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***Studies on Surface Modified Metal Oxides Nanofibers and Thin Films  
for Solar Energy Conversion and Storage***

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One alternative energy resource available worldwide is solar energy. The earth receives 120,000 TW of energy from the sun in the form of sunlight per day. This energy is around four orders of magnitude higher than the yearly current and projected total energy consumption.<sup>1-3</sup> The density of solar energy (irradiance) though is not concentrated; with an annual average of  $170 \text{ W m}^{-2}$  at the surface of the earth. Also, the irradiance varies with geographical location, but this concern is not as significant to production economics as that of the distribution of oil reserves. Some Northern European countries which have lower irradiation than those located near the equator are finding applications of solar energy to be economically viable.<sup>4</sup>

The most extensive use of solar energy is the photosynthetic conversion of carbon dioxide to energy in the form of carbohydrates, or chemical energy, by plants and microorganisms. Humans, on the other hand, have long employed solar energy in the form of heat into the lifestyle as ancient civilizations used sunlight for water heating and warming of homes.<sup>5</sup> But it was not until 1839, when Becquerel discovered the photovoltaic effect and until 1954, when the first practical photovoltaic module was developed by Bell Laboratories, that solar energy could be directly converted to electricity.<sup>6</sup> However, the current cost of solar to electric conversion technologies makes them hardly competitive with the low-cost, base-loadable, fossil based electricity. In order

for solar energy to be truly practical as a primary energy source, its conversion and storage must be done in a cost-effective and efficient manner.<sup>7</sup>

Current commercial single crystal silicon photovoltaic modules are at 16-18% efficiency.<sup>8</sup> But even if these expensive modules operate near the theoretical limit of 70% efficiency, the cost of fabrication, storage, and dispatching energy still hinders the use of the technology since sunlight is an intermittent resource in a geographical area.<sup>1</sup> Many research efforts are already addressing these problems, however. Low-cost and/or high-efficiency photovoltaic device concepts like the excitonic solar cells are being developed. Solar thermal technologies are reaching a mature stage of development and have the potential of becoming competitive for large energy supply systems. Intermittency is being addressed by extended research efforts in energy storage devices, such as batteries, other electric storage systems, thermal storage, and in the direct production of solar fuels (typically hydrogen). All these are valuable routes for enhancing the competitiveness and performance of solar technologies.<sup>6</sup>

In this work, one-dimensional and thin film metal oxide materials are developed for devices used in the conversion and storage of solar energy. In particular, this research is mainly focused on: (a) the preparation and optimization of metal oxide (strontium titanate) based nanofibers for the photocatalytic production of hydrogen; and (b) the design and/or modification of one-dimensional and thin film metal oxides for electrodes of excitonic solar cells and lithium ion batteries.

The make-up of metal-oxide based nanofiber photocatalysts and the optimum configuration and design of their use as electrodes of excitonic solar cells and batteries may help provide significant information and help mark another milestone towards the large-scale implementation of solar production of hydrogen and electricity. The efficient

conversion of solar energy to hydrogen and electricity may help ease mankind's dependence on fossil fuels for the majority of its energy needs. On a more specific application, the efficient production of hydrogen may allow for its use as an alternative for fossil based automotive fuels.

The preparation and modification of one-dimensional and thin film metal oxides as electrode materials of excitonic solar cells and their application to photovoltaic devices may provide additional insights on the fabrication process and functional mechanisms of excitonic solar cell devices. Such mechanisms and efficiencies may support studies in the construction of highly efficient yet cost-effective photovoltaic modules.

The preparation and application of one-dimensional metal oxides as anodes of lithium ion batteries may lead to safer and yet higher performing devices. The process used in the fabrication and characterization of these anodes may yield the needed steps and data towards the design and construction of more efficient batteries for high power applications.

For the photocatalytic production of hydrogen, strontium titanate ( $\text{SrTiO}_3$ ) nanofibers were prepared, optimized, characterized, and tested.  $\text{SrTiO}_3$  nanofiber-based photocatalysts were chosen in the study since  $\text{SrTiO}_3$  has been shown to have band levels suitable for hydrogen production *via* the photocatalysis of water.<sup>9</sup> Pure  $\text{SrTiO}_3$  crystals have been shown to produce hydrogen from alkaline solutions<sup>10</sup> or in the presence of sacrificial reagent that act as hole scavengers like methanol.<sup>11</sup> Among nanostructures, the nanofiber morphology was selected since it has previously been established that anatase  $\text{TiO}_2$ , a highly researched photocatalyst, have been shown to have higher hydrogen production with a nanofiber morphology compared to a nanoparticle morphology.<sup>12</sup>  $\text{SrTiO}_3$  nanofibers were prepared in the study *via* the hydrothermal reaction of electrospun

titanium dioxide (TiO<sub>2</sub>) nanofibers with strontium hydroxide and the direct electrospinning of solutions containing both strontium and titanium salts.

