

**NASA-EPSCoR Whitepaper Proposal**

**Title: Nanotechnology Assisted Solar Water-Splitting, Solar-Cell, and Fuel-Cell**

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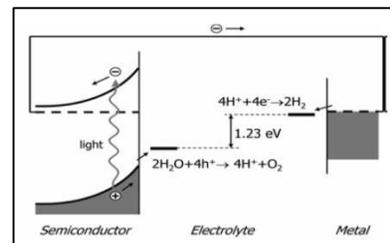
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## PROJECT DESCRIPTION AND CONTENT.

### A. Motivation and Purpose.

Developing new science and technologies for solar water-splitting, solar cell, and fuel-cell can help boost the economy (e.g. logistics-heavy businesses such as Walmart, Tyson Foods, J. B. Hunt, etc.) and K12-STEM education in Arkansas and USA. New findings can help NASA meet future mission-critical need in solar-energy conversion and utilization because water, for instance, could be found from heating water-containing minerals (besides ice) from deep-space, including planets like Mars.

Conventional solar water-splitting (*Figure 1*), for example, relies on shining sunlight onto a semiconductor photoanode in a photoelectrochemical cell in an acidic or alkali electrolyte to generate electron-hole pairs. In the electrolyte, the holes in the photo-anode split  $2\text{H}_2\text{O}$  into  $4\text{H}^+$  and  $\text{O}_2$ . The  $4\text{H}^+$  cations move to the metal cathode, receive electrons, and form two  $\text{H}_2$  molecules as sketched in *Figure 1*. Traditionally, a semi-conductor such as Si is used as the photoanode, and chemically inert but catalytically active precious metals – typically Pt or Au – are used as the electrocatalyst. Enormous work has been put on prolonging the semiconductor lifespan and using lower-cost metals or alloys.



*Figure 1. Conventional Water Splitting*

This team has seamlessly worked together for four years. Uniquely, we developed new  $\text{MoS}_2$ <sup>1</sup> nanostructures for hydrogen evolution reaction (HER), >20 prototypes of  $\text{MoS}_2$ - and CIGS-based solar-cells<sup>2</sup> (12.4% efficiency),  $\text{H}_2$ -based proton exchange membrane fuel cell (PEMFC, temp >200 °C, see Task-VI), and the LTCC technology (see Task-VII), each truly leading in its field. Most recently, we made new perovskite materials that can boost the solar-cell efficiency to ~ 20% (higher than IBM best product's).<sup>3</sup>

### B. Goals and Anticipated Results:

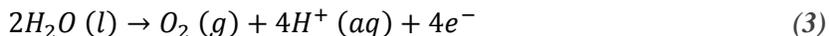
On this basis, we hereby propose to further develop new nanomaterials, and to deliver industry-viable prototypes of these devices' integration for benefiting both NASA and USA household. In the proposed work within the next three-years, we will boost the solar-energy conversion with the new nanostructured semiconductive perovskite, and replace the precious-metal catalyst with low-cost high-efficiency metallic  $\text{MoS}_2$  nanosheets. This new combination will practically lower the cost of water-splitting and improve HER efficiency greatly. In addition, we will integrate our pre-existing metallic  $\text{MoS}_2$  nanosheets and perovskite-based solar conversion technology into the water-splitting, with a practical goal to deliver a water-splitting prototype with a solar conversion efficiency >15%. In parallel, new PEMFC prototypes will be developed to effectively utilize the water-split  $\text{H}_2$  from the hydrogen HER, in which a hydrogen-storage technology will be developed and integrated into the PEMFC for the first time in the field.

The proposed prototypes, to be high disruptive in the market, were never reported in literature. This is because such teamwork demands not only materials chemists and physicists to work seamlessly and extensively with nanodevice-engineer, but also extensive experiences and knowledge in the related fields for all the team-members, which is why our team was formed to do the proposed work below.

### C. Task-I. Development of New Nanostructured Catalysts for Solar Water-Splitting. (Chen and Tian)

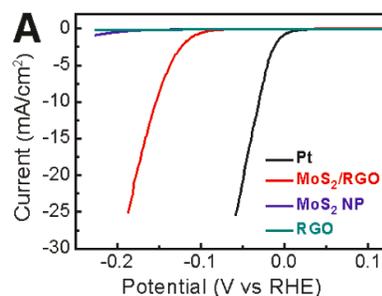
By using an advanced catalyst HER, the overpotential can be reduced and the resulting electrochemical process efficiency will be increased. In general, the catalytic rate of the HER is two to three orders of magnitude greater in an acidic (pH = 1) solution than in an alkali (pH = 13) solution<sup>4</sup>. In an acidic solution, the three reaction mechanisms involved in the water splitting process are





The overall reaction equation for the electrolysis of water is shown in *Equation (1)*. The cathode and anode half-reactions are given in *Equations (2) and (3)* respectively. In the cathode half-reaction, electrons combine with the hydrogen cations to form hydrogen gas. In the anode half-reaction, an oxidation reaction occurs resulting in the release of oxygen and electrons for the anode. As the latter producing hydrogen and oxygen is thermodynamically unfavorable, the reaction can only be facilitated through the use of an electrocatalyst such as the previously mentioned platinum. As a result of this electrochemical limitation, widespread and cost-effective H<sub>2</sub> fuel is commercially unfeasible without replacing the use of platinum and other precious metal electrocatalysts with low-cost, abundant alternatives.

In the search for alternative materials for HER, the free energies of several replacement materials were calculated and MoS<sub>2</sub> was found to be comparable to platinum<sup>5</sup>, especially for MoS<sub>2</sub> nanoparticles supported on graphite. Thus, the latter may provide a new class of materials suitable as the electrocatalyst for higher-efficiency HER. As shown in *Figure 2. Polarization curves with several catalysts as Pt, MoS<sub>2</sub>/RGO, MoS<sub>2</sub> NP and RGO.*, our previous studies have demonstrated that the performance of hybridized MoS<sub>2</sub> and graphene oxide is still inferior to platinum for HER, especially in the generation of electric current at a lower reversible hydrogen electrode (RHE) potential. Thomas et al. have found that for semiconductor MoS<sub>2</sub>, the catalytic active sites are found at the edges of the MoS<sub>2</sub> nanosheets<sup>6</sup>. Thus challenges still remain in the search for better, lower-cost catalysts to replace platinum and other precious metals for HER.



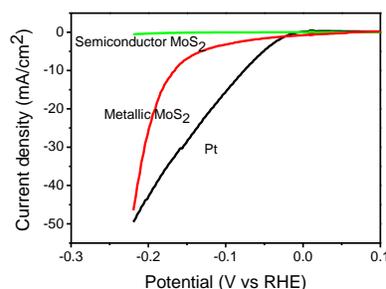
*Figure 2. Polarization curves with several catalysts as Pt, MoS<sub>2</sub>/RGO, MoS<sub>2</sub> NP and RGO.*

#### **D. Task-II. Further Development of New Nanostructured Metallic MoS<sub>2</sub>. (Chen, Tian, and Ang)**

As the semiconductor phase of MoS<sub>2</sub> is thermodynamically favored, metallic phase MoS<sub>2</sub> does not exist in nature. Metallic phase MoS<sub>2</sub> is merely metastable and can easily transition to its semiconductor phase due to its weak sulfur-sulfur van der Waals interaction. However, metallic MoS<sub>2</sub> has a higher electric conductivity than its semiconductor counterpart and is hence preferable<sup>7,8</sup> for use as an HER electrocatalyst.

Despite the requirement of metallic MoS<sub>2</sub> for higher-efficiency HER, achieving stable metallic phase MoS<sub>2</sub> is a significant hurdle. Over the past few decades, no effective approach has been found for attaining stable, high-purity metallic phase MoS<sub>2</sub>. The only known method for preparing large amounts of metastable metallic MoS<sub>2</sub> is through the exfoliation of intercalated semiconductor phase MoS<sub>2</sub><sup>7-9</sup>. However, this method includes its own problems – producing the dangerous intermediary product Li<sub>x</sub>MoS<sub>2</sub> which self-heats in air<sup>10</sup>, producing a heterogeneous mixture of metallic and semiconductor phase<sup>11</sup> MoS<sub>2</sub>, requiring three or more days to complete the process, and the resulting metallic portion of the mixture can easily revert to its semiconductor phase. For the abovementioned reasons, preparing a large quantity of stable metallic phase MoS<sub>2</sub> requires an efficient synthesis process that avoids aggregation, maintains stability, and results in a high level of purity.

It is in this regard that our group's recent fabrication of metallic MoS<sub>2</sub> in water may prove fruitful. Our fabrication was the



*Figure 3. Electrochemical performance of metallic phase MoS<sub>2</sub> (1T MoS<sub>2</sub>) and Semiconductor phase MoS<sub>2</sub> (2H MoS<sub>2</sub>) nanosheets.*

first time that metallic MoS<sub>2</sub> was synthesized directly in water without the application of pressure. The properties of our metallic MoS<sub>2</sub> are promising. *Figure 3. Electrocatalytic performance of metallic phase MoS<sub>2</sub> (1T MoS<sub>2</sub>) and Semiconductor phase MoS<sub>2</sub> (2H MoS<sub>2</sub>) nanosheets.* demonstrates the electric current density versus RHE potential curves for our samples when used as the HER catalyst. It would seem that the curve for our metallic MoS<sub>2</sub> sample (in red) are much closer to platinum (in black) than that of semiconductor MoS<sub>2</sub> (in green).

