tin oxide ceramic disc (the ratio $\text{In}_2\text{O}_3$ to $\text{SnO}_2$ is 90 : 10 wt.%, Alfa Aesar) was used as a target material for sputtering. Indium acetate ($\text{InAc}$, $\text{In(CH}_3\text{OOO)}_3$), indium chloride ($\text{InCl}_3$), stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), stannic chloride ($\text{SnCl}_4 \cdot x\text{H}_2\text{O}$), triethylamine ($\text{TEA}$, $N(\text{CH}_2\text{CH}_3)_3$), monoaminoethanol ($\text{MEA}$, $\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$) and 2-butanol were purchased from Alpha Aesar and used as received as precursors for sol-gel formation. Ethanol ($\text{C}_2\text{H}_5\text{OH}$), toluene($\text{C}_7\text{H}_8$), tetrahydrofuran($\text{THF}$, $\text{C}_4\text{H}_8\text{O}$) and hexane($\text{C}_6\text{H}_{14}$) were purchased from CALEDON and used as received. Polystyrene(48,000)-block-poly(2-vinylpyridine)(70,000) (PS-b-P2VP) polymer was purchased from Polymer Source Inc. and fritted to use in the reverse micelles deposition approach.
3.2 Indium Tin Oxide formation

3.2.1 Sputtered Indium Tin Oxide film

DC magnetron sputtering was performed in a sputtering system (NRC - 3116 vacuum coater), shown in Figure 3.1, with a base pressure of about $10^{-5}$ Torr. The vacuum chamber is equipped with a water cooled electrode (target holder), gas ports, and thermo couples. A substrate holder is located horizontally parallel to and vertically above 15 cm from the electrode. It also has a heater, and a thermo couple to measure the substrate temperature. The ITO target was pre-sputtered for 10 mins to eliminate the surface oxide layer before every sample deposition trial. In order to produce ITO film with high quality, several parameters such as argon pressure (15 - 20 mTorr), sputtering power (100 W) and deposition time (5-15 mins) were varied. After deposition, some samples were annealed at 350°C in a nitrogen flowing furnace; others were deposited with substrate temperatures held above 300°C to achieve high crystallinity.[25, 29]

3.2.2 Indium Tin Oxide synthesis in solution process

ITO sol-gel films were synthesized using recipes from Seki et al. [10] for the acetate route and Devi et al. [18] for the chloride route, as detailed below. The ITO solution was synthesized with both indium and tin precursors dissolved in alcoholic solvents under inert gas (N$_2$) environment using a glove bag (Aldrich Atmos Bag) due to reaction between water and chloride precursors. Reactions were performed in 10 mL flip top vial (Fisherbrand, GmbH, snap-on lid bottle) cleaned in acetone and ethanol using the ultrasonic cleaner, following the standard cleaning procedure.
Solutions were left stirring on a magnetic stirrer at 500 rpm during synthesis, unless stated otherwise.

**Acetate route**

0.30 mL of monoaminoethanol (MEA) (determined by the molar ratio of InAc and MEA at 1:4) was poured in a 3.00 mL of vial of ethanol. Seki et al. [10] suggest 6.4 % Sn in ITO, therefore the amount of material chosen was 300 mg of InAc and 15.8 mg of SnCl$_2$. The solution was stirred for 30mins. The final transparent solution is ready for deposition or further processing.

**Chloride route**

Devi et al. [18] suggest 15% Sn in ITO, therefore the amount of 0.34 g of InCl$_3$ and 0.09 g of SnCl$_4$ were added to 4.00 mL of 2-butanol. After 20mins, 0.79 mL of triethylamine (TEA) was added to the solution under stirring resulting in immediate
precipitation. After an additional 20mins of stirring, the solution was centrifuged (Eppendorf 5804) at 15000rpm for 3mins. The solution was pipetted off and the precipitated emulsion was collected by a spatula to put into a new vial. Acetone was added into the collected emulsion and stirred until the mixture turned to an emulsion. The final solution was again centrifuged at 15000rpm for 3mins and the precipitated emulsion was collected. The final emulsion was dried in the ambient environment for 1hr.

### 3.2.3 Indium Tin Oxide nanoparticle synthesis in PS-b-P2VP

To achieve the calculated stoichiometric ratio from the sol-gel approach described above, the amounts for various reagents were fixed at 0.03 g of In salt (InAc or InCl$_3$), 1.85 mg of SnCl$_2$ and 0.30 mL of ethanol for the acetates route or 8.39 mg of SnCl$_4$ and 0.43 mL of 2-butanol for the chloride route. Further experiments to tune the In/Sn ratio in the final nanoparticles used different stoichiometric ratios, stirring times and dilutions as discussed in chapter 7.

**Polymer fritting**

Prior to dissolving in toluene, the diblock copolymer PS-b-P2VP was fritted to remove undesirable oxidation. Twice the volume of tetrahydrofuran (THF) relative to a polymer was added in a polymer (PS-b-P2VP) containing vial. The vial was sonicated for 30mins until all the polymer was dissolved. The solution (polymer dissolved in THF) was filtered using glass fiber and precipitated into 200 mL of hexane stirred at 500rpm. The hexane solution was vacuum filtered using a “fine” pore size filter funnel (Figure 3.2 Right). The filtered precipitation was dried overnight in the
ambient environment. The dried powder was used to form the reverse micelles as described below.

![Image](hexane_setup.png)

**Figure 3.2**: Left: picture of a set up for precipitation in hexane. Right: picture of filtering though the filter funnel

**Reverse micelles formation**

10 mL vial (Fisherbrand, GmbH, snap-on lid bottle) was cleaned in sequential ultra sonic baths of 30 mins each of acetone and ethanol. After cleaning with solvents, the vial was dried with N\textsubscript{2}. To achieve reverse micelles formation above the critical micelles concentration (3 g L\textsuperscript{-1}), 15 mg of PS-b-P2VP was dissolved in 5 mL of toluene and stirred for 18hrs. The size of reverse micelles in solution were determined by dynamic light scattering using Zetasizer Nano (Malvern) and confirmed by atomic force microscopy (Nano Scope IIIa, Veeco) after dynamic spin coating onto Si substrates, as described in Chapter 3.3 and Chapter 3.4.

In order to form nanoparticles of ITO, each of the reagents were added sequentially
to the micelle solution and kept under magnetic stirring at 1500 rpm for 2 days for each reagent. In between each addition of reagent, the solutions were decanted into Eppendorf tubes and centrifuged for 8 mins at 15000 rpm to remove unloaded salts. The supernatant solution from the tubes were pipetted back into the original vial, which had been rinsed with toluene. The typical sequence followed In salts (2 days stirring), Sn salts (2 days stirring) and alcohol (2 days stirring) before post processing as described in 3.3. A similar procedure was followed with fully formed ITO nanoparticles in place of the initial reagent, as described in Chapter 6.

3.3 Post processing

3.3.1 Coating on substrate

The substrates used were glass, silicon, and ITO. Prior to use, all substrates were cleaned in an ultrasonic bath of 30 minutes each of acetone and ethanol sequentially. After cleaning with solvents, all substrates were dried with N\textsubscript{2}. The solutions were then coated on to the substrates using spin coating or drop casting approaches. For spin coating, 3 µL-5 µL of micellar solution was dynamically spin coated on substrates for 45s, using a Laurell Technologies Spin coater(WS-650MZ-23NPP). The spin coating rate was varied from 2000 to 4000 rpm. To change the dispersion and achieve mono-layered micelles coating, the 3 g L\textsuperscript{-1} micellar solution was diluted with toluene to 2 g L\textsuperscript{-1}. For drop casting, 3 µL-5 µL of micellar solution was pipetted and cast directly onto substrates. The toluene residues on the substrates were left to evaporate in the ambient environment.
3.3.2 Plasma etching

The specimens were plasma treated under oxygen to remove the polymeric micelles and leave ITO particles on the substrates with Harrick Plasma cleaner (PDC-001-HP) or Thierry Zepto Plasma System. Etching condition for either systems was set as 29.6 W power, 5 mbar \( \text{O}_2 \) gas pressure, and 30 sccm \( \text{O}_2 \) gas flow rate for 90mins.

3.3.3 Post annealing

After plasma etching, the specimens were heat treated using a Lindberg tube furnace at 600\( ^\circ \)C for 1 hr in flowing nitrogen. Specimens were kept on an alumina boat which was pushed into the middle of the furnace tube. For the furnace tube, a standard mullite tube (2 inch outer diameter, and 36inch length purchased from Cole-Pamer) was used. We designed and had added glass tubing parts at both ends in order to flow nitrogen gas during heating(Figure 3.3).

![Figure 3.3: Left: picture of a furnace set up with a mullite tube. Right up: picture of a glass tubing for gas outlet. Right down: picture of a glass tubing for gas inlet](image-url)
3.4 Analysis technique

3.4.1 Atomic Force Microscope (AFM)

Two different AFMs were used to examine the samples depending on the purpose. To examine the surface morphology, a Nano Scope IIIa, Veeco was employed in tapping mode. The silicon tips used had a resonance frequency of 300 (200-400) kHz or 150 (170-210) kHz, and a force constant of 42-45 Nm.

AFM characterization for mechanical properties was performed using Bioscope Catalyst, Bruker in Peak Force QNM in Air mode with a silicon tip with a resonance frequency of 150 (170 to 210) kHz, and a force constant of 45 (30 to 76 N m$^{-1}$). The AFM images were processed with WSxM, Nano Tec[89] and NanoScope Analysis, Bruker.

3.4.2 Dynamic Light Scattering (DLS)

Zetasizer Nano, Malvern Instruments Ltd. were used for DLS measurement. A quartz cuvette should be used because quartz cells are not affected by a toluene solution. The detector used Non-Invasive Backscattering (NIBS) optics with scattering angle 173°, and a He-Ne laser (4.0 mW) used as a light source with wavelength 633 nm. Reference values for polystyrene (refractive index = 1.59) which makes up the corona of micelle was used for the optical parameter, and the micelles solution (0.54 cP) value was used to account for the viscosity value of dispersion[90].
3.4.3 Ellipsometer

Optical measurements were performed by a VASE ellipsometer (J.A. Woollam Co., Inc.) and a single wave length ellipsometer (Philips). VASE ellipsometer measured thickness and refractive indices at different angles (45° to 75°) at 643.8 nm. Single wave length ellipsometer was used to plot 3D maps of the surface using the refractive index and thickness determined from VASE.

3.4.4 Fourier Transform Infra-red Spectroscopy (FTIR)

Fourier transform infra-red spectroscopy was performed in a VERTEX 80/80v FT-IR spectrometers, Bruker, equipped with MIR source, KBr beam splitter, and a DLaTGS detector in transmittance mode at room temperature. FTIR requires a set of a cuvette to contain the micelles solutions with KBr windows which can be used in the range of 800 cm$^{-1}$ to 2000 cm$^{-1}$.

3.4.5 Scanning Electron Microscopy(SEM)

Scanning electron microscope (SEM, JEOL JSM-7000F) images were taken using a field emission gun at 3.0 keV. Non-conductive surfaces were pre-coated with carbon to be conductive.

