

## **Role of Fractal Patterns on New Materials for Solar Energy Applications: Inorganic Clusters, Films and Fractal Geometry Simulations**

Darren W. Johnson and Richard P. Taylor, University of Oregon  
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### Project abstract

The overarching, long-term goal of the proposed research is to simulate, fabricate and measure novel solar devices that exploit the solar efficiency of Nature's fractal patterns. This goal will be achieved by a team of theoretical physicists (led by Richard Taylor) and inorganic materials chemists (led by Darren Johnson) who seek in the short-term to deliver fundamental advances in *both* the chemistry and physics of materials for solar energy conversion. The three research thrusts are: 1) to simulate the electrical properties of solar devices with a fractal geometry in order to predict the fractal parameters that will provide efficient, novel solar devices, 2) to synthesize new inorganic clusters for use as inks for solar materials; and 3) to unite these two thrusts in the design of new solar materials with fractal geometries predicted to have properties mimicking the light-harvesting fractal patterns found in Nature. Research thrusts 1 and 2 have been initiated in the PIs' laboratories and offer basic science advances leading to new solar materials, while thrust 3 is higher risk and will unite the two teams of researchers towards designing new fractal materials for solar energy conversion. Collaborations with regional industry, centers and facilities will complement the PIs expertise. The University of Oregon's active internship programs in the Materials Science Institute (<http://internship.uoregon.edu/partners.html>) teams the PIs with companies such as Nanosolar, SolarWorld, SpectraWatt and Voxel, among others with R&D efforts in materials for solar energy conversion. This provides researchers on the project additional expertise and long-term potential for commercialization.

### **STATEMENT OF THE PROBLEM AND SCIENTIFIC SIGNIFICANCE OF PROPOSED RESEARCH:**

The scientific significance of this proposal lies in an integration of novel and fundamental approaches to enable long-term goals of improving solar device performance:

- *We propose to use fractal analysis to predict nanoscale patterns that will provide efficient, novel solar structures;*
- *We propose to synthesize new inorganic clusters (e.g., Cu-containing analogs of our known Ga/In clusters) for use as precursors/inks for such new solar materials;*

- *Combining these approaches, we propose to synthesize new solar materials with fractal geometries predicted to have properties mimicking the light-harvesting fractal patterns found in Nature.*

The concept of solar cells based on nature's fractal patterns represents a significant advance on traditional solar cell designs. For the first time, solar cells will directly exploit the efficient light-collection properties of trees by incorporating fractal branches within the device's architecture. By adopting self-assembly fabrication processes, the electrodes and the photoactive material will form interlocking fractal patterns. This 'natural' architecture will establish an optimal balance of providing a large surface area of the photoactive material (to maximize the collection of light) and also providing a large interface with the electrodes (allowing an efficient collection of the electricity from the photoactive material). Simulations will be employed to optimize the scaling properties of the fractal branches in order to maximize these two geometric properties and thus the device's performance.

On the chemistry side, the proposed research offers to provide new synthetic routes to aqueous inorganic cluster compounds. This team has developed new approaches to synthesize previously inaccessible nanoscale inorganic clusters in gram scales, and we propose to expand those methods to prepare clusters that will be of interest as precursors ("inks") for solar thin film materials. This will be accomplished by: 1) ion exchange of the counterions on known nanoclusters to add novel functionality and provide new "nanocomposites"; 2) development of new mononuclear precursors; and 3) anion exchange on the films directly. Furthermore, these methods will provide fundamental new routes for nanocluster synthesis that could have application in many fields of materials science.

The proposal joins the University of Oregon (UO) group of Richard Taylor in physics, who specializes in understanding and predicting the relationship between fractal device architectures and their performance, with the group of Darren Johnson in chemistry, who specializes in preparing inorganic cluster compounds for materials applications. This multidisciplinary approach to addressing a scientific problem of crucial significance to society is expected to have high educational value and provide a platform for public outreach activities. In line with this expectation, the majority of the project's budget will be devoted to funding graduate students.

This work will be performed under the auspices of three regional centers that provide complementary resources to the PIs. (1) The Photovoltaics Laboratory of the Oregon Support Network for Research and Innovation in Solar Energy (Oregon SuNRISE, <http://camcor.uoregon.edu/sunrise/index.shtml>), a network of shared facilities and expertise serving the Oregon University System and industry collaborators that seeks to provide infrastructure for PV research and enhance the education, collaboration and innovation opportunities for PV researchers in Oregon. The facility also has an active graduate internship program (<http://camcor.uoregon.edu/sunrise/workforce.shtml>) to provide supplemental training in the chemistry, physics and engineering of photovoltaic processing. UO has a long history and culture of doctoral students performing off-campus internships during their studies, and it is expected that students working on the proposed Scialog project will perform internships as part of their research and education efforts. (2) The Fractals Research Laboratory (FRL), an internationally renowned group that develops practical applications of fractals. (3) The Center for Green Materials

Chemistry (CGMC), an NSF Phase 1 Center for Chemical Innovation (CCI) recently awarded to UO and Oregon State University (OSU) that seeks to study and develop new solution-based materials and process chemistries that provide direct pathways to the deposition of dense, high-quality inorganic films of technological interest.