Compared to platinum and other current precious metal-free catalysts, our proposal of using metallic phase MoS<sub>2</sub> as the catalyst has five unique advantages:

1. the metallic phase MoS<sub>2</sub> can be directly synthesized in water and our solution-based preparation of layered materials is relatively low cost despite having unique properties for practical application,
2. metallic phase MoS<sub>2</sub> is produced without the presence of semiconductor MoS<sub>2</sub> and, as shown in *Figure 3. Electrocatalytic performance of metallic phase MoS<sub>2</sub> (1T MoS<sub>2</sub>) and Semiconductor phase MoS<sub>2</sub> (2H MoS<sub>2</sub>) nanosheets.*, metallic phase is highly preferable to semiconductor MoS<sub>2</sub>,
3. the incremental interlayer spacing provided by the weak sulfur-sulfur van der Waals interaction between adjacent layers and the layers of water on both sides of the nanosheet of metallic phase MoS<sub>2</sub> prevents it from aggregating and keeps it phase-stable in water,
4. the suspension of metallic phase MoS<sub>2</sub> can be easily dispersed in water through simple sonication and this dispersion may allow MoS<sub>2</sub> to mix with graphene and reduce graphene oxide in water,
5. the catalytic active sites may be identified by dropping the metallic MoS<sub>2</sub> onto a copper grid and silicon substrate for high-resolution transmission electron microscopy (HRTEM) and scanning tunneling electron microscopy (STM) studies.

For the above reasons, we believe that the proposed metallic phase MoS<sub>2</sub> has the potential to be a significant breakthrough in the development of solar-powered water splitting. In our proposed project, we aim to improve the stability of the metallic MoS<sub>2</sub> for use as an electrocatalyst for HER.

### **E. Task-III. Further Development of the Perovskite Photovoltaics. (Chen and Tian)**

Perovskite-based materials have been successfully used as light absorbers for photovoltaic cells. By controlling the formation of the perovskite layer and carefully choosing the other materials to suppress carrier recombination in the absorber, facilitate carrier injection into the carrier transport layers, and maintain good carrier extraction at the electrodes, the power conversion efficiency (PCE) of perovskite-based thin film photovoltaic devices has increased from 3.8% to more than 19% in the past 5 years<sup>3,12-14</sup>. Currently the highest efficiency is approximately 19.3% and was obtained through film. This efficiency could be further improved through the use of nanostructured perovskite.

Flexible perovskite solar cells could be fabricated with PCEs greater than 10%<sup>15</sup>. In their paper, Liu et al. reported that a thin layer of ZnO nanoparticles was used as an electron-transport layer for perovskite-based CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> solar cells. The incident photon-to-current efficiency (IPCE) spectrum of devices fabricated on polyethylene terephthalate (PET) displays a broad peak at 450 nm with a pronounced shoulder at 680 nm. This illustrates a substantial loss of photocurrent in the 500 to 800 nm range relative to comparable devices fabricated on glass. Developing an excellent conducting, transparent top layer to replace the gold electrode of the device to allow for more incident light is an important step toward increasing solar efficiency.

In our project, we intend to approach development from both sides. As perovskite has been found to be an excellent material for sunlight absorption, we will use perovskite-based semiconductors as sunlight absorbers to generate electron-hole pairs. Additionally, we intend to use graphene – a nearly transparent material with an electrical conductivity at least one order of magnitude greater than that of ZnO – as the electrode for our solar cells. A single layer of graphene has a transparency greater than 97% of incidental

sunlight. For this reason, graphene will be employed as the top electrode for flexible perovskite solar devices which will yield higher photovoltaic and electrical efficiencies.

#### F. Task-IV. Exploring New H<sub>2</sub>-Production Science for Solar Water-Splitting. (Chen and Tian)

Solar-powered water splitting is both an ambitious goal and the natural culmination of the aforementioned processes. This can be accomplished through two strategies – (1) direct conversion of solar energy to chemical fuel, and (2) indirect conversion of solar energy to fuel through photovoltaic-to-hydrogen production. In the former case, an applied bias voltage is required for the photoelectrochemical water splitting process or the efficiency of hydrogen production is relatively low. For example, a system using TiO<sub>2</sub>/MoS<sub>2</sub>/graphene as co-catalysts in a 1M Na<sub>2</sub>SO<sub>4</sub> aqueous solution for photo-catalytic H<sub>2</sub> production under UV irradiation at 0.5 V versus Ag/AgCl which produces a photocurrent response in the TiO<sub>2</sub>/MoS<sub>2</sub>/graphene that is less than 0.1 mA/cm<sup>2</sup><sup>16,17</sup>. This photocurrent is significantly lower than the 10 mA/cm<sup>2</sup> from MoS<sub>2</sub>-based electro-catalytic systems with a low overpotential of -187 mV relative to RHE<sup>7</sup>. For this reason, the study of sunlight use without an external bias may be a necessity for improving the efficiency of the first method.

For the second method, the highest water photolysis efficiency is approximately 12.3% and has been attained via perovskite photovoltaic devices and NiFe-layered double-hydroxide catalysts<sup>18</sup>. In this case, the performance of the NiFe-layered double-hydroxide/Ni foam electrode is much better than bare Ni foam and slightly better than Ni(OH)<sub>2</sub>/Ni foam, but still worse than the standard Pt/Ni foam electrode. In conclusion, a better, higher-efficiency catalyst is required for indirect solar hydrogen production.

We propose the development of direct-sunlight water splitting devices without the use of expensive apparatuses by integrating perovskite photovoltaic cells and metallic phase MoS<sub>2</sub>. The proposed integrated device would be assembled on the same indium-doped tin oxide (ITO) coated glass and PET substrate including a perovskite solar cell and metallic MoS<sub>2</sub> catalyst. The proposed project may also speed up the understanding of catalytic active sites within metallic MoS<sub>2</sub>, a subject that has been attractive to study but remains yet unexplored. The efficiency of our proposed direct-sunlight water splitting project is anticipated to reach at least fifteen percent (15%).

#### G. Task-V. Integrating H<sub>2</sub>-Storage and Pressure-Regulating Technologies into the Fuel-Cell. (Tian and Ang)

Hydrogen (H<sub>2</sub>) is an attractive option as a fuel for fuel cells because (1) it has high-energy content (120 kJ/g vs. 44 kJ/g for gasoline) and (2) clean product (i.e. water) is produced during the operation of H<sub>2</sub>-based fuel cells. The United States Department of Energy (USDOE) predicts that adsorptive or chemical storage, provided with further technological improvement, can store H<sub>2</sub> more effectively than the currently widely used technologies of compressing or liquefying hydrogen. Integrating a hydrogen-storage MOF into a PEMFC, which was seldom discussed in literature, should have the great advantage on regulating H<sub>2</sub>-pressure and H<sub>2</sub>-molecule's diffusion for developing future smart-PEMFC.

Metal organic frameworks (MOFs) are composed of metal ions or small metal-containing clusters connected by multidentate organic ligands, and are porous in crystal structures. They have been considered a very promising candidate of storing H<sub>2</sub> for fuel cells<sup>19</sup> for the following reasons.

First, MOFs are chemically stable and their structures can be widely tuned through varying metal ions/cluster, ligands, and connection modes to afford exceptionally high surface areas and thus optimize H<sub>2</sub> adsorption. Second, MOFs store H<sub>2</sub> through physical adsorption and the adsorbed H<sub>2</sub> can be much more easily released than those stored through chemical adsorption since the bond enthalpies of the former (less than 20 kJ/mol) are much lower than the latter

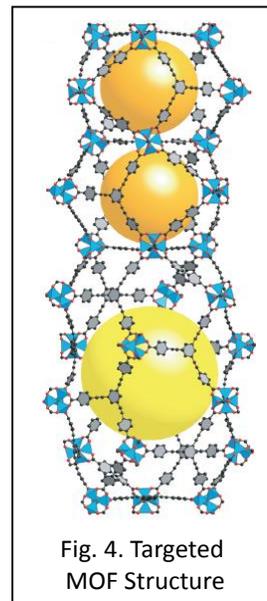


Fig. 4. Targeted MOF Structure

(250–500 kJ/mol).<sup>20</sup> Third, MOFs have no dead volume and thus the non-accessible volume can not induce storage-capacity loss.

Currently, most of the MOFs materials crystallize in tens to hundreds of micrometers in dimension and thus can be characterized by single-crystal X-ray diffraction (XRD). Their nanomaterials counterparts should have significantly boosted surface areas and thus H<sub>2</sub>-storage capacity.