3.4.6 X-ray Spectroscopy (XPS)

X-ray photoelectron spectroscopy was performed on a Thermo K-alpha x-ray photoelectron spectrometer at Koç University and PHI Quantera II Scanning XPS Microprobe at McMaster University. Both XPS were equipped with a monochromatic Al
Kα source(1476.7 eV). The samples were characterized by a hemispherical analyzer using 50 eV pass energy, with a nominal analysis area of 400 cm². All spectra were corrected for charging using adventitious C at 284.8 eV. The atomic concentrations of the elements were determined from In3d, Sn3d, O1s, and Si2p core level peak areas. Data analysis was performed using the software Thermo Avantage. A main analysis of the data will be the quantitative analysis by measuring the peak intensities and areas of each peak. As x-ray beams are sensitive to the atomic number, we need relative sensitivity factor (RSF) to scale the measured peak areas; therefore, the variations in the peak areas can represent the amount of material in the sample surface. The areas of the curves were obtained by peak fitting function. This process defined the best fit for the peak shaped by Gaussian-Lorentzian function with smart background subtraction. With the intensity and RSF, the relative concentrations of the elements can be obtained. The atomic percentage, $C_x$ can be expressed by[91]

$$C_x = \frac{n_x}{\sum n_i} = \frac{I_x/S_x}{\sum I_i/S_i}$$  \hspace{1cm} (3.1)

where $n$ is the the number of atoms of the element, $I$ is relative peak area of photoelectrons from element, and $S$ is the RSF of the element.

### 3.4.7 X-ray Diffraction (XRD)

X-ray diffraction measurements were performed in a Bruker Smart 6000 2D area detector with a Rigaku Cu-Kα rotating anode source(50 eV, 90 mA) and a cross-coupled parallel beam ($\lambda = 0.1543$ nm). The detector distance was calibrated to 16.740 cm. The chi($\chi$) degree is fixed at 54.804°, and 2 theta($\theta$) is in the range of 20° to 80° 2 theta($\theta$). Data analysis was performed using the softwares DIFFRAC.SUIT
Figure 3.4: 2D frame of XRD result with converted 1D intensity: $2\theta$ from 29° to 55° and $\gamma$ from 75° to 105°

EVA and TOPAS. The results from the measurement shows 2D frame data. In order to analyze the 2D data, this should to be converted into 1D intensity scan by Chi integrating of data as shown in Figure 3.4. Chi integration is the summation of counts within the defined $2\theta$ steps ($\Delta 2\theta$) and $\gamma$ values as described in Figure 3.4. The end results will be intensity counts as a function $2\theta$. $\gamma$ integration is explained as

$$ I (2\theta) = \int_{\gamma_1}^{\gamma_2} J (2\theta, \gamma) \, d\gamma \quad 2\theta_1 \leq 2\theta \leq 2\theta_2 \tag{3.2} $$

where $J (2\theta, \gamma)$ is the 2D intensity in the 2D frame and $I (2\theta)$ is integrated intensity as a function of $2\theta$. For phase analysis, the experimental data was compared to the references obtained from Inorganic Crystal Structure Database (ICSD).
Chapter 4

Sputtered ITO film

4.1 Introduction

DC magnetron sputtering deposition has been commonly used for large area and mass production of ITO\cite{8}. Therefore, our first attempt was to control the roughness by growing ITO films on glass. As described in Chapter 3.2.1, DC sputtering was performed in a dedicated chamber equipped with an ITO sputtering target.

<table>
<thead>
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<th></th>
<th>Vacuum (Torr)</th>
<th>DC power (W)</th>
<th>Ar gas (mTorr)</th>
<th>Deposition temp. (°C)</th>
<th>Deposition time (min)</th>
<th>Post-annealing Temp. (°C)</th>
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<td>10</td>
<td>350</td>
<td>30</td>
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<tr>
<td>5</td>
<td>2.80 × 10^{-5}</td>
<td>100</td>
<td>20</td>
<td>292</td>
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<tr>
<td>6</td>
<td>1.40 × 10^{-5}</td>
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<td>20</td>
<td>305</td>
<td>5</td>
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<td>-</td>
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<tr>
<td>7</td>
<td>1.20 × 10^{-5}</td>
<td>100</td>
<td>20</td>
<td>301</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
4.2 Results

A number of parameters were varied to try to obtain high quality transparent ITO films on glass substrates using DC sputtering. By tuning the Ar gas pressure, sputtering power, and deposition time, as summarized in Table 4.1, we attempted to obtain crystalline films of 10% Sn, 150 nm thickness and 1 nm to 20 nm roughness according to the literatures [93, 94]. Initially, though the films looked adequate visually, samples grown without deliberate substrate heating showed open circuit, using a multi-meter, indicating no conductivity. As described in Chapter 2.1, this is likely due to the amorphous crystal structure of as-deposited films. Previous studies of sputter deposited ITO films [24] have shown that post-deposition annealing can yield highly crystalline, and therefore conductive, films for ITO with less than 20% Sn.

Thus, these samples required a post-annealing process to obtain crystallinity and high conductivity. Although conductivity of the sputtered ITO films was observed after a furnace annealing using a Lindberg tube furnace at 300 °C for 1hr (confirmed using the multi-meter), cracks in the glass substrates are observed with post-annealing as seen in Figure 4.1(a). Since Latz et al. [26] achieved crystallinity by deposition at
high substrate temperature, we tried to deposit ITO at high substrate temperatures rather than post annealing to prevent cracking on the glass substrates. This resulted in conductive ITO films without cracks, as shown in figure 4.1 (b).

Figure 4.2: (a) a thickness contour plot of ITO14, (b) a 3D surface plot of ITO14, (c) a thickness contour plot of ITO15, and (d) a 3D surface plots of ITO15. Cross-hatched regions represent areas where the sample holder potentially blocked the deposition, and were excluded from the average thickness calculations.

The 3D surface images and contours of thickness are obtained from single wave length ellipsometry of two selected samples (ITO14 and ITO15) deposited at high
Table 4.2: Average thickness and roughness of ITO thin films (14-15) obtained with similar deposition parameters

<table>
<thead>
<tr>
<th></th>
<th>Ellipsometry</th>
<th>AFM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thickness (nm)</td>
<td>Refractive index (n) at 632.8nm</td>
</tr>
<tr>
<td>ITO14</td>
<td>143.3 ± 0.6</td>
<td>1.80</td>
</tr>
<tr>
<td>ITO15</td>
<td>137.2 ± 0.5</td>
<td>1.80</td>
</tr>
</tbody>
</table>

temperature without post annealing (Figure 4.2 (a)-(d)) to confirm the surface thickness uniformity. The film thickness summarized in Table 4.2 was determined by averaging the measured values from the 2D map of the surface. As the high and low peaks at right and left edge were located near the sample holders in the sputtering chamber, those parts were ignored in calculating the thickness (as shown by the cross-hatched areas in Figure 4.3). As can be seen in Figure 4.2, uniform ITO films can be obtained (ITO14); however, the second attempted sample (ITO15) with similar parameters had different thickness and uniformity (Figure 4.2). This suggests a high degree of sample variation from similar deposition parameters. Such large sample to sample variation, as well as the non-uniformity on the surface, indicate that sputtering may not have the level of accuracy required to study roughness effects on devices. Detailed roughness of ITO14 was analyzed by AFM and SEM. From the SEM image, we determined that the ITO film consists of approximately 25 nm to 35 nm nano-sized grains. Figure 4.3 (a) and (b) show ITO AFM morphology images, and height distribution, respectively. The micrograph indicates that the surface of these samples have nano-sized grains with measurable average height around 13 nm. Additionally, the height distribution can be well described by a Gaussian distribution, indicating a randomly rough surface[95]. For the purposes of this project, random roughness is not desirable. It will be difficult to correlate the influence the roughness with the electrical and optical properties, as would be possible for a uniform periodic array, as
Figure 4.3: (a) AFM micrograph of ITO14 (b) height distribution histogram (c)SEM image of ITO14 described in Chapter 2.4.

4.3 Summary

Sputtering was initially chosen to produce ITO films with different roughness as it has been commonly used to grow ITO films. We optimized the sputtering parameters to produce highly crystalline, conductive and transparent ITO films. Though we successfully fabricated rough ITO films, ellipsometry maps demonstrate large sample
variation with inconsistent results; moreover, AFM micrographs confirmed a Gaussian
distributed rough surface. As a result, the sputtering technique was determined to
be unsuitable to control roughness for ITO films for this project.
Chapter 5

Solution processed ITO film

5.1 Introduction

Previously, we fabricated ITO film from sputtering which produced Gaussian distributed grains. For a more controllable approach to roughness, we examined routes to achieving nano-scale and crystalline ITO films from solution process approaches, which exist in the literature. Before discussing the method to control the roughness using nanoparticles, solution processed ITO films are demonstrated in this chapter.

5.2 Experimental

ITO films are synthesized from colloidal ITO in solution produced by two different routes: one based on an acetate precursor[10] and one based on a chloride salt[18].
Acetate route ITO

The simple reaction of InAc, SnCl₂, and ethanol was demonstrated by Seki et al. [10] in an aqueous environment. The reaction is described in equation 5.1. To achieve crystalline film, the molar ratio of SnCl₂·2H₂O to (In(CH₃OOO)₃+SnCl₂·2H₂O) was chosen, as described in Chapter 3.2.2, to achieve Sn doping 0.06(6%) Sn. The details of the volumes and stirring protocols are given in chapter 3.2.2. During the reaction, SnCl₂ was directly soluble in ethanol while monoaminoethanol (MEA) was needed to increase the decomposition of InAc.

\[
\text{In(CH}_3\text{OOO)}_3 + \text{SnCl}_2\cdot 2\text{H}_2\text{O} + \text{NH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{C}_2\text{H}_5\text{OH} \\
\rightarrow \text{In}_{(1-x)}\text{Sn}_x(\text{OH})_3 - \text{heat treatment} \rightarrow \text{In}_{(1-x)}\text{Sn}_x\text{O}_3
\]

Chloride route ITO

The chloride route uses InCl₃, SnCl₄, and 2-butanol as precursors as described by Devi et al.[18] The molar ratio of SnCl₄·×H₂O to (InCl₃+SnCl₄·×H₂O) was chosen to achieve Sn doping of 0.15(15%) Sn, using the volumes described in Chapter 3.2.2. Triethylamine(TEA) is used as a stabilizer which optimizes the pH values of the solution to control the size of nanoparticles[16]. The reaction is illustrated in equation 5.2.
InCl$_3$ + SnCl$_4$ \cdot xH$_2$O + N(CH$_2$CH$_3$)$_3$ + C$_4$H$_{10}$O

\rightarrow In_{1-x}Sn_x(OH)_3 \quad \text{heat treatment} \quad \rightarrow In_{(1-x)}Sn_xO_3

(5.2)

All specimens from both the acetate route and the chloride require heat treatment (600 °C), as described in Chapter 3.3.3, to reduce the hydroxide(In$_{(1-x)}$Sn$_x$O$_3$) to oxide and promote crystallization [34, 97]. As described in Chapter 3.2, the acetate route results in a hydroxide loaded transparent solution. 3 g L$^{-1}$ to 5 g L$^{-1}$ ITO solution of the acetate route was spin coated on the 1 × 1 cm$^2$ Si substrates for further characterizations. The solution was spin coated at 2,000rpm for 45s (Laurell Technologies). Prior to use, all substrates were cleaned in an ultrasonic bath of 30 minutes each of acetone and ethanol sequentially and then dried with N$_2$. As described in Chapter 3.2, the end result of the chloride route is an insoluble powder. After calcination, this powder was used for further characterizations without substrates.

