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Work function tuning of tin-doped indium oxide electrodes with solution-processed lithium fluoride

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ABSTRACT

Solution-processed lithium fluoride (sol-LiF) nanoparticles synthesized in polymeric micelle nanoreactors enabled tuning of the surface work function of tin-doped indium oxide (ITO) films. The micelle reactors provided the means for controlling surface coverage by progressively building up the interlayer through alternating deposition and plasma etch removal of the polymer. In order to determine the surface coverage and average interparticle distance, spatial point pattern analysis was applied to scanning electron microscope images of the nanoparticle dispersions. The work function of the sol-LiF modified ITO, obtained from photoelectron emission yield spectroscopy analysis, was shown to increase with surface coverage of the sol-LiF particles, suggesting a lateral depolarization effect. Analysis of the photoelectron emission energy distribution in the near threshold region revealed the contribution of surface states for surface coverage in excess of 14.1%. Optimization of the interfacial barrier was achieved through contributions from both work function modification and surface states.

1. Introduction

The ability to tune the electrode work function by the insertion of an interlayer has enabled the optimization of charge injection and collection efficiency in organic electronics [1]. In particular, charge selectivity and improved energy level alignment has motivated the development of various interlayers, such as n-type oxides, e.g., TiO_2 and ZnO, for preferential electron transport [2] and p-type oxides, e.g., MoO_3, WO_3, NiO_x, for hole transport [3]. Self-assembled monolayers of organic dipolar molecules have also been presented as a means for controlling the surface dipole of the electrode; the polarization strength can be tuned by careful selection of the functional groups on both ends to specify the desired shift of the modified electrode work function [1,4,5]. More recently, conjugated polyelectrolytes, which appear to have dynamic dipoles that can switch direction depending on the direction of the applied electric field, have been used in organic light emitting diodes and transistors [6,7]. However, some of the most widely used interlayers have been thermal evaporated LiF and other alkali halides and alkali metals [8], where the exact mechanism by which these materials enhanced charge collection/injection remains the subject of debate [9,10].

Meanwhile, rapid advances in the low-cost solution processing of organic electronics [11], as exemplified by the roll-to-roll manufacturing of polymer solar cells [12], have motivated the development of a solution processed alternative to thermal evaporated LiF [13]. In contrast to thermal evaporated LiF, which decreases the surface work function of tin-doped indium oxide (ITO), solution-processed LiF (sol-LiF) actually increases the work function [13]. In fact, incorporation of the sol-LiF at 14.4% coverage into a conventional ITO/sol-LiF/poly(3,4-ethylenedioxythiophene:poly(styrene sulfonate) layer (PEDOT:PSS)/poly(3-hexyl-thiophene):[6,6]-phenyl C61-butyric acid methyl ester (P3HT:PCBM)/thermal LiF/Al photovoltaic device showed a 6-fold increase in photon conversion efficiency over the same device without sol-LiF [14]. Since LiF interlayers have been shown to enhance charge collection efficiency at both electrodes, they are most likely providing a means to fine-tune the energy level alignment between the electrode and the organic active layers.

The work function, Φ, is the difference in energy between an electron at the Fermi level just inside the surface and at rest in vacuum [15], and a key technique to measure it is photoelectron emission yield spectroscopy. When irradiated with a UV source, electrons with a kinetic energy greater than the apparent photoemission threshold, φ, will be ejected from the specimen. The fastest, i.e. most energetic,

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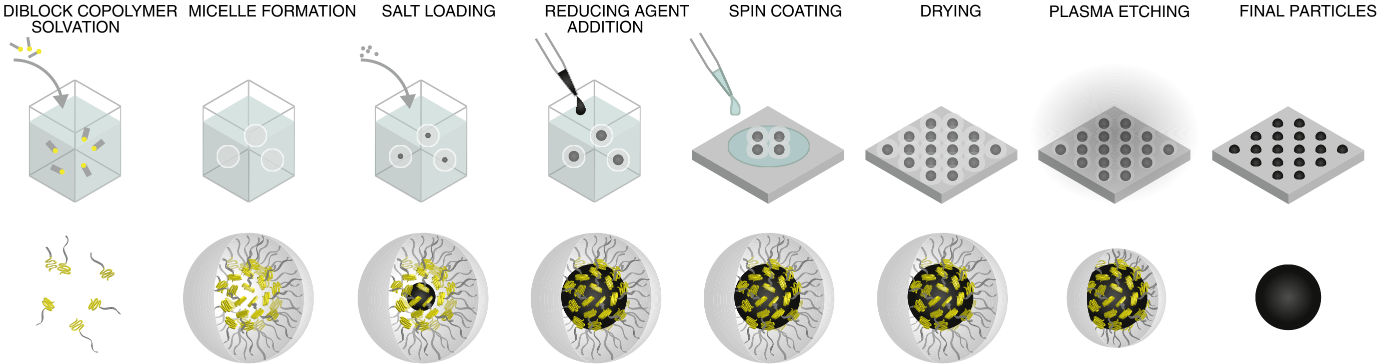

Fig. 1. The synthesis LiF nanoparticles in solution in reverse polystyrene-*block*-poly2vinylpyridine diblock co-polymer reactor vessels.

electrons would be those at the Fermi level, while the slowest electrons would be those with energy equal to Φ. A negative deviation of φ from Φ can be attributed to emission from surface states [16,17].