We aim at preparing nanomaterials of those MOFs that, in their bulk forms, already demonstrate the highest H<sub>2</sub>-storage capacities (**Figure 4**). MOFs of interest include but not limited to (1) NU-100 (NU = Northwestern University, Cu<sub>3</sub>(TCEPEB)(H<sub>2</sub>O)<sub>3</sub>, TCEPEB = 1,3,5-tris[(1,3-carboxylic acid-5-(4-(ethynyl)phenyl)ethynyl)-benzene] which has a high Brunauer–Emmett–Teller (BET) surface area of 6143 m<sup>2</sup>/g, the highest excess H<sub>2</sub> storage capacity 99.5 mg/g at 56 bar and 77 K, and a total capacity of 164 mg/g at 77 K and 70 bar.<sup>21</sup> (2) MOF-210 (Zn<sub>4</sub>O(bte)<sub>4/3</sub>(bpdc), H<sub>3</sub>bte = 4,4',4''-[benzene-1,3,5-triyl-tris(ethyne-2,1-diyl)]tribenzoic acid and H<sub>2</sub>bpdc = biphenyldicarboxylic acid) which has a BET surface area of 6240 m<sup>2</sup>/g and the highest total H<sub>2</sub> storage capacity (176 mg/g) at 77 K and 80 bar.<sup>22</sup>

Conventional methods for nanomaterial synthesis, such as template synthesis, seeded growth, and layer-by-layer technique, will be employed to prepare MOFs nanomaterials. Our goal is to meet the 2015 H<sub>2</sub>-storage standard set by USDOE<sup>23</sup> which includes the following parameters: (1) a H<sub>2</sub>-storage capacity of 40 g H<sub>2</sub>/L, (2) 10 min or less time for H<sub>2</sub> refueling, (3) a lifetime of at least 1000 refueling cycles, and (4) operational from 30 to 50 °C.

The HiDEC has experiences in making pressure-sensing microdevices. For the first time, this H<sub>2</sub>-pressure monitoring will regulate H<sub>2</sub> diffusion and pressure-surge in developing a much smarter PEMFC.

### **G. Task-VI. Optimizing Catalyst-stabilizing, Thermal-stable, Nanofiber-Nafion-Graphene Composite PEM. (Tian and Ang)**

**Background:** For decades, governmental/industrial/academic labs worldwide have been putting countless efforts on blending inorganic moieties into Nafion, in the hope to form a new composite with the key properties (e.g. proton conductivity, thermal stability, mechanical strength, etc.) much better than the Nafion's. To date, however, not much progress has been made in creating such an ideal composite that can simultaneously meet all these criteria for running the new FC at the low temperatures (e.g. <150 °C) and intermediate temperatures (e.g. 200 °C – 300 °C).

Our team started seamlessly in 2009 to try to meet these Nafion's long-unmet challenges. We propose to use our patented titanate nanofibers to develop entangled freestanding membrane can form a composite with Nafion based on the following intuitions/logic/ideas:

- The titanate nanofiber's clay-like layered crystal lattice can allow the protons to conduct easily along the nanofiber's longitudinal surface, which was not reported in literature then;
- The nanofiber's one-dimensional morphology can guide the Nafion-polymer's backbone to crystallize better, and tune the nanocomposite's crystallinity and in turn its thermal stability and mechanical strength, which was well established in many nanocomposites but not such PEM at that time;
- The controllably reduced graphene oxide (rGO) and surface-functionalized graphene oxide SFGO with widely tunable surface redox properties may enable us to fine-tune the nanocomposite's proton-/electron-/heat-conductivities, hydrophobicity/hydrophilicity level, and the PEM's surface functional groups and pore-shape/size (for optimally supporting the catalyst nanoparticles);
- The nanofiber-Nafion-rGO composite PEMs can stabilize the catalysts even after the fuel-cell's 1,000 times of cycling in between room-temperature and the intermediate operational temperatures.

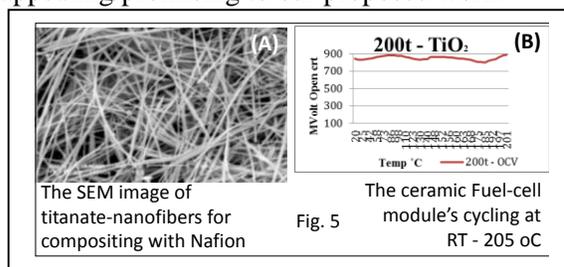
**Preliminary Data and Objectives:** Our FC-module's nanofiber-Nafion PEMs (**Figure. 5**) don't show the longstanding problems of membrane's swelling/deterioration, etc. in normal PEMFC- or intermediate temperature FC (ITFC)-stacks. This is attributed to that our nanofiber itself is thermally stable above 400 °C, and its layered lattice has high proton-exchange and surface-functionalization capacities, which will afford a high proton-conductivity (like those in rechargeable Li-ion battery) and a high corrosion-resistance when compositing with Nafion, in theory and intuition. Further, each nanofiber will induce the Nafion polymer-backbone to crystallize well (i.e. a higher crystallinity) around it which in turn will drastically improve the resultant PEM's mechanical strength, thermal stability, and blockage to fuel-/water-molecules. These are unavailable to spherical ceramic particles thus appealing/promising to our proposed work.

Moreover, the nanofiber-Nafion PEM-based ITFC showed that our nanocomposite-PEM prevented the catalytic Pt-clusters from sintering and kept the ITFC operational above 200 °C. This can be attributed to the nanofiber-enabled pore-structures and proton-passages widely tunable across the PEM, which prompts us to explore the highest operational temperature and fuel-to-electricity efficiency for the ITFC. According to reports

in literature, blending fully/partially reduced graphene-oxide (rGO) into the PEM may substantially improve the PEM's proton-conductivity, mechanical strength, thermal-stability, and resistance to the fuels- and water-crossovers, since the rGO is hydrophobic. Thus, we propose that the rGO-enriched PEM may prevent the 3–5 nm sized (the ideal size-range known for PEMFC) Pd-nanoparticles (or Pd-NPs) from migration (or sintering) at elevated temperatures over **1,000 cycles** of operation, and simultaneously minimize (i) the fuel-/water-crossover, (ii) PEM swelling, and (iii) the catalyst oxidation or poisoning by sulfur-containing molecules in fuels, to name but a few which may be challenging for pure Nafion.

**Task-VI-1: Optimizing the low-cost nanofiber's synthesis, crystal lattice and surface:** Our patented synthesis of straight nanofibers is done around 240 °C in a 125-ml autoclave vessel containing TiO<sub>2</sub>-powder in a 10M NaOH solution, which imposes a challenge in scaling up to the metro-tons level. Thus, we will try to use a reflux synthesis near 100 °C –150 °C, to hopefully result in a new synthetic route faster and cheaper than the higher-temperature autoclave method, and more suitable for future large-scale production. At the same time, microwave- and IR-based fast heating will be tried, which is promising based on our preliminary data. Here, KOH will be used for replacing NaOH in order to result in curved nanofibers that may composite differently or even better with the Nafion. Here, XRD, SEM, and TEM will be used for characterizations. In parallel, the nanofiber's diameter will be varied from 10 nm to 100 nm while the length from 100 nm to 100 μm, in order to test which diameter/length would best composite with the Nafion polymer-backbone. Here, the diameter/length control was shown, in our own work, to be determined by controlling the time/temperature and starting-materials' concentration in the autoclave environment, in which thinner nanofibers are usually in short lengths and vice versa. The diameter/length combination will determine the nanofiber's entanglement in the composite, and in turn the pore-structure in the PEM, which will be monitored using on-campus SEM and TEM.

In addition, the nanofiber's negatively charged crystal-lattice framework will be doped with similarly sized cations such as Al(III) or V(V), so as to replace the Ti(VI) in the lattice to fine-tune the lattice's overall charge density across the nanofiber's length and diameter. The doping will be conducted by, for instance, mixing the substituting cations in the solution over the time in the autoclave rather than in air, in which the hydrothermal condition may speed up the ion-exchange process. The optimized charge-density is believed to be critical to optimally conducting the protons, electrons, heat, and also to stabilizing the catalyst-nanoparticles in a programmable/optimal distribution on the nanofiber without the unwanted migration (since the migration can sinter the nanoparticles and reduce the catalyst-activity) even at the



The SEM image of titanate-nanofibers for compositing with Nafion

The ceramic Fuel-cell module's cycling at RT - 205 oC

elevated temperatures. The XRD pattern may tell the lattice-constant change from the doping, and SEM-EDX and ICP-MS will help us determine dopant concentrations.

At the same time, the nanofiber's lattice intercalation via cation-exchange will be systematically studied in order to make the resultant surface's isoelectric point optimal for stabilizing the catalyst NPs over the cycling. The science is because the temperature-change over the cycles will make those physically adsorbed NPs delaminate from the nanofiber, due to the difference in thermal expansion coefficient between the NPs and the nanofiber. In other words, only those NPs chemically bonded on the nanofiber can sustain the temperature cycling from the PEMFC's practical on/off in operation. In this part, protons occupying the inter-layer space throughout the inner-lattice and surface as one extreme, while laying proton only on the surface only (i.e. leaving the inner-lattice sites being occupied by other cations such as Na(I) ) such that the overall lattice isoelectric point and thermal-stability can be balanced. This work will be based on such a fact that 100% proton-exchanged nanofiber can lose water easily at the elevated temperature (~300 °C) to form TiO<sub>2</sub>-B or even anatase that are hard to keep the 1D-nanofiber structure. In turn, the isoelectric point and surface-cation type will greatly affect the charge-transfer and catalyst-NP impregnation, which will be studied coherently with the diameter/length/lattice/surface optimizations mentioned in the above. Likewise, XRD, SEM-EDX, and ICP-MS will help us characterize the samples from this step.

