Pushing the Efficiency Limits of Solar Cells with Molecular Photon Upconversion

Summary: The abundant and sustained nature of sunlight leaves little doubt that access to inexpensive solar energy conversion technology will play a pivotal role in future global health and sustainability. As such, it is necessary to generate less expensive cells and/or increase solar cell efficiencies in order to decrease module costs per energy generated ($/kWh). As a step towards this goal we have introduced an entirely new solar energy conversion strategy that incorporates molecular photon upconversion directly into a solar cell. Photon upconversion (UC)—combining low energy light to generate a higher energy light—is a strategy to efficiently utilize the previously unharnessed, low energy portions of the solar spectrum. Our efforts thus far have demonstrated that the mechanism is feasible but the proof-of-concept device efficiency is low. Here we propose the steps necessary to significantly increase device performance. If successful, this integrated upconversion solar cell will be a lower cost alternative to traditional silicon solar cells which could have far reaching global implication for the distribution and utilization of inexpensive renewable energy.

I. Description of invention: Dye-sensitized solar cells (DSSCs) are a promising alternative to traditional silicon solar cells because they can be generated using low cost, solution processable manufacturing. Since the mid-1990s the record DSSC efficiency has increased from 11% to 14.1%[1] through incremental variation in the composition of the materials but the photocurrent generation mechanism remains largely unchanged. The record efficiency, while impressive, falls short of the competitive commercialization goal of 15%.[2] Systems analysis indicate that harnessing photon upconversion via triplet-triplet annihilation (TTA-UC) can increase the maximum theoretical solar cell efficiency from 31% to greater than 43%.[3] Actual device performances are lower than the theoretical limit but successful implementation of TTA-UC could increase DSSC performance from the current 14.1% to upwards of 20% (well above the 15% commercialization goal) but with much lower manufacturing cost than current solar cell technologies. With this goal in mind, the Hanson research group has introduced self-assembled bilayers on metal oxide surfaces (Figure 1) as an effective strategy for combining TTA-UC molecules[4] and directly harnessing TTA-UC in a DSSC.[5] Our prototype bilayer TTA-UC film/device is composed of a high surface-area semiconductor, an acceptor molecule (blue in figure 1), a sensitizer molecule (red in figure 1), a redox mediator, and counter electrode. We have definitively established that bilayer films effectively harness sunlight and generate photocurrent via low energy light absorption by the sensitizer molecule, followed by triplet energy transfer, TTA-UC, and electron injection from the upconverted state.

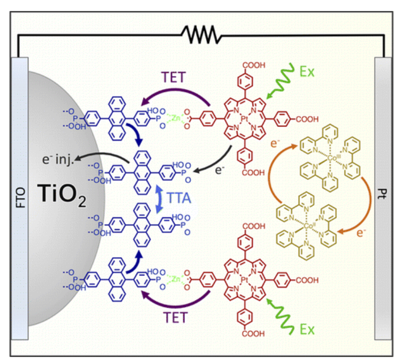

Figure 1. Schematic of the self-assembled TTA-UC DSSC.

II. Importance in the area of science, environmental conservation, or patient care and experience: The realization of an efficient TTA-UC could have a major impact on numerous applications, such as photodynamic therapy, photocatalysis, bioimaging, photoactuators, and, in particular, solar energy conversion. Access to low cost, renewable solar energy will 1) reduce

CO_2 emissions, 2) lessen the need for mining/fracking/drilling for fossil fuel, and 3) improve the quality of life for millions of people around the globe. The later point being particularly important in that inexpensive energy/electricity can be used for water and air purification, cooking, indoor lighting, recycling materials, as well as the production and distribution of medical equipment/technology.

III. Stage of invention: We have generated an integrated TTA-UC DSSC using self-assembled bilayers and have definitively supported that we are able to harness a new photocurrent generation mechanism via TTA-UC. Our first published TTA-UC DSSC efficiency is low (η_{UC} = 1.6 × 10^{-5} %, η_{total} = 7.0 × 10^{-3} %) but does demonstrate proof-of-concept. Now that we have established a mechanism we are positioned to significantly improve device performance by: 1) Incorporating near-IR absorbing sensitizer and acceptor pairs into the film to maximize solar spectrum overlap and UC solar cell efficiency, 2) generating multi-sensitizer bi- and tri-layer films to increase broad band light absorption, 3) modifying the acceptor molecule structure to maximize electron injection yield and cross-surface energy transfer/TTA rate, and 4) incorporating earth abundant sensitizer molecules into the TTA-UC DSSCs.

IV. Current funding: The research thus far has been entirely supported by start-up funds provided by the FSU Energy & Materials initiative. This startup account will be closed on August 2017. We currently have two pending grants (NSF-CHE-MSN and ONR-YIP) to gain fundamental mechanistic insights into the energy/electron transfer dynamics in the film. These pending proposals do not focus on increasing device efficiencies (although the insights gained will help in future materials design).