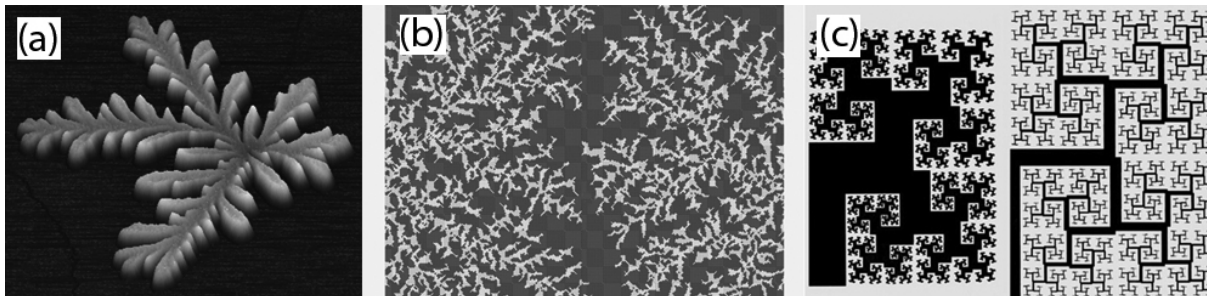
An advantage of our Scialog project will be to pool funding, resources and expertise with these existing projects. In particular, the techniques developed to fabricate, model and measure films/materials (CGMC) or fractal electronic circuits (FRL) are readily adaptable to the solar cell geometries proposed below.

## PLAN OF PROCEDURE

### Richard Taylor – Exploiting Fractal Geometry for Generation of Solar Energy.

*Preliminary Results.* Fractal patterns are prevalent throughout nature (e.g., in natural environments, biological systems and human physiology)[1,2] because they possess a number of highly desirable functional properties. In particular, the repetition of patterns at many size scales builds highly complex structures with unprecedented surface area/volume ratios. Nature exploits this property, for example, in trees where the maximal area of the branches allows unprecedented collection of solar energy. In addition, these multidirectional surfaces are exposed to light from many directions, allowing collection of solar energy throughout the entire day. Fractal patterns also have high connectivity properties, facilitating efficient collection and transport of thermal and electrical energy. We plan to use the same approach for designing novel solar structures based on fractal geometry.

Fractal patterns are relatively easy to fabricate and are expected to be prevalent in future nano-electronics applications. Many nanoelectronic systems are formed using “self-assembly”, where “natural” growth processes are harnessed to fabricate the devices or circuits under investigation. For instance, the generic “fingerprint” pattern of self-assembled nanoscale systems is expected to be fractal.[3] By harnessing these processes to build the fractal patterns, self-assembly represents an efficient way of building the complex architectures that result from the integration of millions of intricate nanoscale components. Despite the high potential of fractal nanoscale devices for solar applications, there has been little previous research into these systems, in part due to the multi-disciplinary challenges involved. Fortunately, the PIs are well-placed to pioneer these studies.