On this basis, nanofiber surface will be functionalized using silane-coupling reactions with thermally stable molecules tailed by functional groups (from commercial sources such as Gellest) similar/identical to that in the Nafion. The proton-conducting functional groups densely packing on the proton-surfaced nanofibers will make the proton-hopping distance much shorter than that in the Nafion-polymer backbone, so as to boost the proton-conductivity.

The surface-functionalized samples will be mixed with KBr powder and then pressed into pellets for FTIR tests for studying the functional groups. In addition, temperature-programmed desorption (TPD, to be built from a tubular-furnace and a GC acquired in this project), Mass Spectroscopy, XPS, AFM, and HRTEM will be used for studying the surface-functional groups.

#### **Task-VI-2. Optimizing the ceramic nanofiber-rGO and the nanofiber-SFGO composites**

Based on the above idea of using carbon-free catalysts, the rGO's and SFGO's roles in advancing new rechargeable batteries and fuel-cells should be a new topic in fuel-cell science, thanks in part to the GO's tunable charge-conduction across its surface that can be functionalized with abundant molecules and methods well established in literature and observed in our lab. It's believed that the rGO's surface functional groups can indeed act much like that of the oxide nanofiber as mentioned earlier. In this work, rGO's reduction degree will be tailored, by varying not only the temperature and time in the reductions (e.g., different methods of heating), but also the concentration/temperature and power of the reducing agents (e.g. NaBH<sub>4</sub>, LiAlH<sub>4</sub>, hydrazine, etc.). In parallel, SFGO will be developed using surface-functionalization reactions, e.g. silane-coupling reactions in methanol.

Next, the rGO and/or SFGO will be blended with or anchored onto the nanofibers, so as to hopefully wrap (or coated) on each nanofiber's surface in an optimal fashion (e.g. densely standing or laying-laminated on the nanofiber-surface), based on what we have exploited in the past three years. Ideally, a strong oxide-alike bond between the rGO (or SFGO) and the nanofiber surface will be formed upon a controlled heating, via releasing H<sub>2</sub>O. Here, the rGO's and SFGO's size/shape and density on the nanofiber-surface will be systematically varied, which will affect the optimization of the next-step impregnation of the catalysts-nanoparticles and the proton-conduction. Again, simulation and modeling of Task E will greatly help to reduce the amount of experimental work needed to deliver the result, and microRaman, diffuse-reflectance FTIR, FESEM and TEM will be used for characterizing the optimized nanofiber-rGO composites timely.

**Task-VI-3. Optimizing structure/surface of the ceramic nanofiber-rGO-Nafion composite:** This task is not just simply to mix or blend the nanofibers, rGO (or SFGO) and Nafion-polymer-solution into one pot. First of all, an optimal composition of the three components will need to be found from a systematic

variation of a large matrix of fabrication parameters (e.g. temperature, concentration, time, ratios, and the mixing method) based on our previous experiences in the related work, which could be time-consuming and challenging. Second, casting the nanocomposite into PEM will be focused on controlling the PEM's thickness and the nanofiber/polymer-backbone crystallinity in the PEM. Since the PEM's fabrication recipes vary widely in literature, we will test if a certain percentage of the highly hydrophobic graphene (GA) inside the PEM will help maximize the proton-conductivity and minimize the long-term solvent crossover and swelling for the new ITFC. The anticipated high-toughness PEM will sustain in addition the pressure formed by fuel and the resultant H<sub>2</sub>O at the high temperature, which is the steaming environment in which catalyst-supports made of 100% ceramics (e.g. zeolites) may not survive/work.

In order to cast the PEM optimally, "doctor-blade", brushing, spray-coating, and even roll-to-roll (R2R) printing methods will be used to help us rationally identify the best/cheapest method or the optimal combination of methods. The resultant PEM's thickness, thermal stability, mechanical strength, proton-conductivity, and electrical conductivity will be characterized by means of AFM, FESEM, HETRM, EDX, tensile-strength tester, diffuse reflectance FTIR, TGA/DSC, GC-MS, four-probe tester (van der Pauw's method), impedance tester, FTIR, XRD, XPS, and microRaman.

**Task-VI-4. Optimizing impregnation of catalyst-nanoparticles on new PEM:** Indeed, the NP-impregnation on/in the new PEM will dictate the success/failure of the new PEMFC. Here, simply pressing the NPs onto the PEM may be too crude to improve much for the catalytic-PEM. In fact, the NPs will be anchored onto the nanofiber-surface before casting the PEM, or mixed into the mixture before the PEM-formation, or transferred onto the PEM after the PEM's formed. These three ways will be studied in parallel.

In order to anchor the NPs onto the nanofiber surface, we will try to functionalize the nanofiber-surface with the thiol-tailed molecules, because the thiol-group can bond strongly with the NP. Moreover, the pore-structure on/in the PEM will be fine-tuned accordingly, in order to envelope/encage the catalytic NPs optimally so as to discourage the heat-induced NP migration (i.e. the unwanted NP-sintering). In this sub-task, we will evaluate whether the highest loading of NPs on the nanofiber-surface would be the best, for cost-effectiveness and for minimizing possible side-reactions at the elevated operation temperature for the intermediate temperature PEMFC.

Mixing the NPs inside the mixture to form the composite PEM will be systematically studied at the same time. Basically, we will vary the order of mixing, optimize the NP's wetting on the polymer-backbone in the mixture (so as to avoid possible unwanted phase-separation), and choose a proper shear-mixer for not breaking but well dispersing the NPs and nanofibers and for not inducing much heat during the blending of the viscous mixture. If too much heat is generated in order to get the mono-dispersed NPs and nanofibers, a cooling (e.g. ice bath) will be used. Here, we will also try to solve a longstanding puzzle regarding the NPs optimal locality/distribution on/across the PEM.

The resultant NP/nanofiber/Nafion composite will obviously have a high-content of the catalytic NPs. Hence, we will try to coat a thin-layer of the composite on a pre-cast PEM inside which there is no such NP, so as to help us to differentiate which design would be the low-cost.

Directly pressing the NPs onto the PEM would be another route that we will study, based on our up-to-date experience on Pt-NPs instead. This method will probably use the least amount of the catalytic NPs, which will enable us to compare with the PEM-coating mentioned in the above paragraph. For stabilizing the NPs on the PEM, the NP-suspended/dispersed liquid will be sprayed directly onto the PEM, then dried in air or through a mild-heating, and then mechanically pressed to force the NPs imbed into the thin-crust of the PEM-surface. The entire process will be repeated for a few times to have enough loading of the NPs on the PEM, which will be optimized via adjusting the NP-content in the suspension and how many times of the spraying. Moreover, timely PEM testing will guide us quickly to move toward optimizing the catalytic PEM fabrication. In addition, findings from this sub-task will be fed back to the catalyst-NP's design/development in Task B, so as to enable us to integrate our sub-tasks in a more efficient manner.

## **H. Task-VII. Miniaturization and Integration of Smart Fuel-Cell Modules. (Ang and Tian)**

***Background/Objectives:*** Based on our decades of experience in developing microsystem-integration technology at the UAF's High-Density Electronics Center (an integration center started initially by a DARPA grant from 1991–2001 at UA), we plan to optimize a manufacturer-viable, durable and low-cost modular fuel cell system integrated with various nanostructured membranes, catalysts, and electrodes. Three dimensional interconnects and cavities afforded by low-temperature co-fired ceramic (LTCC) technology enable fuel cells to be completely integrated within a thin ceramic slab structure<sup>24-25</sup>. This leads to smaller module size, enables operation in extreme environments (LTCC is capable of operation at 850°C and corrosion resistance), and paves the way for integration of additional electrical power management devices (LTCC is used for hermetic electronic package applications) or mechanical on-board functions (sensors and actuators can be integrated onto LTCC substrates).

The LTCC technology gives us the flexibility of current collector cavity sizes from under 0.5" x 0.5" all the way through 8" x 8", the largest size of available commercialized ceramic materials (green ceramic tapes). In this way the active area of the fuel cell can be controlled by design to apply to applications from portable power in consumer electronics, automobile power sources, to stationary applications. The structure of the LTCC-based fuel cell consists of gas channels and anode/cathode current collectors embedded in thin LTCC ceramic structure. Two ceramic halves are mated to form the assembly that houses the gas diffusion layer and the gas barrier membrane as well as the membrane electrode area (MEA). The MEA functions to separate electrons at a conductive anode and to conduct the electrons to an external circuit. This must be done while allowing the hydrogen ions to pass through a gas barrier to the cathode so that it may recombine with electrons and ultimately balance the reaction. Many variables affect cell performance including gas channeling methods, diffusion layer construction, electrode-to-diffusion layer interface, and electrode conducting material<sup>26</sup>.