The nanofibers obtained from the hydrothermal reaction of TiO<sub>2</sub> nanofibers with strontium hydroxide were characterized to have composite structures containing both SrTiO<sub>3</sub> and TiO<sub>2</sub> nanocrystals with morphology and composition dependent on the crystallinity of the TiO<sub>2</sub> nanofibers used in the hydrothermal reaction. The best performing composite nanofiber structure prepared had a hydrogen production rate of 127  $\mu\text{mol}\cdot\text{h}^{-1}\text{g}^{-1}$  under majorly visible light irradiation, with 10% methanol present as a sacrificial agent. The measured hydrogen production rate was even higher than that of commercial SrTiO<sub>3</sub> nanoparticles which had the activity of 19  $\mu\text{mol h}^{-1}\text{g}^{-1}$ . The higher hydrogen production rate of the prepared nanofiber sample was attributed to it being closer to the ideal Ti/Sr ratio, smaller crystallite size, and its mesoporous structure. However, although the prepared composite SrTiO<sub>3</sub>/TiO<sub>2</sub> nanofibers have higher hydrogen production rate than commercial SrTiO<sub>3</sub> nanoparticles, properties important to photocatalytic activity were shown to change depending on the hydrothermal reaction conditions. Since the doping of metals into SrTiO<sub>3</sub> were shown to lead to higher hydrogen evolution rates, visible light photocatalysis,<sup>13,14</sup> and photocatalytic decomposition without the use of sacrificial agents,<sup>15-17</sup> the preparation of homogenous SrTiO<sub>3</sub> nanofibers become more critical.

The preparation of pure and homogenous SrTiO<sub>3</sub> nanofibers were optimized *via* the electrospinning of solutions containing both strontium and titanium salts. Homogeneous SrTiO<sub>3</sub> nanofibers with high hydrogen production photocatalytic rates were reproducibly prepared *via* the electrospinning of clear precursor solutions, which contained: polyvinylpyrrolidone as the polymer guide, acetylacetone, titanium butoxide and

equimolar amounts of strontium acetate in acetic acid. Calcination was done at 700°C. The prepared nanofibers were found to have a hydrogen production rate of 167  $\mu\text{mol h}^{-1} \text{g}^{-1}$  or a quantum yield of 0.339% under majorly visible light irradiation, with 40% methanol present as a sacrificial agent. Like the composite nanofibers prepared after the hydrothermal reaction of  $\text{TiO}_2$  nanofibers with strontium hydroxide, the prepared pure  $\text{SrTiO}_3$  nanofibers have a higher hydrogen production rate than the commercial nanoparticle (32  $\mu\text{mol h}^{-1} \text{g}^{-1}$ , or quantum yield of 0.064%). The improvement in photocatalytic performance was found to be because of better crystalline properties, ideal Ti/Sr stoichiometric ratio, higher surface areas, and the mesoporous nature of the nanofibers brought about mainly by the optimization of the electrospinning technique and significantly by the morphological difference of the nanofibers and nanoparticles since the nanofibers were used in powder form during the photocatalytic characterization. Although the electrospinning technique can easily be used to prepare nanofiber-based solid electrodes and have a higher hydrogen production rates than nanoparticle-based solid electrodes because of better charge transport, the surface area required to have the same equivalent loading (as powder photocatalysts) for the photoreaction makes such electrodes impractical. Higher hydrogen production rates for the nanofiber-based powder photocatalysts are expected in large-scale reactors wherein evolved gases are constantly removed from the reactor. Also, since  $\text{SrTiO}_3$  are essentially anodes, the addition of metal co-catalysts in conjunction with the nanofibers or even the direct doping of the metal onto the nanofibers can give higher photocatalytic performance. The use of metal co-catalysts during photoreactions have been shown to improve hydrogen production rates of the electrospun nanofibers. However, even if the improvement in photocatalytic rates was already remarkable, the methodology of co-catalyst loading when used in larger scale

may prove to be difficult especially in the recycling and the separation of the photocatalyst and the co-catalyst. This difficulty however can be resolved by the loading of metal salts into the electrospinning solutions. Metal-doped SrTiO<sub>3</sub> nanofibers were also shown to have improvements in hydrogen production rates.