The characterization of the ITO film from solution was evaluated using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), as described in Chapter 3.4.6 and Chapter 3.4.7.
5.3 Examination of ITO film

5.3.1 Acetate route ITO

To confirm the formation of ITO, XPS (Figure 5.1(a)) and XRD (Figure 5.3(a)) was performed. Survey scan consisted of peaks that could be assigned to In3d and O1s from the ITO film, and Si2s and Si2p from the substrate. A small amount of adventitious C was also visible. Even though Sn3d is not visible in the survey scan, high resolution core level scans do show the presence of Sn3d (Figure 5.2(b)). Since a thin film of ITO was deposited on a Si substrate, survey scan shows weak peaks from the ITO film and large peaks from the Si substrate. All core level peaks were curve fitted. The In3d_{5/2} peak binding energy (BE) of 445.15 eV and Sn3d_{5/2} peak BE of 487.24 eV are assigned to indium tin oxide (ITO) [98–100]. The ratio of Sn3d to (In3d + Sn3d) is 0.21 (21 %). The XPS spectra in O1s region is located at 532.35 eV and is assigned to O1s from SiO₂ [101]. Due to the strong peak from the Si substrates as discussed from survey scan, O1s peak expected at 530 eV in ITO [98–100] is overshadowed by O1s in SiO₂. Moreover, the Si2p core level in Figure 5.2
Figure 5.2: The acetate route XPS results of (a) In3d (b) Sn3d (c) O1s and (d) Si2p

(d) shows contributions from atomic Si and SiO₂ [27, 102]. The ratio of O1s (SiO₂) to Si2p (SiO₂) is 2.3, supporting the idea that the O1s peak can be assigned completely to SiO₂. The XRD patterns (Figure 5.3 (a)) shows good agreement with the standard data of crystalline ITO (ICSD #50849) which also confirms the formation of crystalline ITO.

Table 5.1: Atomic percentages of Sn in ITO

<table>
<thead>
<tr>
<th></th>
<th>Sn/(In+Sn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac route</td>
<td>0.213</td>
</tr>
<tr>
<td>Cl route</td>
<td>0.359</td>
</tr>
</tbody>
</table>
Figure 5.3: XRD results for (a) the acetate route ITO solution and (b) the chloride route ITO powder (blue) compared to reference SnO$_2$ (red) and ITO (black), and the experimental data refined to ITO (orange)

5.3.2 Chloride route ITO

Survey scan of the chloride routes are shown in Figure 5.1 (b) with In3d, Sn3d, O1s, C1s, N1s and Cl2p easily identified. As in the case for the InAc route, the In3d 3/2 peak BE of 445.41 eV and Sn3d 3/2 peak BE of 486.99 eV are assigned to indium tin oxide (ITO)[98–100]. The ratio of Sn3d to (In3d + Sn3d) is 0.35 (35 %). Additionally, due to the absence of the Si substrate, we were able to observe in the O1s core level a peak assigned to lattice oxygen in the crystalline ITO[99]. Although we were successful in identifying ITO, there was significant contamination in these samples. As seen in Figure 5.4(c), the O1s scan also had a significant component at 531.73 eV, assigned to oxygen double bonded carbon (C=O)[99]. All core level peaks were curve fitted. The C1s scan (Figure 5.4 (d)) was resolved into two regions, 284.8 eV and 286.5 eV, assigned to carbon contamination (C-C) and oxygen or nitrogen single-bonded carbon (C-O or C-N), respectively[99]. As N1s was also found at 400.60 eV, the C1s contamination at 286.48 eV is assigned to an amide group (RCONH$_2$) formed by reaction of TEA with oxygen contamination[99]. As discussed in Chapter 3, the
reaction was performed under an inert gas\((N_2)\) environment inside a glove bag. However, the glove bag has a limitation to reduce oxygen and moisture contamination levels below \(2\%\) (10000 ppm) which is 1000 times higher than the oxygen levels required for chemical synthesis \((\leq 10\text{ppm})[103]\). The Cl2p peak visible in the survey scan is likely a result of unreacted InCl\(_3\). Hong et al.[34] observed that solutions including InCl\(_3\) require high temperature heat treatment above 600\(^\circ\text{C}\) to completely remove the chloride. As Devi et al.[18] used 400\(^\circ\text{C}\) to 600\(^\circ\text{C}\) to obtain crystallized ITO, we only annealed our powder at 600\(^\circ\text{C}\). Though we did not subsequently check with higher temperature annealing, it is likely that this can explain the presence of
Cl$_2$p in the survey scan as the residue from InCl$_3$. From the XPS data, the chloride route seems to require heat treatment above 600 °C to remove unwanted Cl, and an undesirable reaction seems to have occurred between the stabilizer and oxygen contamination.

In Figure 5.3 (b), the XRD pattern of the ITO powder from the chloride route shows only two diffraction peaks between 32° and 55° 2θ. The experimental diffraction pattern was compared to both ITO(ICSD #50849) and SnO$_2$(ICSD #84576) diffraction patterns, which are the possible outcomes from the chemical reaction. Though the peaks are broad, suggesting very small crystallites, they do not coincide with SnO$_2$. This suggests that the experimental diffraction pattern results from ITO. The orange line in 5.3 (2), extracted from a refinement of the data, does appear consistent with ITO with peak at 2θ= 32° corresponding the (222) plane and the one at 55° to a convolution of (400) and (622) planes.

5.4 Summary

ITO was synthesized by sol-gel processes as a preliminary step to verify the formation of ITO from solution. Two routes from the literature were attempted: the acetate route and the chloride route. XPS and XRD data illustrate that the acetate route can successfully form crystalline ITO, while the chloride route contains residues from the precursors and stabilizer, and limited crystallinity. Even though the chloride route seems unfavourable, we initially attempted to apply both routes for nanoparticle formation.
Chapter 6

Formation of ITO nanoparticles using micelles

Published in modified form Can. J. Phys. 2014, 5, 1-5[50]

6.1 Introduction

Another approach for controlled roughness is to use ITO nanoparticles. In this chapter, we introduce a nano-scaled ITO deposition method from the recipes from the previous chapter, using diblock copolymers to control the size of the particles. ITO nanoparticles can be synthesized by using micelles deposition in a manner similar to other nanoparticles[40, 41]. Diblock copolymers are known to form core-corona micelles spontaneously in selective solvents[38, 42]. The hydrophilic block typically has high affinity to coordinate with metal reactants allowing control of nanoscale chemical reactions and nanoparticle growth. A key advantage of such a technique is that the micelles strongly stabilize the nanoparticles in solution, limiting the need
for conventional stabilizers[38]. In this chapter, the best approach for forming the nanoparticles is examined, as shown in Figure 6.1: one where the pre-formed ITO is introduced into the micelles (nano-stabilizer) and another where the micelles are used as the nano-scale vessel for the reaction to occur (nano-reactor).

6.2 Experimental

Polystyrene-block-poly-2-vinylpyridine (PS-b-P2VP) diblock copolymer was dissolved in toluene and kept under vigorous stirring for 18 hours. Pre-formed ITO is produced from the two routes, as described in Chapter 3 and Chapter 5. Indium acetate, stannous chloride and ethanol were used for the acetate route following the approach of Seki et al. [10]. Indium chloride, stannic chloride and 2-butanol were used for the chloride route, following the approach of Devi et al [18].

For the first approach using micelles, prepared ITO solution loaded micelles, a measured amount of the prepared ITO solution was dissolved in the toluene based micelle solution. For the chloride route, ITO solution (emulsion form) was precipitated to ITO powder by centrifuging and dried. The ITO powder was dissolved in
2-butanol first to encourage segregation into the micelles. The solution was stirred for 48 h and centrifuged to remove undissolved particles before spin coating on silicon substrates.

For the second approach, indium salts, tin salts and alcohol are sequentially loaded in the toluene based micelle solution. To ensure that the salts were fully loaded, the solution was stirred for 48 h between addition of each reactant. Unloaded salts were removed by centrifuging, before adding the next reactants. After a final stir of all reactants, the solution was spin coated onto silicon substrates. Toluene was allowed to evaporate during coating.

The specimens were plasma treated under oxygen to remove the polymeric micelles and leave ITO particles on the substrates. The ITO layer was then annealed at 600 °C for 1 hour in flowing nitrogen. The micelles and nanoaprticles were analyzed as described in Chapter 3.4. Briefly, the diameter of micelles in suspension was confirmed using dynamic light scattering. To validate the formation of the particles inside of the micelles, Fourier transform infrared spectroscopy was performed. The size of ITO nanoparticles was analyzed using atomic force microscopy in tapping mode.

### 6.3 Precursor loaded micelles

The micelles were used in two ways to produce nanoparticles of ITO: (1) as a nano-stabilizer, with a pre-formed ITO solution and (2) as a nano-reactor where the reagents were added sequentially. The method of reverse micelle deposition relies on the formation of core-corona reverse micelles. In such a system, a diblock copolymer consisting of a hydrophilic block and a hydrophobic block are dissolved in a non-polar
solvent, such as toluene. In our system, the hydrophobic polystyrene block forms the outer block and the hydrophilic 2-vinylpyridine (2VP) is the inner block.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Water solubility (g L$^{-1}$) at 25°C</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin chloride</td>
<td>2698</td>
<td>[104]</td>
</tr>
<tr>
<td>Indium chloride</td>
<td>467</td>
<td>[104]</td>
</tr>
<tr>
<td>indium acetate</td>
<td>65</td>
<td>see Chapter 7</td>
</tr>
<tr>
<td>2-butanol</td>
<td>125</td>
<td>[105]</td>
</tr>
<tr>
<td>ethanol</td>
<td>miscible</td>
<td>[105]</td>
</tr>
<tr>
<td>indium tin oxide power</td>
<td>insoluble</td>
<td>[106]</td>
</tr>
</tbody>
</table>