In each such fuel cell module, many of these fuel cells are integrated, connected in series or parallel configurations through internal module interconnections (**Figure 6**). When connecting the modules to a central power bus, a "power pack" system is formed that can be scaled up or down, like playing Lego, in order to meet the customer's changing needs of current-outputs from 100s to 1,000s of amperes, so as to be disruptive in the market. Due to the batch processing nature of the LTCC technology, the cost of manufacturing is significantly reduced as thousands of these fuel cell modules can be precisely fabricated in a single production batch with high throughput. Moreover, the investment for the thick film processing facilities is a small fraction (<1%) of those conventional semiconductor thin-film processing facilities.

The assessment of the present capabilities of our LTCC fuel cell module technology includes:

- Smaller, lighter fuel cells with a higher power density.
- Cells that can be rebuilt, repaired, and recycled. Our current design allows the LTCC 24-cell module to be changed out and repaired or recycled.
- Fuel cartridges that can be changed out and/or refilled for portable applications. Solid storage allows for the quick exchange of spare canisters and can be refilled using a fresh metal hydride hydrogen source for portable application.

- Minimal hazardous waste, since all materials can be reused.
- Green: Zero emission with no toxic gas and only water vapor as by-product.

The proposed technology will provide increased capability through:

- The ability to be applied to many form factors for portable applications for automobiles or stationary platforms.
- The ease with which the modules can be ganged together to allow various output configurations.
- Easy re-configuration or connections with different voltages can be delivered to allow a wider range of devices to be powered.

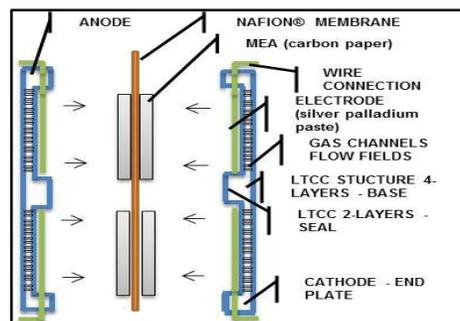


Fig. 6. Cross section of 4-cell end plate.

**Task-VII-1. Module Design:** Cell construction will begin with MEAs built using carbon cloth on carbon paper doped with  $0.5 \text{ mg/cm}^2$  of a platinum/ruthenium (Pt/Ru) in a 1:1 ratio. Fuel channel size is the first variable taken into consideration when designing the cells. It is already known that channel shape and size has a significant effect on output levels.<sup>27</sup> In order to establish a starting point, 20 mil round holes will be selected using a  $0.5 \text{ mm} \times 0.5 \text{ mm}$  grid layout for the gas flow fields. A ceramic structure will be designed that anchors four MEAs, channels the fuel, integrates the collectors, and provides the necessary electrical interconnect for multiple cell configurations.

The collector cavity size of these ceramic fuel cell modules will be varied from  $< 0.5'' \times 0.5''$  to  $8'' \times 8''$ , depending on the application needs. **Figure 7** shows the LTCC structure with four single current collectors built into a single ceramic plate (anode). Here, LTCC technology will provide the needed isolation and separation that standard metal plates could not, in addition to being lower in weight and smaller in size<sup>24</sup>.

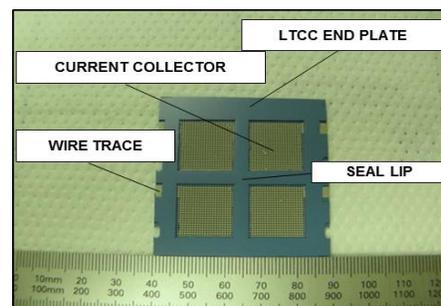


Figure 7. Current collectors in one plate.

**Task-VII-2. Module Construction:** DuPont 951 Green Tape with a 10 mil thickness will be used for fabrication of the cells. This tape available in multiple thicknesses will be designed for use as an insulating layer.<sup>28</sup> As seen in Figure 6, both the anode and cathode plates will have a similar build sequence, thus easing the batch processing requirements. Each plate will begin with a four-layer tape base. An AutoCAD software will be used to design the artwork used for fabrication. The artwork will be converted to run on an automatic tape-punching tool, where layers will be then punched automatically. Following this, the four layers will be laminated together to form 40 mil-thick unfired end plates. The LTCC surfaces will then metallized by applying a paste mixture of silver and palladium. This conductive paste will be used to form the current collectors and the conductors that will connect to the outside of the cell. Following this step, additional layers of tape will be laminated to the structure so to form a sealing edge.

The ceramic pieces will then be fired in a furnace. After firing, the plates will measure 1.2 mm thick. **Figure 8** shows the completed 4x4-cell fuel cell modules with external connection wires that form the 8-cell module. The fuel chamber made from acrylic will be replaced, and made from additional layers of LTCC tape. The center area will be open to form a cavity that can withstand several hundred psi and hold the MOF's or solid source hydrogen storage. Feed and supply tubing along with controls will be

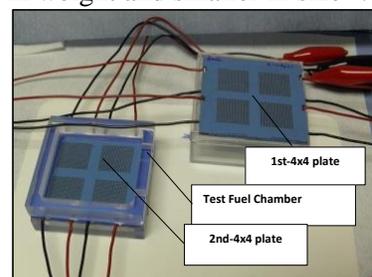


Figure 8. Two 4x4 plates with fuel chamber comprise the 8-cell module.

integrated between the layers that form the storage chamber. The whole fuel cell will be scaled up or down, in order to fit different applications.

### I. Partnership and Interactions.

Since 2008, our team has been working with NASA-Ames Center on developing new nanomaterials and nanotechnologies. This collaboration started from developing electrochemical gas-sensors using new nanomaterials and nanotechnologies, and recently shifted to developing new energy-nanotechnologies. Through this collaboration, Dr. Jing Li has been serving as an adjunct faculty in the UAF's Microelectronics/Photonics PhD Program, and Dr. Mayya Mayypan has been advising the UAF-UALR NSF-EPSCoR External Advisory Board and a junior faculty member in the UAF's Mechanical Engineering Department. Both scientists from the NASA-Ames, each internationally renowned in nanotechnologies, will continuously and closely work with the team for addressing the NASA-mission critical needs in short- and long-terms. Both scientists from the NASA-Ames, each renowned in nanotechnologies, will be continuously and closely worked with and consulted by the team for addressing the NASA-mission critical needs in short- and long-terms.

### J. Timeline.

<b><i>TIMETABLE</i></b>	<b>MONTHS 1-6</b>	<b>MONTHS 7-12</b>	<b>MONTHS 13-18</b>	<b>MONTHS 19-24</b>	<b>MONTHS 25-30</b>	<b>MONTHS 31-36</b>
<b>TASK-I</b>	■	■	■	■	■	■
<b>TASK-II</b>	■	■	■	■	■	■
<b>TASK-III</b>	■	■	■	■	■	■
<b>TASK-IV</b>	■	■	■	■	■	■
<b>TASK-V</b>	■	■	■	■	■	■
<b>TASK-VI</b>	■	■	■	■	■	■
<b>TASK-VIII</b>	■	■	■	■	■	■

### K. Sustainability.

After the three-years, the highly complementary three teams will move beyond the scope of the proposed objective, in which the most appealing topic of our common interest is to co-tackle longstanding problems in energy-storage such as rechargeable batteries at very low cost and ultra-high energy density. On this basis, new courses will be co-offered to the two campuses and beyond, and stimulate minority students to study STEM majors on both campuses. The findings from the proposed work will help the teaming labs and campuses to develop new projects with the NASA-Ames collaborators on meeting NASA's mission-critical need for not only sustainable energy source in space-exploration but also growing economy and job-market in Arkansas and USA. In parallel, new ideas of high practicality will be proposed to other funding agencies such as DOE, EPA, DOD, etc., by us alone or through collaboration with regional industries. For example, Eagle Picher in Joplin, MO has been working with the HiDEC for >20 years and grown into an international leader in manufacturing batteries for >90% of NASA need (e.g. that on the Hubble Telescope) and 80% DOD need, and the company most recently got \$20M grant from DOD for developing new batteries. As another example, Walmart is increasingly interested in testing our new technologies that can save their electrical bill, because Walmart is the largest domestic customer for the grid-electricity. Using a new solar-cell or fuel-cell to recharge the batteries for minimizing the grid-electricity consumption, for instance, has been long-overdue for industrial giants such as Walmart, which will provide us with an opportunity for sustaining our teamwork in future.

### L. Dissemination.

Activities for outreaching K12 students statewide will be developed and executed, using the infrastructure that was developed under the NSF-EPSCoR projects. The proposed prototypes to be on-time delivered in three years will substantially reduce not only the logistics cost for the Walmart, Tyson Foods, JB Hunt, and farmers in Arkansas, but also the air-pollution and green-house gas-emission from the truck-engines that burn the fossil fuel. These new technologies will help NASA further develop new version suitable for exploring deep space such as Mars.