Aside from metal-doping, other techniques can be used to improve properties of metal oxides to match requirements of specific devices. In the fabrication of excitonic solar cells, metal oxides are used for three main functions.<sup>18</sup> The first one is as electrode materials. Metal oxides which have wide band gap can be employed as transparent conducting films used as the top electrode of excitonic solar cells.<sup>19</sup> The second function of metal oxides in excitonic solar cells is as selective hole or electron transport layer. The third function of metal oxides is as electron acceptor materials during the exciton dissociation at the interface with an organic donor material.<sup>18</sup>

As a top electrode, metal oxides like the transparent indium tin oxide have surface energies quite incompatible with the hydrophobic polymeric materials used in the active layer of organic solar cells. Aside from this, the work function of indium tin oxide varies depending on the source, preparation method,<sup>20,21</sup> and surface treatment<sup>22</sup> and is usually not high enough when paired with polymeric active layer materials used in organic solar cells. Thus an interfacial material between the anode and the active layer like the conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is usually employed to stabilize and increase the anode work function.<sup>23</sup> However, although PEDOT:PSS-modified indium tin oxide anodes were found have a more uniform electrical property, better electron blocking, and enhanced hole collection,<sup>24-27</sup> PEDOT:PSS was found to undergo phase separation after casting, leading to lower conductivity.<sup>24,28,29</sup> Also, its acidity has been found to etch the indium tin oxide

surface leading to lower current injection.<sup>30</sup> As an alternative to the more common PEDOT:PSS, the use of self-assembly monolayer (SAM) molecules to modify the indium tin oxide surface has been also shown to increase the wettability of the ITO surface, promote charge injection and shift the anodic work function.<sup>31-34</sup> Properties of SAM-modified anodes can vary depending on the attaching group and its dipole moment.<sup>23,35</sup>

In this work, different SAM molecules were surveyed in order to improve photovoltaic properties of organic solar cells with an active layer based on the bulk heterojunction of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM). Benzoic acid (BA), 2-naphthoic acid (NA), 1-pyrenecarboxylic acid (pCA), 4-(thiophen-2-yl)benzoic acid (tBA), 4-cyanobenzoic acid (cBA), phenyltrichlorosilane (PTCS), and phenylphosphonic acid (PPA) were the SAM molecules used for indium tin oxide modification. All devices with SAM-modified anodes except for that with PTCS modification resulted to improvements in terms of short-circuit current density ( $J_{SC}$ ) when compared to devices with bare indium tin oxide anodes. The increase in  $J_{SC}$  may be due to better charge injection or wettability of the active layer on the anode. Anodes modified with SAM molecules have increased water contact angles indicating a more nonpolar surface, indicating better matching with the polymeric active layer. Improvements in terms of the open-circuit voltage ( $V_{OC}$ ) were achieved for devices modified with SAMs which have its perpendicular dipole moment pointing into the indium tin oxide surface. The reverse was the case for SAM-modified anodes when the SAM molecules used have its perpendicular dipole moment pointing out of the indium tin oxide surface. The orientation of the perpendicular dipole affect  $V_{OC}$  as the dipole generates an electric field either supports or suppresses the built-in electric field of the device. The SAM molecule that resulted to the best performing indium tin oxide anode for organic solar cells was BA



which gave the highest power conversion efficiency (*PCE*) of 0.717% (as compared to the *PCE* of 0.143% of bare ITO anodes). The *PCE* obtained though was still lower than devices modified with PEDOT:PSS. Devices modified with BA and cBA with a PEDOT:PSS layer resulted to higher *PCEs* than unmodified ones with PEDOT:PSS (1.885%, 1.871%, and 1.592%, respectively).

Aside from the modification of the metal oxide with organic molecules, the properties of the metal oxide can be matched to device requirements *via* the modification of its morphology. For metal oxides used as electron acceptor materials in hybrid solar cells, the interface area between the metal oxide and the *p*-type conducting polymer is crucial since the exciton in the *p*-type conducting polymer has a short lifetime corresponding to a diffusion range of only up to 10 nm,<sup>36</sup> requiring a large interface area for dissociation before recombination happens. Aside from this, continuous percolation pathways in the metal oxide are essential for the transport of the charge, generated upon exciton dissociation, to the electrode.<sup>37</sup> Thus the design of the morphology that have both a high surface area and continuous pathways for charge transport is crucial in the improvement of the performance of hybrid solar cells.