### 6.3.1 Reverse micelles as nano-stabilizer

In the nano-stabilizer system, pre-formed ITO solution was loaded into the micelles solution. The oxide itself is insoluble in water (as shown in Table 6.1), suggesting that it will not preferentially segregate into the micelles. This was readily observed, especially in the chloride route, where the pre-formed powder had to be dissolved in 2-butanol to prevent direct precipitation when added to the micelles solution. Although the alcohol has a solubility of $\sim 125$ g L$^{-1}$ (Table 6.1), the similarity of the FTIR spectrum (Figure 6.2(a) and (c)) before and after loading suggests that the hydrophobic oxide preferred the toluene solution. Upon loading with the preformed ITO nanoparticles from either route, no change in FTIR spectrum can be observed, suggesting no interaction. Figure 6.2(c) shows some change at 1450 cm$^{-1}$ probably resulting from the interaction of the excess alcohol and P2VP in the chloride route. As can be seen in DLS images (Figure 6.3), ITO solutions did not load into the reverse micelles, supporting the FTIR results. Two peaks are visible in the spectrum, one corresponding to the empty micelles, likely at the smaller size and the other to the ITO particles in suspension. This is also readily understood if the water solubility...
Figure 6.2: FTIR results for empty and loaded micelles (a) the acetate route ITO solution loaded micelles (b) the acetate route salts loaded micelles (c) the chloride route ITO solution loaded micelles (d) the chloride route salts loaded micelles

is taken as a sign of hydrophilicity: the ITO particles would be hydrophobic and remain in the toluene. After removing the polymeric micelles, deposition was tracked using AFM. Figure 6.4 (a) and (d), for the ITO solution loaded micelles, show bare Si substrates, without any evidence of nanoparticles or ITO films. In addition, resistivity measurements from a multi-meter show open circuit in both cases. Analysis of FTIR, DLS, and AFM suggests that the micelles do not act as nano-stabilizers.
6.3.2 Reverse micelles as nano-reactor

Typically, when indium and tin salts are loaded into micelles, one would expect metal acetate and chloride ligation with the P2VP through nitrogen-metal coupling\[41, 42\]. Kaleli et al. [107] suggest that the filled metal $d$ ($d_{xz}$ or $d_{yz}$) orbital gives electrons to the empty $p$ orbital, introducing $\pi$ back bonding. The normalized FTIR transmittance spectrums of pristine and reactants loaded micelles are given in Figure 6.2. The peak in the range of 1400 cm$^{-1}$ to 1600 cm$^{-1}$ corresponds
to the pyridine stretching mode. The absorption band in the range of 1500 cm$^{-1}$ to 1800 cm$^{-1}$ is assigned to the C-C bonding and C=C bond stretching of the aromatic ring in both pyridine and styrene[107, 108]. With loading of InCl$_3$ and SnCl$_4$, changes can be observed in the pyridine stretch mode, with a broadening of the peak and increasing intensity around 1450 cm$^{-1}$ to 1475 cm$^{-1}$ (6.2(d)). This suggests that there was indeed some ligation with the pyridine. With loading of the 2-butanol, the peak shape and intensities resemble that of the original micelles. In this case, 2-butanol was added to the micelle solution, fully reacting with the In and Sn compounds and likely not interacting strongly with the P2VP. For the acetate route precursors (indium acetate, tin chloride and ethanol), however, very little change was observed in the FTIR spectrum, implying no ligation. Even if there is no reaction with the micelle ligands, due to the hydrophilic nature of the inner block, the reactants are all expected to preferentially segregate inside the micelle. This is supported by the DLS measurements (Figure 6.3). The in-situ formation approach shows that the size of micelles from unloaded to fully reactant loaded micelles increased from about 75 nm (empty micelles) to 88 nm for the acetate route and to 93 nm for the chloride route from DLS (Figure 6.3). Again, the hydrophilicity can explain this effect, as all the reagents are hydrophilic. Although the precursors are all hydrophilic, they are not equally likely to infiltrate the micelles. Nanoparticles produced from both routes show signals (Figure 6.5) from In3d$^{3/2}$ (BE of 445.28 eV and 445.37 eV for the acetate and chlorides routes respectively) and Sn3d $^{3/2}$ and BE of 487.08 eV and 487.22 eV for the acetate and chloride routes respectively which can be assigned to indium tin oxide(ITO)[98–100]. The tin concentrations of ITO nanoparticles, however, are high, 74% and 97%, respectively for the two precursor routes (Table 6.2). This can
be explained by assuming that the hydrophilicity of the reactants can be estimated through the water solubility (Table 6.1). As the solubility of tin chloride is so much higher than the other precursors, the concentration of Sn in the micelle core should be expected to be higher than that predicted by the stoichiometry. Sn, due to this higher infiltration into the micelles, could be expected to form more PS-b-P2VP-Sn complexes with the pyridine. These results suggest that the resultant nanoparticles are unlikely to be crystalline or conductive, as they have much higher Sn doping than the 20% needed for successful ITO for electrodes.

Figure 6.4: AFM image of ITO nanoparticles after heat treatment (a) the acetate route ITO solution loaded micelles (b) acetate route salts loaded micelles (c) particle size histogram for Fig. 4(b) (d) the chloride route ITO solution loaded micelles (d)
Figure 6.5: XPS image of ITO nanoparticles from the nano-reactor route (a) In3d and (b) Sn3d from the acetate route and the chloride route

Table 6.2: Atomic percentages of Sn in ITO from the nano-reactor route

<table>
<thead>
<tr>
<th></th>
<th>Sn/(In+Sn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac route</td>
<td>0.74</td>
</tr>
<tr>
<td>Cl route</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The in-situ reaction (Figure 6.4 (b) and (e)) shows a complete film of nanoparticles. Both routes show complete coverage of the surface. The particle size distributions were determined by randomly selecting particles in the AFM images. More than 100 particles were analyzed to obtain a statistical representation of the entire population of the particles[109]. Gaussian distribution functions were fitted to eliminate unexpected small and large particles to obtain precise statistical values. By limiting the reaction region to within the micelles, a mean size of (9.32 ± 2.90) nm, (11.35 ± 3.50) nm are achieved for the acetate and chloride routes respectively. Polydispersity indices (relative standard deviation from AFM height histograms) of 0.3 were achieved for both routes. As a small polydispersity with similar particle sizes
were consistently achieved, the results in Figure 6.4 can be considered as representative of particles produced by this method. The Gaussian distributions show ultra fine size particles similar to ITO nanoparticles from the hot injection approach[14]. The particles were more mono-disperse and smaller than most other solution approaches to ITO nanoparticles[9, 13].

6.4 Summary

ITO nanoparticles were deposited on silicon using diblock reverse micelles (PS-b-P2VP). We attempted two routes, the acetate route and the chloride route, from two approaches: ITO solutions loaded into micelles and ITO synthesized within the micelles. DLS images and FTIR spectrums reveal that only in-situ formation of nanoparticles within the micelles shows incorporation with pyridine and completely migrated reactants, forming nanoparticles. By using this approach, uniform ultra fine size nanoparticles are achieved, without the additives common to other approaches. Even though FTIR, DLS, and AFM indicate formation of nanoparticles, Sn concentration in the nanoparticles for the acetate route and the chloride route are 74% and 97%, respectively. The XPS results indicate that the nanoparticles are unlikely to be crystalline or conductive, as they are much higher than 20% Sn doping needed for successful ITO sol-gel film. Previously, in Chapter 5, XPS and XRD results indicate that only the acetate route successfully can produce ITO. From the study in this chapter, it appears that nanoparticle synthesis process is also likely to be most successful using the acetate route with the nano-reactor approach. However, using the stoichiometric ratios suggested in the literature failed to produce crystalline ITO nanoparticles due to the high tin concentration.
Chapter 7

Optimize ITO composition

7.1 Introduction

As demonstrated in previous chapters, ITO produced from the acetate solution route has a successful In to Sn ratio (23%) and crystallinity for high electrical conductivity needed for a successful electrode. However, when the reaction was performed inside of micelles, XPS experiments reveal higher Sn concentration ($\geq 25\%$), resulting in an amorphous phase.

Polystyrene-block-poly-2-vinylpyridine (PS-b-P2VP) diblock copolymer forms reverse micelles in a non-polar solvent. The hydrophilic nature of the inner block has high affinity to coordinate with reactants that have high water solubility. As stannous chloride ($\text{SnCl}_2$) has higher water solubility than indium acetate (Table 6.1), it is likely that Sn is able to penetrate into the micelles with greater ease than In. Due to the solubility differences, the amount of reagent put into the solution for the solution processed ITO should be modified in the nanoparticles formation in order to achieve the desired stoichiometry in the nanoparticles. In this chapter, several parameters
were changed with the aim of increasing the penetration of indium acetate (InAc) to optimize the ITO composition: the micelles size, micelle solution concentration, and stoichiometry. Additionally, the reproducibility of the formation of ITO nanoparticle stoichiometry was examined.

### 7.2 Experimental

Polystyrene-block-poly-2-vinylpyridine (PS-b-P2VP) diblock copolymer was dissolved in toluene and kept under vigorous stirring as described in Chapter 3. InAc, SnCl₂ and ethanol were used for the acetate route following the approach of Seki et al.[10]. The reference sample (np1.1) was synthesized using the parameters in Chapter 6. Table 7.1 shows the detailed list of parameter modifications attempted: the np1 sample set shows the different stirring times of the solution, the np2 sample set shows different micelles concentrations, the np3 sample set shows different orders of salts loading, and np4 sample set shows different amount of InAc loading.

<table>
<thead>
<tr>
<th>Name</th>
<th>micelles concentration (g L⁻¹)</th>
<th>micelles stirring time (days)</th>
<th>InAc weight (mg)</th>
<th>InAc stirring time (days)</th>
<th>SnCl₂ weight (mg)</th>
<th>SnCl₂ stirring time (days)</th>
<th>Ethanol volume (mL)</th>
<th>Ethanol stirring time (days)</th>
<th>sequence</th>
</tr>
</thead>
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<td>1(18hr)</td>
<td>30</td>
<td>2</td>
<td>1.8</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>SnCl₂ → InAc → ethanol</td>
</tr>
<tr>
<td>np1.2</td>
<td>3</td>
<td>4</td>
<td>30</td>
<td>2</td>
<td>1.8</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>SnCl₂ → InAc → ethanol</td>
</tr>
<tr>
<td>np1.3</td>
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<td>SnCl₂ → InAc → ethanol</td>
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<td>np1.4</td>
<td>3</td>
<td>1</td>
<td>30</td>
<td>4</td>
<td>1.8</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>SnCl₂ → InAc → ethanol</td>
</tr>
<tr>
<td>np1.5</td>
<td>3</td>
<td>1</td>
<td>30</td>
<td>4</td>
<td>1.8</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>SnCl₂ → InAc → ethanol</td>
</tr>
<tr>
<td>np1.6</td>
<td>3</td>
<td>1</td>
<td>150</td>
<td>2</td>
<td>0.8</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>InAc → SnCl₂ → ethanol</td>
</tr>
<tr>
<td>np1.7</td>
<td>3</td>
<td>1</td>
<td>150</td>
<td>2</td>
<td>0.9</td>
<td>1</td>
<td>0.4</td>
<td>2</td>
<td>InAc → SnCl₂ → ethanol</td>
</tr>
<tr>
<td>np2.1</td>
<td>3</td>
<td>1</td>
<td>150</td>
<td>2</td>
<td>0.9</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>InAc → SnCl₂ → ethanol</td>
</tr>
<tr>
<td>np2.2</td>
<td>4</td>
<td>1</td>
<td>150</td>
<td>2</td>
<td>0.9</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>InAc → SnCl₂ → ethanol</td>
</tr>
<tr>
<td>np3.1</td>
<td>3</td>
<td>1</td>
<td>15</td>
<td>2</td>
<td>0.9</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>SnCl₂ → InAc → ethanol</td>
</tr>
<tr>
<td>np3.2</td>
<td>3</td>
<td>1</td>
<td>15</td>
<td>2</td>
<td>0.9</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>SnCl₂ → InAc → ethanol</td>
</tr>
<tr>
<td>np3.3</td>
<td>3</td>
<td>1</td>
<td>15</td>
<td>2</td>
<td>0.9</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>InAc &amp; SnCl₂ → ethanol</td>
</tr>
<tr>
<td>np3.4</td>
<td>3</td>
<td>1</td>
<td>15</td>
<td>2</td>
<td>0.9</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>ethanol → InAc → SnCl₂</td>
</tr>
<tr>
<td>np4.1</td>
<td>3</td>
<td>1</td>
<td>30</td>
<td>2</td>
<td>1.8</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>SnCl₂ → InAc → ethanol</td>
</tr>
<tr>
<td>np4.2</td>
<td>3</td>
<td>1</td>
<td>150</td>
<td>2</td>
<td>1.8</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>SnCl₂ → InAc → ethanol</td>
</tr>
<tr>
<td>np4.3</td>
<td>3</td>
<td>1</td>
<td>300</td>
<td>2</td>
<td>1.8</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>SnCl₂ → InAc → ethanol</td>
</tr>
<tr>
<td>np4.4</td>
<td>3</td>
<td>1</td>
<td>510</td>
<td>2</td>
<td>1.8</td>
<td>2</td>
<td>0.4</td>
<td>2</td>
<td>SnCl₂ → InAc → ethanol</td>
</tr>
</tbody>
</table>
All specimens were plasma treated under oxygen to remove the polymeric micelles and leave ITO particles on the substrates. The ITO layer was then annealed at 600 °C for 1 hour in flowing nitrogen. To confirm the ITO composition, X-ray photoelectron spectroscopy (XPS) was performed. The size of ITO nanoparticles was analyzed using atomic force microscopy (AFM), as described earlier in Chapter 3.3 and Chapter 3.4. The structures of the samples were analyzed with grazing incidence x-ray diffraction with 0.5° incidence angle and the sample was exposed to x-ray for 6hr.