#### **M. Budget and Budget-Justification.**

##### **1). Budget.**

For supporting the proposed work, we request a yearly budget of \$215,000 or a three-year total budget of \$645,000 from NASA-EPSCoR Office. On a 2:1 ratio for the cost-sharing, UAF's Vice Provost for Research and Economic Development has committed to provide a matching fund of \$322,500 over the three-year period. Under the support of Arkansas NASA-EPSCoR Office, the team will confidently and timely deliver the prototypes by the end of the year-3 of the proposed work, on a total budget of \$862,500 (after the \$105,000 overhead to the Arkansas NASA-EPSCoR Office).

##### **2). Budget Justification.**

The budget will be almost equally distributed to the three teaming labs under the help from the Arkansas NASA-EPSCoR Office. The requested grant will be used for mainly supporting personnel in the work, and will not be for buying any major equipment. Thus-doing will maximize the productivity of the proposed work, because the existing infrastructures on the two teaming campuses can meet all needs for performing the proposed work and delivering the prototypes. Thus, each lab's budget of \$93,800/year (including 21.2% overhead) will be mainly for supporting one graduate student and one postdoctoral researcher, including \$3k - 5k for materials and facility user-fees.

**N. Prior NASA-EPSCoR Research.** None for all the three teaming labs.

#### **RELEVANCE OF THE PROJECT TO NASA'S CURRENT AND FUTURE MISSIONS.**

In light of the volatile pricing and ultimately finite quantities of fossil fuels and their related environmental impacts, global government bodies have extensively sought for clean, renewable "green" energy sources. Among the current array of clean technologies – wind, hydro, geothermal, and solar – solar power is the most feasible generic energy solution as it lacks the constraints in place with the other energy sources, is renewable with a source that will outlast the Earth itself, and is clean and abundant. The two primary methods for harnessing solar power are 1) direct conversion of solar energy into electricity through photovoltaic devices and 2) hydrogen gas product via sunlight. Both methods have been extensively studied and advanced over recent decades.

The former method requires the use of significant quantities of semiconductors to build solar arrays which may be costly. The latter requires a setup for the solar energy to split water into H<sub>2</sub> and O<sub>2</sub> and a means to safely and effectively collect the resulting gasses which are both combustible. However, a well-designed solar water splitting device could last for a longer period of time if the proper materials are used. Additionally, hydrogen fuel could prove easier to transport and deliver than electrical storage media. For these reasons, solar water splitting may have an advantage over direct photovoltaic electricity generation.

According to NASA, liquid hydrogen is the "fuel of choice for space exploration"<sup>29</sup>. With the recent focus on a manned mission to the moon and eventually to Mars, NASA's demand for hydrogen fuel will likely continue for the foreseeable future. NASA is also pursuing a variety of alternative power sources for aerospace vehicles. One of those alternatives is hydrogen fuel cells. With significant advances by both the Department of Energy (DOE) and the private sector in the development of Proton Exchange Membrane (PEM) fuel cells using hydrogen and air as fuel and oxidant for ground-transportation applications and emerging Solid Oxide Fuel Cells (SOFC) for ground-based power generation, NASA is also building upon

existing developments to dramatically advance fuel cell technologies to provide compact, reliable high-energy power sources for aerospace applications. NASA is the largest consumer of liquid hydrogen at 10 million pounds of liquid hydrogen per year.

Our proposed research project for improving the efficiency and commercial feasibility of both mundane water splitting and solar water splitting as well as fuel cell technologies to increase the efficiencies of and reduce the costs of hydrogen fuel. This should fit well within the collection of research projects and programs sponsored by NASA.

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**BIOGRAPHICAL SKETCH—Z. Ryan Tian**

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 Institution: Board of Trustees, University of Arkansas

**EDUCATION:**

B.S. Chemistry (Major: Catalytic Chemistry), Fudan University, Shanghai, China, 1982  
 Ph.D. Chemistry (Minor: Chemical Engineering), University of Connecticut, Storrs, CT, 1998

**EXPERIENCE:**

2010–present Assoc. Prof., Chem/Biochem; Inst. of Nanoscale Mat. Sci./Engr., Cell/Molecular Biol., Microelectronics/Photonics, U. of Arkansas (UARK), Fayetteville, AR  
 2006–2010 Assistant Professor (Courtesy), Biomed. Engr., UARK, Fayetteville, AR  
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 2002–2004 Postdoct Fellow, Chemical Syntheses & Nanomaterials, Sandia Nat'l Labs, NM  
 2000–2001 R&D Manager, Production/Technology Transfer Manager, AXT, Inc., Fremont, CA  
 1998–2000 Research Associate, Dept. of Chem. Engr. & Mater. Sci., U of California, Davis, CA

**RESEARCH INTEREST:**

- Developing complex, heterostructured, & self-assembled nanomaterials for healthcare uses

**PROFESSIONAL ACTIVITIES:**

- Cofounder/Associate Editor, Journal of Nanotechnology for Engineering and Medicine
- Member: ACS, MRS, ECS, ASNM

**SELECTED PRODUCTIONS:** (out of 50+ papers)

- 1) Y. Zhang, H. Zhou, S. Liu, Z. R. Tian, M. Xiao, Second-harmonic Whispering-gallery Modes in ZnO Nanotetrapod, *Nano Lett.*, 9 (5). 2109-2112 (2009).
- 2) H. S. Sharma, S. Ali, Z. R. Tian, R. Patnaik, S. Patnaik, P. Lek, A. Sharma, T. Lundstedt, Nano-Drug Delivery and Neuroprotection in Spinal Cord Injury. *J. Nanosci. Nanotech.*, (invited review paper)9, 5014-5037 (2009).
- 3) K. Geren, S.W. Liu, H.J. Zhou, Y. Zhang, R. Tian, and Min Xiao, Second-order Susceptibilities of ZnO Nanorods from Forward Second-harmonic Scattering, *J. Appl. Phys.*, 105, 063531 (2009).
- 4) W. Dong, T. Zhang, J. Epstein, L. Cooney, H. Wang, Y. Li, Y-B. Jiang, A. Cogbill, Z. Ryan Tian, Multifunctional Nanowire Bioscaffolds on Titanium, *Chem. Mater.*, 19, 4454-4459 (2007).
- 5) T. Zhang, W. Dong, R. Njabon, V. K. Varadan, Z. Ryan Tian, Kinetically Probing Site-Specific Heterogeneous Nucleation and Hierarchical Growth of Nanobranches, *J. Phys. Chem. C.*, 111, 13691-13695 (2007).
- 6) W. Dong, A. Cogbill, T. Zhang, S. Ghosh, Z. R. Tian, Multifunctional, catalytic nanowire membranes and the membrane-based 3D devices, *J. Phys. Chem. B.*, 110, 16819-16822 (2006).
- 7) T. Zhang, W. Dong, M. Brewer, S. Konar, R. N. Njabon, Z. R. Tian, Site-Specific Nucleation and Growth Kinetics in Hierarchical Nanosyntheses of Branched ZnO Crystallites, *J. Am. Chem. Soc.* 128, 10960 (2006).
- 8) J. W. P. Hsu, Z. R. Tian, N. C. Simmons, C. M. Matzke, N. A. Missert, J. A. Voigt, J. Liu, Directed spatial organization of zinc oxide nanorods, *Nano Lett.* 5(1), 83 (2005).
- 9) Z. R. Tian, J. A. Voigt, J. Liu, B. Mckenzie, M. J. Mcdermott, M. A. Rodriguez, H. Konishi, H. Xu, Complex and oriented ZnO nanostructures, *Nature Materials* 2, 821 (2003).
- 10) Z. R. Tian, W. Tong, J. Y. Wang, N. G. Duan, V. V. Krishnan, S. L. Suib, Manganese oxide mesoporous structures: Mixed-valent semiconducting catalysts, *Science* 276 (5314), 926 (1997).

**SYNERGISTIC ACTIVITIES:**

- 1) Honorary Recognitions, by Vice Chancellor for Student Affairs and Dean of Students, for

“significant impact on the ability of a student to maintain focus on his/her academic pursuits”, University of Arkansas, 2008, and 2010.

- 2) Outstanding Mentor Award, University of Arkansas, 2010; 2012; 2014
- 3) Developed curricula for courses, “Nanomaterials Chemistry” (to science/engineering undergrads & grads), “Advanced Inorganic Chemistry” (to science/engineering undergrads), and “Chemistry for the Modern World (to non-science-major undergrads), with up-to-date nanotechnologies, 2004-now;
- 4) Visiting, and giving seminars to faculty in Computer Science/Engineering, Biomedical Engineering, Crop/Soil/Environmental Sciences, Food Science, Animal Science, Physics, Mechanical Engineering, Poultry Science, Chemical Engineering, and Mathematics for developing collaborations, 2005-now;
- 5) Encouraging/convincing high-school students and their siblings to study sciences (e.g. nanosciences), Huntsville High School Career Fair, Huntsville, AR, 2005-now, and local K-12 female/minority student to learn nanosciences under a minority/female graduate student’s supervision in my lab, 2010.