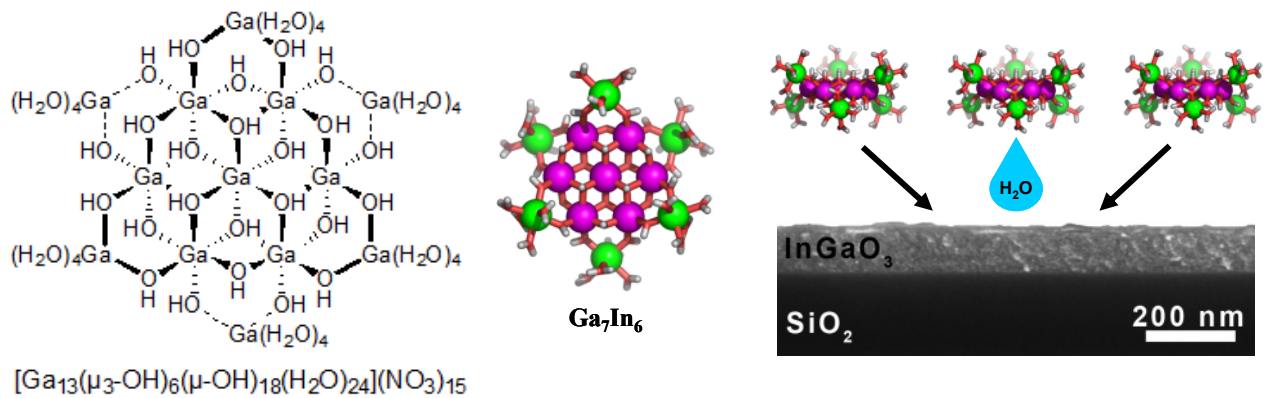
**Figure 1.** (a) A fractal circuit formed using the diffusion-limited aggregation (DLA) growth process, (b) a simulation of the DLA process, used to create metallic, fractal electrodes (light gray) surrounded by photoactive material (dark gray), (c) examples of fractal branches with different scaling properties: the right-hand fractal has a higher ratio of fine to coarse structure than the left-hand fractal. Images span ca. 1  $\mu\text{m}$ , although in principle, there is no physical limit to the size of the patterns grown using DLA.

Figure 1(a) shows an example of a fractal architecture currently being developed in FRL. The pattern is formed by depositing ‘nanoclusters’ of semiconductor material on a smooth substrate. The clusters migrate on the surface until they encounter other clusters, at which point diffusion-limited aggregation (DLA) causes incoming clusters to ‘self-assemble’ into the branch-like pattern shown in Figure 1(a).

### **Darren Johnson – Inorganic Nanoclusters as Materials Precursors.**

*Preliminary Results.* The Johnson lab has developed a new synthetic strategy to prepare inorganic clusters such as  $[\text{Ga}_{13}(\mu_3\text{-OH})_6(\mu\text{-OH})_{18}(\text{H}_2\text{O})_{24}](\text{NO}_3)_{15}\cdot 6\text{H}_2\text{O}$  (**Ga<sub>13</sub>**, Figure 2).[4] Despite their environmental relevance and potential use as precursors for materials (such as  $\text{Ga}_2\text{O}_3$  and IGO),[5,6] applications of Group 13 clusters have been hindered due to inefficient and/or ineffective synthetic strategies. The Johnson lab’s facile synthesis can generate a variety of Group 13 clusters in high yield in several days under ambient, aerobic conditions, and it is amenable to scale-up. These synthetic strategies have also yielded the  $\text{Al}_{13}$  analog,[7] and a series of heterometallic clusters, including six Ga/In and three Al/In clusters with varying compositions.[6,8] All of these clusters are air- and solution-stable, making them ideal for use as inks (i.e., precursors for solution deposition techniques).

The Keszler group at OSU, a close collaborator with the Johnson lab, has pioneered the use of heterogeneous, kinetically stable solution precursors for the production of thin film dielectrics, semiconductors, and metals.[9] In collaboration with the Keszler group, we have developed a new strategy for precursor development using our discrete nanoscale inorganic clusters.[6] The tridecameric cluster **Ga<sub>13</sub>** simply represents the type of condensation product that is likely forming in the thin film precursors that are being developed using the Keszler group’s heterogeneous precursor route. Furthermore, the preorganized nature of the Ga-hydroxide structure represents a desirable starting point for the condensation to  $\text{Ga}_2\text{O}_3$  thin films, while also providing a high-purity ink precursor.  $\text{M}_{13}$  nanoclusters provide much needed fundamental insight into the solution species in the heterogeneous precursors and provide new parameters for deposition control. For example, the heterometallic clusters prepared in the Johnson group provide fine-tuned control, at the molecular level, over the metal ratios in prepared thin films (e.g., **Ga<sub>7</sub>In<sub>6</sub>** in Figure 2). The mixing of the metal precursors at the molecular level prevents potential problems with inhomogeneities resulting from incomplete mixing of bulk precursor materials.



**Figure 1.** (left) Chemdraw representation of the  $Ga_{13}$  nanocluster; (middle) ball and stick representation of the crystal structure of  $Ga_7In_6$ . (right) Solution deposition of heterometallic nanocluster inks provides dense, crack-free IGO thin films (TEM image).

**Aim 1.** The proposed solar cell architecture (Figure 1b) represents a radical advance on traditional solar cell designs. This design exploits fractals by incorporating the efficient light-collection properties of fractal branches within the photoactive material film.[10] Whereas the fractal branches of Figure 1(a) are employed as the active components of the electrical circuits, in the Scialog project they will serve as electrodes, spreading out from a source and drain. The photoactive material film will then be deposited using solution deposition techniques described above such that it occupies the spaces between the branches.