**Solubility test**

Solubilities of InAc in selective solvents of water, toluene, and ethanol were estimated by a student in Dr. Turak’s Group, as there are no values reported in the literature. 500 mL of solvents were prepared and kept under stirring. Small amount of InAc was continuously added to the solvent until the salts could not be dissolved at room temperature. All experiments were performed twice with each solvent. The solubilities of InAc in solvents are listed in Table 7.2. For the purpose of our estimation, insoluble means 0.1 mg could not be dissolved in the 500 mL of solvent. From table 6.1, it can be seen that InAc is much less soluble than tin chloride. Due to the polar nature of micelles core, a precursor that has a higher water solubility would tend to penetrate inside micelles more readily. This can explain the high tin concentrations observed in the nanoparticles compared to those from the sol-gel directly.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility (g L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>65</td>
</tr>
<tr>
<td>Toluene</td>
<td>insoluble</td>
</tr>
<tr>
<td>Ethanol</td>
<td>insoluble</td>
</tr>
</tbody>
</table>
7.3 Method for optimization

7.3.1 Increase the micelles size

When centrifuging the InAc loaded micelles solution, precipitated InAc was left in the Eppendorf tube. One assumption was that if the size of micelles were enlarged, the particle size might increase due to the higher affinity of the micelle core to the salt[41, 54]. According to El-Atwani et al.[41], stirring the micelles solution should increase the size of the micelles. In our study, we stirred the empty micelles solution for 1 and 4 days. Figure 7.1 shows AFM images of empty micelles, stirred for different lengths of time. The size distributions were determined by randomly selected micelles in the AFM images, as described in Chapter 6. Approximately 40 particles were selected to obtain a statistical representation of the entire population of particles.
distribution function was fitted to the resulting histogram to acquire the mean and standard deviations. From Figure 7.1, for micelles stirred for 1 day the mean sizes and polydispersity indices are $\langle 72.00 \pm 10.60 \rangle$ nm and 0.14 respectively. For micelles stirred for 4 days the mean sizes and polydispersity indices are $\langle 75.00 \pm 8.22 \rangle$ nm and 0.10, respectively. The size difference between 1 day and 4 days stirring is within the error range; consequently, the stirring time does not appear to have an effect on the size of micelles.

The micelles size was also analyzed after InAc was loaded, and the micelles solution
was stirred for 2, 4 and 7 days. The AFM images were analyzed in a manner similar to that for the micelles stirring time. Mean sizes of (62.00 ± 6.09) nm, (64.00 ± 6.83) nm, and (63.00 ± 6.07) nm were achieved for 2, 4, and 7 days of stirring time respectively after InAc loading. Polydispersity indices of 0.09 (2 days), 0.10 (4 days), and 0.09 (7 days) were obtained. This suggests that the stirring time of InAc loading does not change the size of micelles. From our examination of stirring times, no significant increase of micelles size was observed.

![AFM topography images of the empty micelles.](image)  
**Figure 7.3**: Right panel: AFM topography images of the empty micelles. Left panel: micelles size distribution (a) np2.1: the solution from 3 g L\(^{-1}\) (b) np2.2: the solution from 4 g L\(^{-1}\)

In the typical protocol to synthesize the micelles solution, 3 g L\(^{-1}\) micelle concentration was obtained from 15 mg of polymer dissolved in 5 mL of toluene\[90\]. For our next set of experiments, the assumption was that if the micelles concentration is increased, the size of micelles would increase\[54\]. For comparison, 4 g L\(^{-1}\) concentration was synthesized from 40 mg of polymer dissolved in 10 mL of toluene, and analyzed by AFM and XPS. Figure 7.3 shows AFM topography images of the empty micelles and
size distributions with fitted Gaussian distribution function. The mean sizes of $3 \text{ g L}^{-1}$ and $4 \text{ g L}^{-1}$ were obtained as $(66.00 \pm 6.20) \text{ nm}$, and $(72.00 \pm 5.74) \text{ nm}$, respectively. The size distributions show that larger size of micelles were observed from $4 \text{ g L}^{-1}$ compared to $3 \text{ g L}^{-1}$ although they are in the same distribution range of error. The nanoparticles produced from these $4 \text{ g L}^{-1}$ high concentration micelle solution were revealed by XPS to contain above 90% Sn. This suggests that the increase of micelles size grants more SnCl$_2$ penetration by replacing the InAc rather than increasing the penetration of InAc.

**7.3.2 Sequence of precursor loading**

Given the results from the micelles size test, we speculate that due to the high water solubility of SnCl$_2$, SnCl$_2$ might penetrate the micelles by displacing the loaded InAc out of the micelles. We studied the different order of precursors loading to confirm the solubility effect on the salt loading. For the reference sample, the sequence of salts loading was InAc, SnCl$_2$, and ethanol, and three difference sequences of loading were implemented (Table 7.3).

<table>
<thead>
<tr>
<th>sample</th>
<th>1st loading</th>
<th>2nd loading</th>
<th>3rd loading</th>
<th>Sn percentage(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>np3.1</td>
<td>InAc</td>
<td>SnCl$_2$</td>
<td>ethanol</td>
<td>68</td>
</tr>
<tr>
<td>np3.2</td>
<td>SnCl$_2$</td>
<td>InAc</td>
<td>ethanol</td>
<td>100</td>
</tr>
<tr>
<td>np3.3</td>
<td>InAc and SnCl$_2$ simultaneously</td>
<td>ethanol</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>np3.4</td>
<td>Ethanol</td>
<td>InAc</td>
<td>SnCl$_2$</td>
<td>100</td>
</tr>
</tbody>
</table>

As can be seen in Table 7.3, when SnCl$_2$ was loaded prior to the InAc, no In was observed in the nanoparticles by XPS. This supports the speculation that due to the higher solubility of SnCl$_2$ to InAc, SnCl$_2$ may displace InAc in the loaded micelles.
For the np 3.3 sample, when InAc and SnCl\(_2\) precursors were loaded simultaneously, both InAc and SnCl\(_2\) tended to segregate into micelles a similar amount as to when they were loaded sequentially (68% vs 63%). Nevertheless, the high solubility salt has more chance to be inside of the micelles, leading to the high Sn percentage (63%). The ethanol first loaded sample (np3.4) has no In element, showing pure SnO\(_2\) in XPS measurement. Based on the solubility experiments in Chapter 7.2, InAc is immiscible in ethanol, while SnCl\(_2\) is highly soluble in ethanol. Filling the micelles with ethanol may prevent the penetration of InAc, and only allow SnCl\(_2\) to dissolve to produce SnO\(_2\). Due to the polar nature of micelles core, a precursor that has a higher water solubility tends to penetrate inside micelles more readily. According to the sequence of precursors loading experiment, due to the solubility difference, SnCl\(_2\) displaces InAc if it is loaded or prohibits InAc from loading. Thus, InAc penetration should be increased to reduce the Sn percentage.

### 7.3.3 Reduce Sn component

The micelles size tests and sequence of loading tests suggests that SnCl\(_2\) has increased penetration, likely replacing the InAc. Previously, we had kept all of the precursors under stirring for 2 days each to ensure full loading. We tried to decrease the SnCl\(_2\) stirring time down to 1 day while maintaining the other parameters to decrease the Sn percentage. The Sn percentage in nanoparticles was determined to be 80%, which is higher than the reference data (70%). Because of the high solubility of SnCl\(_2\), 1 day is clearly enough for full penetration of SnCl\(_2\).
7.3.4 Increase penetration of InAc

Spaeth et al.[54] predicts that the size of nanoparticles increases with the solution stirring time. Previously, the stirring time was varied (2, 4 and 7 days) after InAc was loaded. Using these samples, we attempted to estimate the InAc penetration rate by measuring the amount of precipitate after centrifuging. However, the centrifuged residue weights were more than the amount added. This is possibly due to the binding of InAc to the micelles and by-product of InAc brought out of the micelles, or InAc reacting with toluene. To determine which was the case, XPS of pristine InAc, the precipitated powder from the micelles solution and the precipitated powder after mixing with toluene were analyzed.

Table 7.4: Ratio of oxygen to indium and carbon to indium for the pure InAc, the precipitated powder from the micelles solution, and the precipitated powder after mixing with toluene determined by the area intensities of XPS spectra

<table>
<thead>
<tr>
<th>Sample</th>
<th>O_{531.72}/In</th>
<th>C_{288.67}/In</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine InAc</td>
<td>2.3</td>
<td>0.3</td>
</tr>
<tr>
<td>The precipitated powder from the micelles solution</td>
<td>2.2</td>
<td>0.2</td>
</tr>
<tr>
<td>The precipitated powder after mixing with toluene</td>
<td>2.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The XPS spectra shows that InAc has In, O and C elements. The C1s core level XPS spectrum displays two distinct peaks at BE 288.67 eV and 284.8 eV which correspond to the carboxylate group and carbon contamination, respectively[110]. The O1s spectra show a symmetric peak at 531.72 eV corresponding to the oxygen in carboxylate group. Figure 7.4 shows C1s XPS spectra for pure InAc and the precipitated powders. The carboxylate group C1s shows that the precipitated powder after mixing with toluene appeared to be pure InAc, supported by the $C_{288.67}/In$ ratio in Table 7.4. The precipitated powder from the micelles solution shows a slight change of $C_{288.67}/In$ ratio. Moreover, a N1s peak was observed from the XPS survey scan.
This suggests a reaction between the InAc and the micelles, and no reaction between InAc and toluene. This supports the solubility test showing InAc to be insoluble to toluene.