#### **COLLABORATORS:**

- Ali, Syed (NCTR, FDA, Jefferson, AR)
- Ang, Simon (Electrical Engineering, University of Arkansas)
- Du, Yuchun (Biological Sciences, University of Arkansas)
- Epstein, Josh (University of Arkansas for Medical Sciences, Little Rock, AR)
- Li, Jing (Ames Lab, NASA)
- Sharma, Hari (Surgical Sciences, University Hospital, Uppsala University, Sweden)
- Srivatsan, Malathi (Neurological Biology, Arkansas State University, Jonesborough, AR)
- Suva, Larry (University of Arkansas for Medical Sciences, Little Rock, AR)
- Yang, Xiaodong. (Mechanical Engineering, University of Missouri, Rolla, MO)
- Zhou, Wuzong (Chemistry, St. Andrew’s University, UK)

#### **ADVISORS AND ADVISEES:**

##### (1). Advisors:

- Dr. Jun Liu, Sandia National labs (now at Pacific Northwest National Lab)
- Dr. Alexandra Navrotsky, University of California, Davis, CA
- Dr. Steven L. Suib, University of Connecticut, Storrs, CT

##### (2). Postdoctoral Advisees:

- Dr. Demydov, D. (2014 - now)
- Dr. Dong, W. (Moved to Zhejiang University of Sci and Tech, China as an associate prof.)
- Dr. Ghosh, S. (moved to U. of Wisconsin, Madison)
- Dr. Konor, S. (now a Humboldt Fellow at the Max Plank Institute, Germany)
- Dr. Lee, M. (Moved to the Yonsei University, South Korea as a research faculty)
- Dr. Massoud, A. (2014)
- Dr. Subramanian, R. (2009-now)
- Dr. Yang, Z-Q. (2010-now)
- Dr. Youssef, A. (moved to the NRC in Cairo, Egypt as Research Scientist)
- Dr. Zhou, H. (2007-2014, moved to HiDEC, University of Arkansas)
- Dr. Zhang, T. (2005-2007, moved to the Chinese Academy of Sciences as a Professor)

##### (3). Graduate Advisees:

Algarni, Suad	Almansaf, Z.	Almansaf, D.	Alahmed, H.
Brewer, M. (MS 2009)	Chen, F. (PhD. 2011)	Chowdhury, A. R.	Chism, T.
Horst, J. (MS 2011)	Manoharan, A.	Ozkizilcik, A.	Turgut, H.
Winkelman, J.	Williams, R. (PhD. 2012)	Zhang, Y.-L.	Yang, X.

## BIOGRAPHICAL SKETCH—SIMON S. ANG

### (a) Professional Preparation

University of Arkansas, Fayetteville, AR	B.S.E.E., 1980
Georgia Institute of Technology, Atlanta, GA	M.S.E.E., 1981
Southern Methodist University, Dallas, TX	Ph.D.E.E., 1985

### (b) Appointments

2010-Present	Director, High Density Electronics Center, University of Arkansas, Fayetteville, AR
1995-Present	Professor of Electrical Engineering, University of Arkansas, Fayetteville, AR
1991-1995	Associate Professor, University of Arkansas, Fayetteville, AR
1988-1991	Assistant Professor, University of Arkansas, Fayetteville, AR
1981-1988	Product Engineer, Engineering Manager, Power Integrated Circuit Development, Texas Instruments, Inc., Dallas, TX

### (c) Related Publications (Out of 290)

- 1). Ang, S. S.; Cannon, T.; Tian, Z. R.; Chen, J. Y. "An LI-145 ceramic fuel cell module," Proceedings of the 46th Power Sources Conference, Orlando, FL, June 9-12, 2014, pp. 104-107.
- 2). Cannon, T.; Ang, S. S.; Steger, M.; Porter, K.; Porter, E. V.; Glover, M. "A Ceramic "Power Cube" Fuel Cell," 45th Power Sources Conference, Las Vegas, NV, June 11-14, 2012, 215-218.
- 3). M. Zhang, S. S. Ang, M. Wang, and G. Liu, "Evaluation of Solid-State electrode for the Rapid Detection of Soil Nitrate-Nitrogen," *Advanced Materials Research*, vol. 422, pg. 96-101, 2012.
- 4). Y. Zhang, S. S. Ang, Andrew A. O. Tay, D. Xu, E. T. Kang and K. G. Neoh, P. C. Lim, and A. C. H. Huan "Characterization of Electroless Deposited Copper and Nickel Nanofilms on Modified Si(100) Surface", *Langmuir*, vol. 19, no. 17, pg. 6802-6806, August 19, 2003.
- 5). D. Xu, E. T. Kang, K. G. Neoh, Yan Zhang, A. A. O. Tay, S. S. Ang, M. C. Y. Lo and K. Vaidyanathan "Selective Electroless Plating of Copper on (100)-Oriented Single Crystal Silicon Surface Modified by UV-Induced Coupling of 4-Vinylpyridine with the H-Terminated Silicon", *J. Phys. Chem. B* 2002, 106, 12508-12516, 2003.

### Broader Publications

1. X. Yang and S. S. Ang, "A Hydrophobic/Anti-reflective Coating and a Nano Particle Ethylene-Vinyl Acetate Encapsulation for Solar Cell Packaging" *Advancing Microelectronics*, vol. 39, no. 6, Nov./Dec. 2012.
2. H. A. Mustain, W. D. Brown, and S. S. Ang, "Tungsten carbide as a diffusion barrier on silicon nitride AMB substrates for SiC power devices," *American Society of Mechanical Engineers (ASME) Journal of Electronic Packaging*, vol. 131, pg. 034502/1-3, September 2009.
3. E. B. Liao, A. A. O. Tay, S. S. Ang, H. H. Feng, R. Nagarajan, V. Kripesh, R. Kumar and G. Q. Lo, "Planar microspring – a novel complaint chip-to-package interconnect for wafer-level packaging," *IEEE Transactions on Advanced Packaging*, pg. 379-389, vol. 32, no. 2, May 2009.
4. L. Zhu, Q. Zhang, H. Feng, S. S. Ang, and Wen-Tso Liu, "Filter-based microfluidic device as a platform for immunofluorescent assay of microbial cells," *Lab-on-a-Chip*, no. 4, pg. 337-341, 2004.
5. Q. Zhang, L. Zhu, H. H. Feng, S. S. Ang, F. S. Chou, and W-T Liu, "Microbial detection in microfluidic devices through dual staining of quantum dots-labeled immunoassay and RNA hybridization" *Analytica Chimica ACTA*, vol. 556, no. 1., pg. 171-177, January 2006.

### (d) Synergistic Activities

**Professional Society:** Chair, Division Executive Committee, Dielectric Science and Technology Division, The Electrochemical Society, USA. 1998-2004; **Fellow**, The Electrochemical Society (USA); **Fellow**, Institution of Engineering and Technology (UK); **Fellow**, City and Guilds of London Institute (UK), **Fellow**, Institute of Electrical and Electronics Engineers (IEEE-USA).

## **BIOGRAPHICAL SKETCH—Tar-pin Chen**

### **I. Employment History**

2010-present Professor, Department of Physics and Astronomy, University of Arkansas at Little Rock  
 2005-2010 Professor & Chair, Department of Physics and Astronomy, University of Arkansas at Little Rock  
 1997-2005 Professor & Chair, Department of Physics and Astronomy, University of North Dakota  
 1994-1997 Professor, Department of Physics and Astronomy, University of North Dakota  
 1986-1994 Associate Professor, Head of Solid State of the Condensed Matter Program, Director of Research Center, Department of Physics, Villanova University, Villanova, PA  
 1980-1986 Associate Physicist and Associate Group Leader, Ames Laboratory-USDoE and Iowa State University, Ames, Iowa  
 1978-1980 Research Associate, Department of Physics, Brandies University, Waltham, MA

### **II. Honors and Awards**

#### **i. Invited Speaker:for 2015**

- a. Invited speaker for Forum 5 of the New Energy Industry in the 1<sup>st</sup> Emerging Industry Forum (EIF), June 26-29, 2014 at Dalian, China
- b. Invited speaker at the 4<sup>th</sup> Annual World Congress of the Nanoscience and Technology Conference, October 29-31, 2014 at Qingdao, China
- c. Invited plenary speaker at the 8<sup>th</sup> International Conference on New Theories, New Discoveries, New Materials and Related Application (NEW3SC), June 7-11, 2011, Chongqing, China

### **III.. Membership in professional and honorary Societies**

- a. Member, American Physics Society, Materials Research Society, and Vacuum Science and Technology Society