In this work, hybrid solar cells based on several zinc oxide morphologies were fabricated and tested for its photovoltaic performance. Improvements in  $J_{SC}$  and  $V_{OC}$  leading to high *PCEs* were found for hierarchical substrates based on the combination of ZnO nanofibers and nanorods due to its high surface area and direct charge transport pathways. Better performing devices can be expected with dye-modification of the hierarchical structure,<sup>38</sup> and optimization of the dimensions of the hierarchical substrate.

The morphology of metal oxides is also important in the electrodes of lithium-ion batteries. The preliminary concern is that the chemical potential of the anode must be

below the lowest unoccupied molecular orbital (LUMO) of the electrolyte and the chemical potential of the cathode must be above the highest occupied molecular orbital (HOMO) of the electrolyte to avoid the reduction-oxidation reactions of the electrolyte with the respective electrode.<sup>39</sup> However, anode materials not meeting chemical potential requirement can be employed with certain electrolytes since the reduction reaction of the electrolyte forms a thin layer of insoluble salts, the solid electrolyte interphase (SEI), that blocks electron transport but allows the transport of  $\text{Li}^+$  to passivate further reduction reactions.<sup>40</sup> Because of this, a battery with higher cell potentials can be formed. However on repeated charge and discharge cycles, the breakdown of the SEI due to high cycling rates can cause the formation of Li dendrites that can grow across the electrolyte and cause short circuits, posing safety concerns.<sup>39,41</sup> The metal oxide lithium titanate,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO), operates at 1.55 V (*vs.*  $\text{Li}/\text{Li}^+$ ), which is within the electrochemical window of practical electrolytes. Also, LTO has been shown to allow the insertion of three Li atoms per formula to form  $\text{Li}_7\text{Ti}_5\text{O}_{12}$  which corresponds to a theoretical capacity of 175 A h  $\text{kg}^{-1}$ .<sup>42,43</sup> The insertion of lithium ions into LTO has been shown to have no effect in the lattice parameters (zero-strain),<sup>42</sup> indicating high stabilities under the stresses of numerous charge and discharge cycles and high cycling rates. Aside from this, at low-potential intercalation, LTO has been shown to allow Li insertion exceeding the  $\text{Li}_7\text{Ti}_5\text{O}_{12}$  composition that corresponds to theoretical capacities as high as 293 A h  $\text{kg}^{-1}$ .<sup>44,45</sup> This additional insertion is expected to be energetically unfavorable in LTO due to the short distance between the occupation sites. However for nanosized LTO, additional Li insertion in near-surface regions was reported to lead to higher capacities. The increase in capacities were more pronounced for smaller particle sizes.<sup>45</sup> It has been reported that the additional capacities found for smaller nanoparticles were due to the increase in the

relative amount of the (111) surface, due to the tailoring of the shape. The (111) surface is the surface wherein Li is additionally inserted whereas the (100) surface is the energetically favored surface for normal Li insertion.<sup>46</sup> The effect of the proximity and orientation of the surfaces of the LTO crystals in the nanoparticles can largely affect the voltage profile. It was reported that the smaller nanoparticles have higher irreversible capacity losses as indicated by shorter voltage plateaus in the discharge curves.<sup>45</sup> These losses were attributed to surface effects, since strain and interface energy upon Li insertion is negligible for LTO.<sup>45,46</sup> Thus it is important to prepare an LTO electrode not only having higher surface areas but also having better surface orientation. In this work, highly crystalline LTO nanofibers were prepared *via* electrospinning and tested for electronic performance for lithium ion batteries. LTO nanofibers were electrospun from precursor solutions containing the lithium acetate and titanium butoxide. Electrospun nanofibers subjected to calcination treatment were confirmed to be of the spinel structure ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) *via* XRD measurement and high resolution TEM imaging. Batteries prepared with nanofiber based anodes were found to give higher discharge capacities at high discharge rates than nanoparticle based anodes. Higher capacities at high rates is important for high power applications like electric vehicles. The high capacities are attributed to shorter electron and  $\text{Li}^+$  transport path brought about by the smaller spinel crystallites of the nanofibers as compared to the nanoparticles.

In summary, different methodologies of metal oxide modification can be done to match important requirements of devices used in solar energy conversion and storage applications. Although the performance gains obtained in the prepared devices can not completely answer the requirements need for practical solar energy usage, these small

gains may provide significant information in the design of materials for the efficient solar production of hydrogen and electricity.

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