Ethanol was loaded afterward to form InO$_3$. Figure 7.5 shows AFM images of the nanoparticles on the Si substrates after plasma etching. The mean size of $(20 \pm 4)$ nm was obtained for 3 different stirring time samples. We increased the stirring time with InAc loading micelles; however, the size of resultant InO$_3$ was not changed with different stirring times. This suggests that the penetration of InAc would be similar with different stirring times. Note also that the size of the InO$_3$ nanoparticles were much smaller than those observed after adding SnCl$_2$. 

Figure 7.4: C1s core level XPS spectra of the pure InAc, the precipitated powder from the micelles solution, and the precipitated powder after mixing with toluene
Figure 7.5: AFM topography images of the nanoparticles after plasma etched micelles containing InAc and ethanol. The micelles solution stirring times were varied for (a) 2 days, (b) 4 days, and (c) 7 days.

7.4 Tin oxide samples

We attempted to adjust the stoichiometry by increasing the moles of InAc and keeping that of SnCl₂ to examine the relationship between molar ratios and Sn percentages. El-Atwani et al.[41] state that by raising the nominal Zn to pyridine (Zn/VP) ratios from 0.3 to 0.5, the loading of ZnAc was increased. The reference ITO nanoparticles (np4.1) has the nominal In to pyridine (In/VP) ratio of 1.0, which is 30 mg of InAc. From the solubility table 6.1, the water solubility of SnCl₂ is 41 times higher than the solubility for InAc. With such a ratio, it would be difficult to achieve the desired ≤ 20% stoichiometry without consuming a large amount of material. Instead, we chose four ratios to see if the trend was consistent with our predicted values. As such, we modified the In/VP ratios to 1, 5, 10, and 17. As the weight of SnCl₂ and volume of ethanol were kept constant, we would expect an increase in the penetration of InAc and relative amount of In to Sn in the final nanoparticles(Figure 7.6 black line). We measured the experimental Sn concentrations in the nanoparticles. They are illustrated in Figure 7.6 with the blue dots representing the
Figure 7.6: Plot of Sn concentration in the nanoparticles with different In/VP ratios, 1, 5, 10, and 17. Blue dot represents the averaged experimental data with the error range and black dots represent the expected values based on the solubility difference averaged values measured from the nanoparticles with error. The blue line shows no trend of Sn concentration of as a function of InAc loading, suggesting that different In/VP ratios could not control the Sn concentration. Surprisingly, when 10 times of InAc(300 mg) was loaded, one XPS measurement of the Sn concentration shows 17%, which should have been sufficient to induce crystallinity in the nanoparticles. The X-ray diffraction (XRD) pattern is shown in Figure 7.8 with reference data of ITO and SnO$_2$. The three diffraction peaks at 34°, 38°, and 51° 2θ are assigned to (101), (200), and (211) planes of SnO$_2$, calling into question the XPS results. Additionally the 17-times-InAc-(500 mg) loaded micelles showed no In component at all. As explained below, these results called into question the reproducibility of our approach with increasing the InAc in the solution.
7.4.1 Reproducibility

The unexpected but apparent success of modifying the In/Sn ratio down to 17% by changing the amounts loaded into the micelles solution, but with no indication of ITO crystallinity observed in the produced nanoparticles, and a decrease in measured In concentration with increased loading led to some suspicion of the stoichiometry obtained by XPS for one sample. Therefore, we examined the uniformity and reproducibility of the loading approach. To determine reproducibility, ITO nanoparticles using the In/VP ratio of 10 were synthesized and summarized with different amounts of reagents as described in Table 7.5.

Although the experimental condition and molar ratio were kept constant, the Sn concentrations were inconsistent with an average 53% and a huge standard deviation(23%) given in Figure 7.7. Thus from this data, it appears that changing the amount of material in the solvent does not reproducibly lead to a fixed stoichiometry.
of nanoparticles. Unfortunately, this makes the results of np4.3 difficult to depend on.

In order to check the uniformity of the nanoparticle stoichiometry upon deposition, XPS line scan was performed on sample np4.3 to see if the value measured in one spot was consistent through the whole sample. The XPS spectra were obtained by scanning a x-ray beam of 20 \( \mu \text{m} \) of spot size across the sample horizontally. Figure 7.9 shows the line scan of XPS data acquired for In3d and Sn3d along a single line across the surface of the np4.3 sample. The spectrum could be fitted with the two expected peaks corresponding to \( 3d_{3/2}(452 \text{ eV} \text{ and } 495 \text{ eV}) \) and \( 3d_{5/2}(444 \text{ eV} \text{ and } 486 \text{ eV}) \) for each In and Sn components, as expected. In Figure 7.9, below 1500 \( \mu \text{m} \) in the X range, high intensity of In and low intensity of Sn were observed, while above 5000 \( \mu \text{m} \), it shows low In intensity and high Sn intensity. As a result, the In and Sn ratios were
Table 7.5: ITO nanoparticles using the reduced In/VP ratio of 10

<table>
<thead>
<tr>
<th>Name</th>
<th>InAc</th>
<th>SnCl₂</th>
<th>Ethanol</th>
<th>Sn %</th>
</tr>
</thead>
<tbody>
<tr>
<td>np4.3</td>
<td>300</td>
<td>1.8</td>
<td>0.3</td>
<td>17</td>
</tr>
<tr>
<td>np5.1</td>
<td>58</td>
<td></td>
<td></td>
<td>58</td>
</tr>
<tr>
<td>np5.2</td>
<td>46</td>
<td></td>
<td></td>
<td>46</td>
</tr>
<tr>
<td>np5.3</td>
<td>150</td>
<td>0.9</td>
<td>0.15</td>
<td>45</td>
</tr>
<tr>
<td>np5.4</td>
<td>75</td>
<td></td>
<td></td>
<td>75</td>
</tr>
<tr>
<td>np5.5</td>
<td>80</td>
<td></td>
<td></td>
<td>80</td>
</tr>
</tbody>
</table>

Figure 7.9: XPS contour line scans of np4.3 in (a) In3d and (b) Sn3d regions. The scan in the middle part shows the Sn concentration in the line scan nonuniform over the surface. In addition, the measured Sn concentrations in the line scan were 79, 88, 92, and 92% which was the opposite result (17% from the XPS data of one single spot) to that observed previously. This calls into question the assumption that changing the amount in the solvent would lead to greater penetration of InAc. However, increasing the In/Vp ratio to 10x did appear to have some effect.

7.5 Summary

ITO nanoparticle synthesis inside of micelles has higher Sn concentration likely due to the different water solubilities of the InAc and SnCl₂. We attempted to adjust the In/Sn ratio by altering several parameters including the micelles size, micelle
solution concentration, sequence of precursor loading and stoichiometry. The Sn concentration achieved from all the various methods was more than 25%. Initially, changing the In/VP ratio seemed promising, showing a trend of decreasing Sn concentration with increased fraction of InAc. However, with repeated attempts, it was found to not be reproducible and in fact resulted in a non-uniform distribution of In and Sn components over the surface. XRD measurement of the surface showed only SnO$_2$ crystalline structure, likely due to the average composition of the particles being above 70% Sn. We had no simple way of measuring the InAc penetration. As there was no swelling of the micelles, there was no indication other than forming nanoparticles and measuring the Sn%. Therefore we looked for another measurement of loading, as described in the next chapter.
Chapter 8

Salt loading control

8.1 Introduction

Atomic force microscopy (AFM) has been widely used to measure topological and mechanical properties in nano structured material simultaneously[51, 111–113]. In the tapping-mode, the material composition mapping is possible through an examination of the phase shift of the cantilever vibrations[51, 111, 112]. However, it is generally difficult to extrapolate the mechanical properties solely from phase images. In order to obtain the elastic and adhesive properties of samples, single point force-displace curve[114, 115], force-volume [116], and mechanical mapping[112, 113, 117–119] techniques have been performed. In this chapter, we explore methods of determining salt infiltration on the mechanical properties of the micelles. In the reverse micelles approach, nanoparticles are synthesized by loading the ionic reactants inside micelles core[40, 41]. Since InAc, a stiffer material, is embedded in a softer polymer, the elastic properties of the loaded micelles is expected to vary as a function of the InAc loading.
8.2 Experimental

Polystyrene-block-poly-2-vinylpyridine (PS-b-P2VP) diblock copolymer was dissolved in toluene and kept under vigorous stirring for 18 hours. The loading of InAc is increased from 4.8, 9.6, 14.4, 24.0, and 150.0 mg corresponding to In1, In2, In3, In4, and In5 respectively. The InAc loaded micelles solutions (3 g L\(^{-1}\)) were spin coated on the Si substrates, the solutions were diluted to 2 g L\(^{-1}\) and then spin coated to form a monolayer. AFM characterizations were performed with a resonance frequency of 150 (170 to 210) kHz and a force constant of 45 (30 to 76) N m\(^{-1}\). For the analysis of phase image, a Nano Scope IIIa, Veeco was employed; analysis of the mechanical properties were performed using Bioscope Catalyst, Bruker in Peak Force QNM in Air mode. Details are described in Chapter 3.4.

Prior to the measurement of the samples using Quantitative NanoMechanical (QNM) microscopy, the force constant and the deflection sensitivity of polystyrene(PS) film were measured for calibration. Those values were used to input parameters to calculate the Young’s Modulus. A PS film with a known elastic modulus of 2.7 GPa was measured as 30 GPa by QNM. The calibrated difference was used to facilitate the analysis to eliminate possible error especially from the tip radius. More than 50 nanoparticles were selected and analyzed to obtain the Young’s modulus at the center of the nanoparticles.

8.3 Phase Analysis

In the tapping mode, height images are obtained by measuring the cantilever vibration due to the tip-sample interaction. With different material components on
the surface, the free cantilever phase angle will shift as it vibrates and the contrast variation is recorded in the so-called “phase image”. The phase signal is a measure of energy dissipated by a vibrating tip on the sample surface defined by its viscoelastic and adhesion properties[112, 120]. The brighter the contrast, the larger the phase angle shift. As the stiffness of inorganic salt will be higher than that from the organic micelles, this technique can be used to determine the infiltration of InAc in the micelles, as has been observed for other system[51].

As discussed, the infiltration of salt into the micelles can be reflected by the phase contrast. The empty micelles were compared to In5 in Figure 8.1. As discussed in Chapter 7, the size of micelles is (65 ± 3) nm for the empty micelle through In5. The empty micelles, clearly distinguishable from the Si background, have relatively flat
contrast phase image, with almost no change in the contour plot across the diameter of the micelles. On the other hand, In5 shows high contrast variation over each micelles regions. The brighter region coincides topographically with the core which is loaded with salt, whereas the darker region is the corona of the micelles.