### **IV. Scholarly and Professional Accomplishment**

#### **i. Seleted Publications from a Total of 96 Papers:**

- 1). Xiumei Geng, Wei Wu, Ning Li, Weiwei Sun, Johnathan Armstrong, Alaa l-Hilo, A. Brozak, Jingbiao Cui, and Tar-pin Chen, "Three – Dimensional Structures of MoS<sub>2</sub> Nanosheets with Ultrahigh Hydrogen Evolution Reaction in Water Reduction", *Adv.Funct. Mater.* (2014) 1-7.
- 2). Weiwei Sun, Xuimei Geng, Johnathan C. Armstrong, Jingbiao Cui, Tar-pin Chen, "Experimental and Theoretical Study on Band Gap Tuning of Cu<sub>2</sub>ZnSn(S<sub>1-x</sub>Se<sub>x</sub>)<sub>4</sub> Absorbers for Thin-Film Solar Cells." Photovoltaic Specialist Conference (PVSC), 2014 IEEE 40<sup>th</sup>, page 0421-0424.
- 3). Johnathan C. Amrstrong, Jingbiao Cui, Tar-Pin Chen, "ALD processd MgZnO Buffer layers for Cu(In, Ga)S<sub>2</sub> solar cells.", Photovoltaic Specialist Conference (PVSC), 2014 IEEE 40<sup>th</sup>, page 0304-0307.
- 4). Al-Hilo, A.A., Mohammed, M.Z, Armstrong, J.C.,Tar-Pin Chen, "Enhanced performance core-sell Si/CdS nanowires heterojunction solar cell device.", Photovoltaic Specialist Conference (PVSC), 2014 IEEE 40<sup>th</sup>, page 2447-2451.
- 5). Mohammed, M.Z., AbdulAmohsin, S., Zhongrui Li, T.-p. Chen, "ZnO nanowire/N719 dye/polypyrrole-SWNT nanocomposite solid state dye sensitized solar cells", Photovoltaic Specialist Conference (PVSC), 2014 IEEE 40<sup>th</sup>, page 1510-1514.
- 6). Mohammed, M.Z., Al-Hilo, A.A., Tar-pin Chen, "Double Shottcky of NiOx/graphene/Si for enhance efficiency solor cells." Photovoltaic Specialist Conference (PVSC), 2014 IEEE 40<sup>th</sup>, page 2998-3003.
- 7). Muatez Z. Mohammed, Alaa A. Al-Hilo, Zhongrui Li, Jingbiao Cui, and Tar-pin Chen, "Acid-doped Multi-wall Carbon Nanotube/n-Si Heterojunctions For Enhanced Light Harvesting Solar Energy", *Solar Energy* 106 (2014) 171-176

#### **ii. Funding Received (from a Total of \$7,067,915)**

At UALR-A 5-year \$2,500,000 NSF EPSCoR grant from October 2011 to October 2015 was awarded to UALR for studying solar cell materials and devices (I was the campus leader to form the UALR research team and initiated the proposal in 2008)

### **Tian's Current and Pending Projects**

#### **CURRENT:**

1). Source of Support: Arkansas Science and Technology Authority (from NSF EPSCoR)  
 Title of Project: Vertically-Integrated Center for Transformative Energy Research (VICTER)  
 Total Award Amount: \$ 345,896 (out of a total budget of ~\$6M)  
 Role: Co-Investigator  
 Start and End Dates: 12/1/2010 – 11/30/2015  
 Person-Months Per Year Committed to the Project: 0.5 SM (SM-Summer Month)

2). Source of Support: NSF-REU  
 Title of Project: REU Site: An Interdisciplinary Exploration of the Convergence of  
 Science and Engineering: Micro to Nanoscale Materials,  
 Processing, and Devices  
 Total Award Amount: \$ 359,866.00  
 Role: Co-PI  
 Start and End Dates: 06/2014 – 08/2017  
 Person-Months Per Year Committed to the Project: 0.0 SM (SM-Summer Month)

3). Source of Support: NSF-REU  
 Title of Project: REU Site: Summer Internships in Nanomaterials, Nanomechanics, and  
 Leadership Training in Engineering  
 Total Award Amount: \$ 359,565.00  
 Role: Co-PI  
 Start and End Dates: 06/2014 – 08/2017  
 Person-Months Per Year Committed to the Project: 0.0 SM (SM-Summer Month)

#### **PENDING:**

1). Source of Support: NASA-EPSCoR  
 Title of Project: Nanotechnology Assisted Solar Water-Splitting, Solar-Cell, and Fuel-Cell  
 Total Award Amount: \$ \$645,000  
 Role: PI  
 Start and End Dates: 10/1/2015 – 9/30/2018

2). Source of Support: NSF  
 Title of Project: Engineering Ion-Transport Anisotropy of Arrayed Ternary Oxide Nanowires for  
 Na-ion Battery Electrodes  
 Total Award Amount: \$ 451,566  
 Role: PI  
 Start and End Dates: 7/1/2015 – 6/30/2018

3). Source of Support: US-DHHS  
 Title of Project: Enhancement of light trapping and optical Absorption in Complex ZnO Nanostructures  
 Total Award Amount: \$ 50,000  
 Role: Co-PI  
 Start and End Dates: 1/1/2015 – 12/31/2016

## Ang's Current and Pending

### **CURRENT:**

1). Funding Source: NSF I/UCRC program

Title of Project: NSF I/UCRC: GRid-connected Advanced Power Electronic Systems (GRAPES)

Total Award Amount: \$520,000

Start and End Dates: 10/1/14-8/30/19

Person-Months Per Year Committed to the Project: 0.1 M

2). Funding Source: Arkansas Science and Technology Authority (from NSF EPSCoR)

Title of Project: Vertically-Integrated Center for Transformative Energy Research (VICTER)

Total Award Amount: \$ 234,501.45

Start and End Dates: 12/1/2010 – 11/30/2015

Person-Months Per Year Committed to the Project: 0.2 SM (SM-Summer Month)

3). Funding Source: ABB, Inc. (ONR)

Title of Project: High Power Solid State Circuit Protection for Power Distribution and Energy Storage

Total Award Amount: \$119,930 (\$569,852.00 Phase II)

Start and End Dates: 10/01/13 to 3/30/15

Person-Months Per Year Committed to the Project: 0.05 SM

4). Funding Source: Monolithic Semiconductor Inc. (ARPA-E)

Title of Project: POWER DEVICE MODELING AND PACKAGE DESIGN FOR WIDE BANDGAP DEVICES IN ARPA-E SWITCHES

Total Award Amount: \$85,344

Start and End Dates: 03/20/2014 to 12/2016

Person-Months Per Year Committed to the Project: 0.1 SM

5). Funding Source: GRAPES Industry Membership Funds

Title of Project: Modular Solid-State Transformer (Individual Research Projects)

Total Award Amount: \$ 216,555.55

Start and End Dates: 01/01/13 – 12/31/15

Person-Months Per Year Committed to the Project: 0.5 SMR

6). Funding Source: GRAPES Industry Membership Funds

Project/Proposal Title: Power-Packaging (Individual Research Projects)

Source of Support: NSF through I/UCRC GRAPES

Total Award Amount: \$378,602.64

Total Award Period Covered: 1/1/10 - 12/31/15

Location of Project: University of Arkansas

Person-Months Per Year Committed to the Project: 1.0 SMR

### **PENDING:**

1). Source of Support: NASA-EPSCoR

Title of Project: Nanotechnology Assisted Solar Water-Splitting, Solar-Cell, and Fuel-Cell

Total Award Amount: \$ \$645,000

Role: Co-PI

Start and End Dates: 10/1/2015 – 9/30/2018

2). Source of Support: NSF

Title of Project: Engineering Ion-Transport Anisotropy of Arrayed Ternary Oxide Nanowires for Na-ion Battery Electrodes

Total Award Amount: \$ 451,566

Role: Co-PI

Start and End Dates: 7/1/2015 – 6/30/2018

### **Chen's Current and Pending**

#### **CURRENT:**

1). Funding Source: NSF-EPSCoR  
Grant Amount: \$2,500,000  
Role: Co- Investigator  
Duration: October 2010 to October 2015  
Location of Project: UALR

#### **PENDING:**

1). Source of Support: NASA-EPSCoR  
Title of Project: Nanotechnology Assisted Solar Water-Splitting, Solar-Cell, and Fuel-Cell  
Total Award Amount: \$ \$645,000  
Role: Co-PI  
Location of Project: UALR  
Start and End Dates: 10/1/2015 – 9/30/2018



# UNIVERSITY OF ARKANSAS

*Office of the Vice Provost for Research and  
Economic Development*

January 14, 2015

Dr. M. Keith Hudson, Director  
NASA/EPSCoR Program  
University of Arkansas at Little Rock  
1201 McMath Avenue  
Little Rock, AR 72202-5142

Dear Dr. Hudson:

The University of Arkansas (UA) is pleased to support the proposal entitled "Nanotechnology Assisted Solar Water-Splitting, Solar-Cell, and Fuel-Cell" submitted in collaboration with the University of Arkansas at Little Rock (UALR). This project is lead by Dr. Z. Ryan Tian. If this proposal is selected for funding, the UA will provide the match needed for the required 2:1 cost share.

Sincerely,

James M. Rankin  
Vice Provost for Research and Economic Development

JMR/kms

210 Administration Building • 1 University of Arkansas • Fayetteville, AR 72701  
Voice (479) 575-3845 • Fax (479) 575-3846

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