The design utilizes the principle that the space surrounding a fractal is also fractal – thus the photoactive material assumes the same fractal characteristics as the branches. In terms of fabrication, this is highly desirable: the fractal branches form via self-assembly which allows solution precursors to provide a photoactive material that assumes this same form during deposition. The approach is also desirable in terms of functionality: both components of the device benefit from Nature’s geometry. In particular, the large boundary between the photoactive material and the branch electrodes allows an optimal balance between having a large surface area to collect light and allowing the electrons to quickly exit through the electrodes.

Whereas the basic hypothesis is based on Nature’s proven fractal geometry, there are many challenges to understanding the specific operation of branch-based solar cells. Electrical transport through fractal circuits is a novel field. The proposed research will use accurate simulations of the growth process to generate branched patterns similar to those that have previously been fabricated. The conduction of these simulated patterns will be modeled, to quantify the relationship between the fractal architecture and the current transport through the two fractal components (the electrodes and photoactive material). Preliminary simulations indicate that the two central scaling parameters (the ratio of coarse to fine scale patterns, and the range of size scales) can both be controlled by adjusting growth conditions. These two parameters affect pattern properties such as the length of the boundary between the electrodes and the photoactive material and the photoactive material’s surface area – both are crucial factors for the solar cell operation.

We will develop a generic fractal geometry that can be applied to a wide range of the photoactive thin films. Different material systems adopt different strategies for separating

the charge generated from the light and transporting it to the electrodes. Charge is either separated by a drift of charge under the influence of an electrostatic field, or from high to low concentration zones following the gradient of an electrochemical potential. To encompass all scenarios, we will consider three categories of photoactive materials. In the simplest scenario, the gaps between the electrode branches are filled with a uniform photoactive material (such as precursors in Aim 2) and an externally applied bias transports the charge to the boundaries of the electrodes. In the second scenario, two materials/precursors are deposited, one filling the gaps between the left-hand branches and the other material filling the gaps between the right-hand branches (Figure 1b), with an interface between the two materials running along the gap between the electrodes (i.e. perpendicular to the substrate surface). The third scenario also involves two materials but in an arrangement that more closely aligns to traditional solar cell architectures. In this design, the interface between the two materials runs parallel to the substrate. By simulating the conduction properties of these three designs, a range of today's solar cell materials will benefit from our novel branch architecture.

**Aim 2.** We also propose to synthesize new inorganic clusters for use as inks/precursors for solar thin film and fractal materials (e.g., Cu-containing analogs of known Ga/In clusters in Figure 2). Initial experiments using the **Ga<sub>13</sub>**, **Ga<sub>7</sub>In<sub>6</sub>** and **Al<sub>13</sub>** clusters as inks have led to the successful deposition of dense, crack free amorphous and crystalline Ga<sub>2</sub>O<sub>3</sub>, IGO and Al<sub>2</sub>O<sub>3</sub> thin films, respectively, demonstrating that this approach provides a useful supplement to heterogeneous precursor methods. We propose to expand our synthetic strategy to prepare new clusters for use as CuIn<sub>1-x</sub>Ga<sub>x</sub>S<sub>2</sub>/Se<sub>2</sub> (and related) materials precursors. For instance, can **Ga<sub>7</sub>In<sub>6</sub>** be doped with Cu to prepare a CIGS precursor?[11-13] Work in the Keszlér lab has shown that indium and gallium nitrate can be dissolved in methanol with Cu<sup>0</sup> to prepare inks for such materials – will similar strategies work in the case of the **Ga<sub>7</sub>In<sub>6</sub>** cluster? This section proposes three synthetic routes to access more complex nanoclusters and materials: 1) anion exchange of the nitrate counterions on the M<sub>13</sub> clusters to add functionality; 2) development of new mononuclear precursors; and 3) anion exchange directly on the films once they are spin coated (prior to annealing).

The M<sub>13</sub> clusters are cationic with nitrate counterions as synthesized. A number of copper/sulfur-containing anionic clusters have been reported (e.g., Cu<sub>2</sub>S<sub>8</sub><sup>12-</sup>).[14] Replacement of the nitrate counterions of **Ga<sub>7</sub>In<sub>6</sub>** with a copper sulfide cluster anion such as this offers an attractive new route to develop precursors for CuIn<sub>1-x</sub>Ga<sub>x</sub>S<sub>2</sub> and related materials for solar energy applications. Additionally, we have recently prepared a new Cu cluster, [Cu<sub>4</sub>(μ-OH)<sub>2</sub>(μ-SO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup>, that may prove suitable for these studies. Anion exchange and diafiltration[19] are well-established procedures, with various ion exchange resins and salt metathesis methods available; however, rarely have these strategies been applied to prepare clusters bearing other *clusters* as counterions (sometimes referred to as nanocomposites).[15-17]. Furthermore, these synthetic methods will be applicable in a more general sense: this will provide a direct route to derivatize any of our M<sub>13</sub> clusters for a variety of applications, including semiconductor and solar materials (including using selenium-containing anions to prepare CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> precursors).