To investigate the InAc loading, the phase images in Figure 8.2 show 4.8 to 24.0 mg of InAc added to the solvent to load micelles. There is some change of shape caused by effects of creep due to the thermal drift in the piezoelectric scanner, especially in the In2 sample[121]. At the beginning of a scan after dimension was changed or location was moved, the initial part of the image might be distorted. The contour images on the top of the phase images can indicate the change in the phase shift over the Si and micelles region. In1 shows a relatively gentle slope while In2, In3, and In4 show much steeper slope with similar elevation. The phase angle shift was slightly enhanced after 4.8 mg of loading, and significant change was observed with 9.6 mg of loading. Though after 9.6 mg of InAc loading the phase contrast images showed increase in slope of the contour plot, and higher phase shift in the core, there was no visible difference in the phase images for samples beyond 9.6 mg of loading.

8.4 Quantitative Nano Mechanical properties

The variation in phase angle was observed between empty micelles and micelles loaded with InAc in the micelles core, as had been observed previously for ZnAc[51]. However, the phase images of InAc loaded micelles did not provide quantitative information related to the different amount of InAc loading.
Figure 8.2: Samples spin coated with 3 g L$^{-1}$ Left part: topography AFM images of nanoparticles. Middle part: phase AFM images of nanoparticles. Right part: the contour plot of phase image (a) In1 (b) In2 (c) In3 (d) In4
For quantitative analysis, the material property variation in the InAc loaded micelles were determined by AFM force-displacement measurement. In such a technique, peak force tapping mode is used to collect a force curve at every point to identify the material variation across a topography image. Using PeakForce QNM, quantitative nano scale material properties such as modulus, adhesion, deformation, and dissipation are collected simultaneously with topography for each individual tap[112, 118, 119]. As the modulation frequency was set lower than the cantilever resonant frequency, only a properly chosen cantilever is capable of responding to deflection change from the samples[122]. The Derjaguin-Muller-Toporov (DMT) [123] model that considers adhesion and small deformation is used to extract the Young’s modulus from the force curve and force volume image.

\[
F - F_{adh} = \frac{4}{3} E^* \sqrt{R \left( d - d_o \right)^3} \tag{8.1}
\]

Where \(F - F_{adh}\) is the loaded force (force on the cantilever about the adhesion force), R is the tip radius, \(d - d_o\) is the deformation of samples, and \(E^*\) is the reduced modulus. The Young’s modulus of the samples can be obtained by the equation relative to the tip and reduced modulus

\[
E^* = \left[ \frac{1 - v_s^2}{E_s} + \frac{1 - v_{tip}^2}{E_{tip}} \right]^{-1} \tag{8.2}
\]

where \(v_s\) and \(E_s\) are Poisson’s ratio and elastic modulus of the sample, and \(v_{tip}\) and \(E_{tip}\) are Poisson’s ratio and elastic modulus of the tip. As the tip is much stiffer than the polymeric samples, we assume \(E_{tip}\) is infinite. Thus, the Young’s modulus of the sample can be calculated from the reduced modulus and Poisson’s ratio of the
sample. Using the Poisson’s ratio of the PS film 0.35\cite{124} for the sample, the reduced modulus can be extracted.

Samples of empty micelles, In1, In3, and In5 were measured, and topography images and modulus maps were obtained (Figure 8.3). In Figure 8.3 (a) the empty micelles are observed with good contrast to the Si substrate. However, the Young’s modulus is non-uniform across the micelle. The edge of micelles appear to have increased modulus compared to the core of micelles (Figure 8.4). When a tip first comes across the corona of the micelles, it first interacts with numerous co-polymer strands, which may explain the high modulus. When the tip is tapping at the core of the micelles; however, it only interacts with a few diblock copolymers, leading to a decreased modulus.

In order to analyze the modulus with different InAc loading, the Young’s modulus at the core of all of the individual micelles was collected. The distribution of the adjusted modulus of each sample is shown in Figure 8.5. The mean values of Young’s modulus from samples were obtained from Gaussian fitting as 3.55, 3.54, 4.58, 5.17 GPa with standard deviations less than 1. This result shows that quantitative differences in mechanical behavior results from variations in InAc loading in the micelles. To confirm the results, two sets of measurements were performed, as shown in Figure 8.6. Though the measured values were slightly different, they follow the same trend of increasing modulus with loading of InAc. The only exception appears to be In1, which shows elastic modulus similar or lower than that of the empty micelles. One potential explanation could be the interaction of InAc with the diblock copolymer. When a small quantity of InAc was loaded, they may slightly swell the micelles through intercalation of the metal salt in the PS region. Previous studies
Figure 8.3: Left part: topography AFM images of nanoparticles. Right part: AFM modulus map
have shown that small amount of intercalation between lamella can act as plasticizers in diblock copolymers[125, 126], lowering the Young’s modulus. As the amount of material increases; however, the infiltrated material acts to reinforce the modulus of the copolymer[125, 126].

The relative differences of Young’s modulus of the loaded micelles to the empty micelles were plotted against the weight of loaded micelles in Figure 8.6. The red and green dots represent the first and second set of measurements. The first set was measured from the empty micelles, In1, In3, and In5; the second measurement was acquired from the empty micelles In1, In2, In3, In4, and In5. Both experiments illustrate decreased modulus at 4.8 mg of InAc loaded micelles, In1, and the modulus was increased as a function of InAc loading. From the modulus plot(Figure 8.6), it appears that the modulus was saturated after 14.4 mg of InAc loading. There are two possible explanations. First, that the Young’s modulus is unchanged beyond a certain threshold, or that 14.4 mg is the limit of infiltration of InAc. Given the extremely low amounts of In observed in the nanoparticles, it appears likely that 14.4 mg is
Figure 8.5: Young’s modulus distribution with Gaussian fitting of samples empty micelles, In1, In3, and In5, the blue line shows the difference between the original data and Gaussian fitting.

the maximum loading amount. As a consequence, even though we added much more InAc to the solvent, it is likely that any amount greater that 14.4 mg was precipitated out of solution. Further work with SnCl₂ loading, which we know has much greater loading potential than the InAc, is needed to confirm these results.
Figure 8.6: Young’s modulus ratio of loaded micelles to the empty micelles comparison of In1, In2, In3, In4, and In5

8.5 Summary

We have measured the mechanical properties of empty micelles and InAc loaded micelles using the phase images and the modulus mappings. Both types of measurements were taken simultaneously with the topography images. InAc loaded micelles show phase contrast variation over the micelles region with a large phase shift at the center of the micelles. However, though it is possible to distinguish between loaded and un loaded micelles, there was no visible difference with different InAc loading. The Young’s modulus of the micelles mapped over the surface were much more promising, showing variations as a function of InAc loading to the micelles. Given the values taken from of the center of micelles, the modulus was saturated after 14.4 mg of InAc loading, suggesting a maximum loading amount for InAc.
Chapter 9

Control of ordering in micelles monolayer

9.1 Introduction

One of the inherent benefits of reverse micelles deposition is that micelles can be coated as monolayers forming a hexagonal pattern. Typically, the film morphology depends on the nature of the solution and the parameters chosen for the spin coating process.[127] Factors such as density of solution, volume of solution and spin speed contribute to how the micelles organize. The topography images from atomic force microscopy (AFM) were used to differentiate the degree of order in the micelles array. Typically, nanostructures are characterized by fast Fourier transform (FFT),[128, 129] radial distribution function,[130] and Delaunay triangulation,[131] to assess the ordering of the structure. As FFT requires a lot of particles to give useful results, in this Chapter, we focussed on the radial distribution function and Voronoi diagram. They exhibit characteristics that would allow the researcher to determine how closely
the dispersion corresponds to the hexagonal lattice, even with few particles.

9.2 Experimental

As described in Chapter 3, polystyrene-block-poly-2-vinylpyridine (PS-b-P2VP) diblock copolymer was dissolved in toluene and kept under vigorous stirring for 18 hours. Indium acetate, stannous chloride, and ethanol loaded micelles were used. The micelles solution was spin coated on silicon substrates using different volumes of solution and spin coating speed as listed in Table 9.1. All specimens were plasma treated under oxygen to remove the polymeric micelles and leave ITO particles on the substrates. All the details are described in Chapter 3.

Table 9.1: Altering parameter of nanoparticles loaded micelles

<table>
<thead>
<tr>
<th>Sample</th>
<th>micelles density (g L$^{-1}$)</th>
<th>volume of solution (µL)</th>
<th>spin coating rate (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D332</td>
<td>3</td>
<td>3</td>
<td>2,000</td>
</tr>
<tr>
<td>D333</td>
<td>3,000</td>
<td></td>
<td>3,000</td>
</tr>
<tr>
<td>D342</td>
<td>4</td>
<td>2,000</td>
<td></td>
</tr>
<tr>
<td>D333</td>
<td>3,000</td>
<td></td>
<td>3,000</td>
</tr>
<tr>
<td>D232</td>
<td>2</td>
<td>3</td>
<td>2,000</td>
</tr>
<tr>
<td>D233</td>
<td>3,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D234</td>
<td>4</td>
<td>3,000</td>
<td></td>
</tr>
<tr>
<td>D243</td>
<td>4,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D244</td>
<td>4</td>
<td>3,000</td>
<td></td>
</tr>
</tbody>
</table>

The distribution of ITO nanoparticles was examined using atomic force microscopy (AFM) as described in Chapter 3.4. In order to analyze the particles distribution, all the images were processed with Image J to produce binary images of nanoparticles. Using the binary images, the particle size, the x and y coordinates, the nearest neighbor distance, the particle count, and the total area were obtained. The codes to process the results and perform the spatial distribution analysis (GranSin Tools)
were developed by another member of the Dr. Turak Group. The average nearest neighbor distance, \((65.0 \pm 2.6)\) nm, and the \((35.0 \pm 1.2)\) nm of nanoparticles size were extracted from five samples(D232-D244) and used to determine a desired hexagonal lattice.

### 9.3 Order of micelles

![AFM images of nanoparticles](image)

Figure 9.1: AFM images of nanoparticles from (a) 3 g L\(^{-1}\) and (b) 2 g L\(^{-1}\) micelles solution densities on Si substrates using 4 \(\mu\)L of solution and 3000rpm spin coating rate

In order to determine how much ordering occurred in the micelles arrays, the analysis compared the experimental data to a desired hexagonally close packed pattern. In our ideal distribution, a given particle should be surrounded by six particles, each with center to center distance of 65 nm.

We synthesized the micelles solution initially with 3 g L\(^{-1}\), and the different volume of solution and spin coating rates were used(Table 9.1). Figure 9.1 shows two different nanoparticle distributions using the same spin coating parameters, but different micelles density. The nanoparticles in Figure 9.1 (a) seem to overlap each other and the area of nanoparticles coverage was above 28\%, which is more than the area
Figure 9.2: Right part: AFM images of nanoparticles from 2g L$^{-1}$ on Si substrate by altering the volume of solution and spin rate. Middle part: Voronoi function of left panel of the AFM image, the color code indicates the percent off hexagonal of Voronoi cells. Left part: probability of Voronoi cells in percent off hexagonal(%) (a) D232 (b)D233 (c)D234 (d)D243(e)D244
coverage of the desired hexagonal pattern (23%). This suggests that the sample in Figure 9.1 (a) has more than one layer. Since the spacing between the particles is determined by the size of micelles, particles that are closer together than the ideal distribution implies that micelles were on top of each other.