Adsorbates on the surface can induce surface dipoles [15]. The consequent formation of a dipole layer can also change the emission threshold of the substrate [18]. When the density of these dipoles is increased, mutual interactions reduce the effective dipole moment ("depolarization") [4,19], which is reflected in modulation of φ [15].

An important side effect of the solution process protocol for LiF is the ability to tune the electrode work function, measured by Kelvin probe, via control of the surface coverage. The tuning of Φ by LiF nanoparticles has been attributed to depolarization [13]. The increase in coverage entailed a decrease in interparticle separation, giving rise to increasing depolarizing interaction between surface dipoles induced by the LiF. As the sol-LiF processing enables the progressive build-up of the electrode bilayer, it provides the means to investigate the degree of work function shift with interlayer morphology. The results would reveal insight into how modification of the electrode structure impacts the interfacial properties. In this contribution, we provide further evidence that the degree of increase of the work function of ITO is tunable via its surface coverage by sol-LiF; we also substantiate the participation of surface states in tuning the degree of increase.

2. Experimental details

Details can be found in Aytun et al. [13] for the synthesis of LiF nanoparticles in solution by using reverse diblock copolymer nanoreactors. Briefly, as shown in Fig. 1, polystyrene-*block*-poly 2vinyl pyridine diblock copolymer (P1330-S2VP; Polymer Source Inc., Montreal, Canada) was dissolved in toluene. Lithium hydroxide non-hydrate (Merck KGaA, Darmstadt, Germany) was loaded into the micelle core, and then buffered 40% hydrofluoric acid (Merck KGaA, Darmstadt, Germany) was added to the loaded micelle solution. The micelles loaded with size-monodisperse particles were deposited onto tin-doped indium oxide

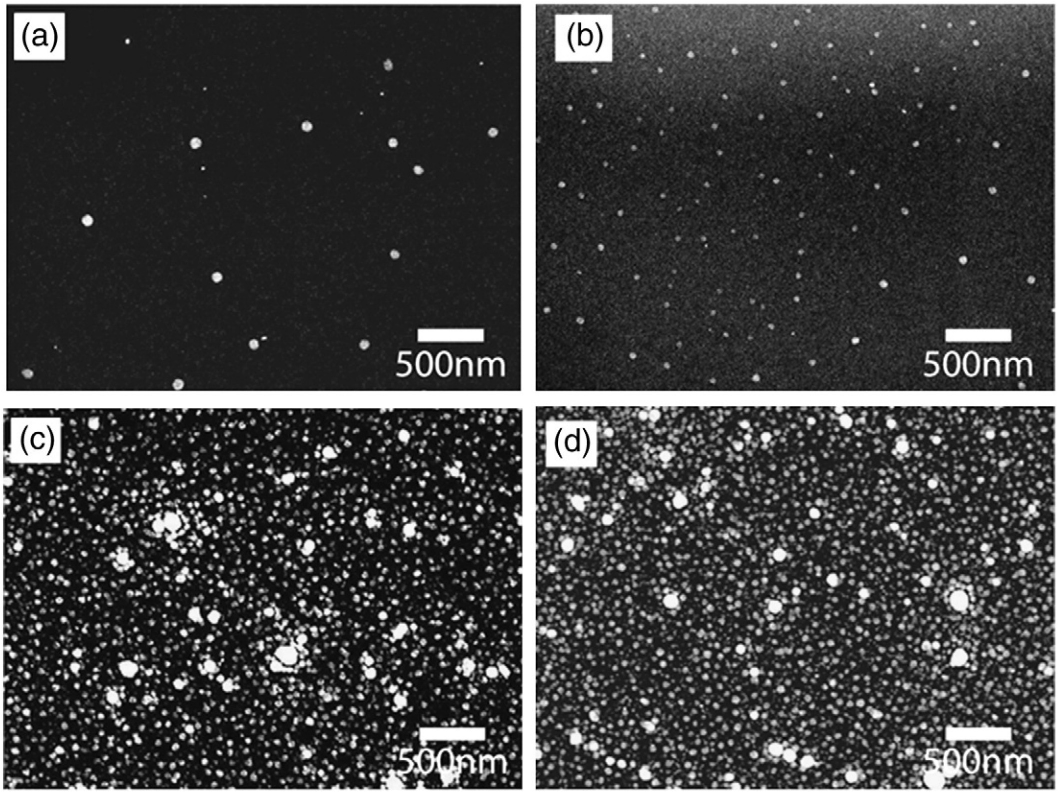

Fig. 2. Images of LiF nanoparticles on single crystal silicon wafer substrates used for spatial point pattern analysis, showing a) 0.5% coverage, b) 1.1% coverage, c) 14.1% coverage, and d) 21.8% coverage.