Another synthetic approach involves ion exchange *prior* to cluster formation. This would necessitate the synthesis of new mononuclear Ga and/or In precursors. This could

be achieved through salt metathesis or by loading  $\text{NO}_3^-$  or  $\text{Cl}^-$  salts of the  $\text{M}^{3+}$  species on an ion exchange column and passing through the desired Cu/S-containing anionic species for cation exchange to prepare a Ga/In-Cu<sub>x</sub>S<sub>y</sub> precursor. This precursor may be an interesting “ink” in its own right, but we will also attempt to prepare the related M<sub>13</sub> cluster.

There are also a number of Cu salts available as starting materials for the direct synthesis of a trimetallic Ga-In-Cu compound. We have investigated some of these already, focusing largely on  $\text{Cu}(\text{NO}_3)_2$ , to maintain a consistent counterion to previous systems. In the case of the procedure developed using Cu metal directly (described above), a molecular precursor was not isolated or characterized; instead, precursor ink solutions were used as prepared to produce semiconductor thin films. We will attempt to isolate such a molecular precursor; however, the ink will be immediately screened to prepare a thin film to fill the interstitial fractal space in the materials prepared in Aim 1 (see Figure 3). In addition, we can prepare the entire series of **Ga<sub>13-x</sub>In<sub>x</sub>** clusters ( $x = 0$  to 6),[8] providing exquisite control of the Ga:In ratio *at the molecular level* in the inks/precursors used for forming new  $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2/\text{Se}_2$  films. This series of Ga/In clusters will also be investigated as components of these new precursor solutions.

As a final route to new materials, it may also be possible to perform the anion exchange directly on the thin films as prepared. We have demonstrated direct anion exchange of nitrate counterions by replacing them with hydroxide once the thin films are prepared. We propose to investigate whether a similar approach may be used with the Cu/S-containing anions and related Se-containing species.

**Aim 3 – Outlook and Summary.** It is conceivable that the condensation from cluster precursors to films itself follows a fractal pathway, as predicted for other self-assembled nanoscale systems.[3] Can fractal materials be trapped prior to complete thin film condensation? Do theoretical models of fractal geometry predict such patterns during the condensation pathway? If such fractal geometries can be trapped using metal clusters relevant to light-harvesting, are these structures useful for applications in solar energy? The requested Scialog funding will enable the PIs to begin to answer these questions and will unite the fundamental studies in chemistry and physics proposed herein.

As an ongoing, long-term goal of the proposed research, we seek to merge the two research thrusts above. Independently, each research lab will make advances in solar energy conversion: The Taylor lab will make fundamental physics discoveries by predicting fractal geometries that provide optimized properties for solar materials applications and the Johnson lab make fundamental chemistry discoveries in the preparation of new inorganic clusters, inks, and thin films. More importantly, the requested Scialog funding unites these two research thrusts to enable the overarching goal of this proposal: to simulate, fabricate and measure novel solar materials that exploit the solar efficiency of Nature’s fractal patterns. This program brings together a team of physicists and inorganic materials chemists to work side-by-side to deliver fundamental advances in both chemistry and physics for potential applications in solar energy conversion. The three year funding would provide preliminary basic science results to contribute to a larger multidisciplinary proposal involving researchers in the CGMC, FRL and SuNRISE. For instance, the aspects of this project falling under the auspices of “green materials chemistry” would likely be adopted as a project in the Phase 2 CGMC

program. In addition, multi-PI proposals to DOE, NSF and/or in state initiatives such as the ARL NanoArchitectures for Enhanced Performance or AFRL Safer Nanomaterials and Nanomanufacturing Initiative are also likely funding agencies for leveraging the initial RCSA investment. Interactions with numerous regional companies, including SolarWorld, Nanosolar, ON Semiconductor and others also provide opportunities for partnership and funding opportunities (such as NSF-GOALI, SBIR, and ONAMI, a state-initiative). Voxel and Sony research lab outposts are also both located in the Lokey Laboratories on the UO campus for further industrial interactions to help enable longterm goals and to enrich the educational opportunities of students working on the requested Scialog project.

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