In order to achieve a monolayer of micelles, we altered the density of the solution. The nanoparticles in Figure 9.1 (b) were formed as a result of the micelle solution diluted from $3 \, \text{g} \, \text{L}^{-1}$ to $2 \, \text{g} \, \text{L}^{-1}$. These are more sparsely distributed with an area coverage of the 12%. They appear to form ideally a monolayer of micelles on the surface, with better distribution but still not in the ideal pattern. In order to modify the ordering and surface coverage, we then changed the volumes and spin coating speeds as shown in the AFM images in Figure 9.2. A monolayer was achieved with the area coverages of 14, 12, 10, 10, and 23% respectively for each sample from top to bottom. By controlling the volume of the solution and spin coating rate, ordering of nanoparticles were manipulated.

For the qualitative analysis of nanoparticles, Voronoi diagrams were plotted and shown in Figure 9.2 middle panel. Voronoi diagram is the decomposition of space, generated by a discrete set of points. For two distinct points that are close to each other, a perpendicular bisector of the line connecting them was drawn. By intersecting half of the planes, boundaries of a region consist of edges and vertices; as a result, they form a polygonal partition of the plane. Hence, this is called the Voronoi diagram.[133] In order to assess how close the particle pattern is to being hexagonal, for each particle, six neighbor particles at the closest proximity will be assigned to form its Voronoi cell. Using the GransimTools developed in the Turak group[132], the Voronoi diagrams were plotted. The color scale describes the percent off hexagonal of the Voronoi cells.
The deep blue, blue, light blue, yellow, orange, and red corresponds to 5, 10, 20, 30 and 40% off hexagonal, respectively. More than half of the 3µL samples show above 20% off hexagonal; on the other hand, more than half of the 4µL samples have less than 20% off hexagonal pattern. Therefore, 4µL solution results in the more effective hexagonal close packed structure.

The pair correlation function $g(r)$ were determined from the probability $K'(r)$ of a pair of points with the inter-particle distance $r$, divided by the corresponding probability for a Poisson process [134] described by

$$g(r) = \frac{K'(r)}{2\pi r}, \quad \text{where} \quad K'(r) = \frac{dK(r)}{dr}$$

(9.1)

where $K(r)$, Ripley’s K-function, is the number of points within a distance $r$ being evaluated. There should be no values below the distance equal to the size of the point, and more points would be evaluated as the distance increase.[134] Figure 9.3 compares the $g(r)$ obtained for AFM images in Figure 9.2 to the $g(r)$ of the desired hexagonal pattern with inter-particle spacing of 65 nm. The peaks at distance $r$ indicate a high probability of finding two particles with this distance between the particles. Although the experimental data do not coincide with the hexagonal pattern, the sample that showed the closest order to the desired hexagonal lattice could be determined by taking the difference in $g(r)$ between the sample and the desired hexagonal lattice. D232 (see Table 9.1) has oscillations at short distances and decays without oscillations at long distance, suggesting clustering,[130] while others have long-range order as their $g(r)$ oscillate with increasing distance. The table in Figure 9.3 shows the root mean square difference ($\Delta$) in $g(r)$ between the sample and desired hexagonal lattice, and the plot shows the $g(r)$ of each sample with the desired hexagonal lattice. The
Figure 9.3: Pair correlation function taken from AFM image in Figure 9.2 with different values between the samples and the hexagonal lattice.
grid lines are plotted relative to the peak maximum center of mass value of \( r \) for the first peak of \( g(r) \) in the desired hexagonal lattice. All samples have the first peak at around 31 nm, roughly the average diameter of the particles, suggesting that some particles are in contact. This may be due to the micelle shells interacting with one another. Two samples spun with 3 \( \mu \)L have the highest intensity at the first maximum and \( \Delta \) larger than 0.58, while the two samples spun with 4 \( \mu \)L have the highest intensity at the second maximum. This peak is found at around 75 nm which is the expected size of the micelles, as confirmed by AFM images of micelles. This supports the Voronoi analysis of the AFM images that more than 50\% of Voronoi cells in D232, D233, and D234 have greater than 20\% off hexagonal pattern; they are very disordered. Interestingly, D234 also has highest intensity in the second maximum, suggesting that even with lower volume it is possible to use the spin speeds to achieve desirable ordering. From the Voronoi diagram and pair correlation function, the nearest neighbor distance was significantly affected by the volume of the solution. By comparison of the \( \Delta \) of the samples D243 and D244, as well as D234, we can see that degree of order was also affected by the spin coating rate. From these analyses, D243, with the smallest \( \Delta \) value represents the highest degree of hexagonal order.

### 9.4 Summary

We illustrate that the inter-particle distance in nanoparticle loaded micelles on the Si substrates strongly depends on the volume of the solution; moreover, the degree of order can be controlled by the spin coating rate. In general, the nanoparticles are dispersed with the inter-particle distance of 83 nm. From the Voronoi diagram and the pair correlation function, the 4 \( \mu \)L and 3,000rpm demonstrated the lowest root
mean square suggested it being closest to the hexagonal lattice pattern.
Chapter 10

Conclusion

Organic electronics are used in displays and lighting sources as OLEDs, and OPVs are in process for further applications. Although high performance of organic electronics have been achieved, some stability and efficiency problems still need to be solved. One factor is the electrode morphology which is directly transferred to the organic layer; hence, the morphology will be crucial to determine the device performances. ITO is the transparent conductive oxide widely used as an electrode. In order to assess the device performances relative to the electrode modification, methods to fabricate the nano-structured ITO were examined.

Initially, sputtered ITO was examined, as it is the most widely used method for producing ITO. Ellipsometry and AFM were performed on the sputtered ITO surface, showing high sample to sample variability and Gaussian roughness, making it unsuitable for further study.

In order to obtain controllable homogeneous roughness, reverse micelles deposition was examined. A 2D array of nanoparticles deposited on a flat the ITO film would lead to uniform roughness over the surface. It was successfully shown, in Chapter 9,
that it was in fact possible to control the degree of ordering in micelle arrays. To assess the nanoparticles distribution, Voronoi diagram and pair correlation function of different distributions were analyzed to compare against the desired hexagonal pattern. The percent of hexagonal probability obtained from the Voronoi diagram gives considerable evidence that 4 µL solutions are more homogeneously distributed than 3 µL ones, and that 2 g L⁻¹ dilutions result in a micelle monolayer. The pair correlation function shows that the spin coating rate can adjust the distribution. Though we were not able to obtain a completely hexagonal patterned 2-dimensional array, as suggested in the literature, the level of control over the distributions suggests that controllable roughness should be possible.

However, in order for the reverse micelle technique to be successful, ITO must be obtained from solution chemistry. Using modified literature derived recipes, we successfully produced ITO from solution, as described in Chapter 5, using either the acetate[10] or the chloride precursor[18]. XPS characterization confirmed synthesis of ITO, showing In3d, Sn3d, and O1s peaks, with Sn concentration of 21% and 35% from the two routes, respectively. The acetate route showed an appreciable ITO bixbyite polycrystalline structure; while the chloride route showed two peaks which are also likely to be from ITO.

We then took two approaches, in Chapter 6, to using the diblock copolymer micelles, PS-b-P2VP, for nanoparticle deposition: a nano stabilizer for pre-formed ITO and as a nano reactor vessel to form nanoparticles. Pre-formed ITO was introduced into the micelles solution for the nano stabilizer approach and In salt, Sn salt and alcohol reactants were added sequentially for the nano reactor route. Loading of salts was confirmed by the change of micelles size analyzed by DLS; the change in the
vibrational modes of the pyridine from the interaction between the precursors and pyridine by FTIR. Both DLS and FTIR demonstrated that the pre-formed ITO did not penetrate into the micelles, likely because ITO is insoluble in water, and only the nano reactor route resulted in nanoparticles formation. However, XPS analysis revealed that both routes had a high Sn concentration ($\geq 20\%$) which would not yield the crystalline ITO.

From the results of solution-based ITO and reverse micelles deposition approaches for nanoparticles, the nano reactor approach using acetate route was chosen as the most likely avenue for successful formation of ITO nanoparticles. With this route, several methods were implemented to increase the In concentration as described in Chapter 7: changing of stirring time, micelles concentration, the order of loading, and stoichiometry of In to Sn. It was found that the stirring time of the micelles solution, the micelles concentration, and the order of loading do not affect the Sn concentration in nanoparticles. Though there was evidence that tuning of the Sn concentration was possible by increasing the In/PV ratio in the solvent, the results were inconsistent, generally with high Sn concentrations, with large sample to sample variation. Line scan XPS measurements even showed that there was considerable non-uniformity between micelles. Furthermore, SnO$_2$ diffraction pattern was obtained for the most promising sample, suggesting the method of increasing the loading of InAc into the solvent does not increase the amount loaded into micelles.

The precursor loading was examined via the mechanical properties of micelles on the substrates. Both qualitative (phase analysis) and quantitative (Young’s modulus) techniques were employed using AFM. Both techniques were able to successfully distinguish between loaded and unloaded micelles. The Young’s modulus approach
further showed a trend of increasing with modulus as the InAc loading increased and saturated after 14.4 mg of InAc loading. With InAc loading above 14.4 mg, it is likely that all excess InAc precipitates in the solution, explaining the low In content in the micelles.

Due to the solubility difference between precursors, and as described in Chapter 7 the SnCl₂ seems to displace InAc during loading, final nanoparticles had high Sn concentration, and even show SnO₂ crystallinity. Though ultimately we were not able to produce the desired 2D array of ITO nanoparticles, this study has shown that it is possible to achieve ITO from solution, that the solubility difference between precursors and their ability to penetrate the micelles is a critical issue in nanoparticle formation, and that significant control of the nanoparticle dispersion is possible. Additionally, we observed that the loading of precursors into the micelles can be tracked quantitatively though Young’s modulus changes as determined by nano-mechanical testing.

Therefore, in this study, the formation of nano-structured roughness by using ITO nanoparticles was seen to be a viable approach for electrode modification in organic optoelectronic devices. For further ITO nanoparticles study, there are few points to be considered: the weight of InAc cannot exceed 14.4 mg; the sequence of precursors loading should be InAc, SnCl₂, and ethanol, due to the solubility differences; nanoparticles should be spin coated on a substrate that will not oxidize under oxygen plasma to confirm the O1s peak in ITO.

It would be interesting to examine the elastic modulus of the micelles with different precursors loaded other than InAc. Moreover, sub-sequential elastic modulus measurements of micelles in between each steps of precursor loading can be studied. In order to optimize Sn concentration in nanoparticles, solvent mixing processes can
be used with a properly selected solvent that is highly soluble to SnCl$_2$ but less soluble to InAc. Thereby, we could potentially decrease the SnCl$_2$ penetration, while keeping the InAc penetration.
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