V. Feasibility: The extensive information already available on both DSSCs and TTA-UC indicate that a >15% efficient TTA-UC DSSC can be realized. The success of this effort requires a broad range of skills including synthesis, thin-film preparation, and device assembly/measurement. Based on our preliminary results, previous publications, and instrumental capabilities we are confident that we have the plan, skill, and know-how to achieve this goal.

VI. Approach for measuring progress during the grant term: Progress in developing this technology can readily be monitored using the device efficiency (current and voltage) relative to the prototype device as well as a control cell that are known to reach 11% in a manufactured device (the same architecture is ~4% efficient in our lab).

References

1) Kakiage, K.; Aoyama, Y.; Yano, T.; Oya, K.; Fujisawa, J.; Hanaya, M. *Chem. Commun.*, **2015**, 51, 15894-15897.
2) Qin, Y.; Peng, Q. *Int. J. Photoenergy* **2012**, 2012, 291579.
3) Cheng, Y. Y.; Fückel, B.; Khoury, T.; Clady, R. l. G. C. R.; Tayebjee, M. J. Y.; Ekins-Daukes, N. J.; Crossley, M. J.; Schmidt, T. W. *Journal of Physical Chemistry Letters* **2010,** 1, 1795-1799.
4) Hill, S.P.; Banerjee, T.; Dilbeck, T.; Hanson, K. *J. Phys. Chem. Lett.* **2015**, 6, 4510-4517.
5) Hill, S.P.; Dilbeck, T.; Baduell, E.; Hanson, K. *ACS Energy Lett.* **2016**, 1, 3-8.

<u>Budget (spreadsheet available upon request):</u>

A. Senior Personnel (Total: $39,855)

One month of summer salary is requested for the PI, Kenneth Hanson, who will devote 1.0 calendar-months effort to this project per year ($10,832). Funds are requested to cover fringe benefits at a rate of 19.03% for faculty. A 3% annual salary increase has been included.

B. Other Personnel (Total: $478,968)

This proposal requests support for one postdoc, three graduate students, and three undergraduate student over the 3-year funding period. The postdoc will be paid at a rate of $47,500 with 2.75% fringe with $15,000 per year for health insurance. Each grad students will be paid at a rate of $23,494.00 for the first year and a 3% yearly increase to account for inflation with 1.3% for fringe benefits as well as $1,662 per year per student subsidy the university-sponsored health insurance plan. Three undergraduate summer research students will be paid at a rate of $5,000 each summer with 1.3% for fringe benefits

C. Travel (Total: $42,000)

We request $8,000 per year in domestic travel costs and $6,000 per year for international travel costs. Funds are requested for the PI, postdoc, and students to attend four domestic conference each per year ($2000 per trip per person) and two international conference ($3000 per trip per person). Example rates are shown below:

<u>Domestic:</u>		<u>International:</u>	
Airfare:	$500.00	Airfare:	$1500.00
Registration:	$1,000.00	Registration:	$1000.00
Lodging: (3 nts @ ~$120/nts)	$356.00	Lodging: (3 nts @ ~$120/nts)	$356.00
Meals: (4 days @ $36/day)	$144.00	Meals: (4 days @ $36/day)	$144.00
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TOTAL/TRIP:	$2,000.00	TOTAL/TRIP:	$3,000.00

D. Materials, Supplies, and Instrument time (Total: $82,810)

We request $34540, $29761, and $24846 in years one, two, and three respectively for materials and supplied to conduct the research. These funds will be partitioned 70% materials and supplies (chemicals, glassware, lamps, etc.) and 30% instrument time (NMR, MS, spectrometers, etc.).

E. Tuition (Total: $100,029)

Funds for tuition costs are requested for 27 credit hours per year per graduate research assistant (9 hours/semester during the fall, spring and summer term). The 2017-18 academic year cost is $11004 and is anticipated to increase by 1%/year in subsequent years.

F. Equipment (Total: $0)

No funds are requested for equipment. All equipment necessary to perform the research described in this proposal are already available in our lab or in user facilities at FSU.

G. Indirect (Total: $75,000)

The grant does not allow for indirect costs as a percentage of the funding. However, FSU will receive a total of $75,000 ($25,000 each year) to offset costs associated with grant management.

Total Requested Funding = $750,000 + $75,000 **= $825,000**
(direct) (indirect) **(TOTAL)**

Kenneth Hanson

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Education/Experience

Florida State University	Assistant Professor	2013-present
UNC-Chapel Hill	Postdoctoral Researcher Research Advisor: Prof. Thomas J. Meyer	2010-2013
University of Southern California	Inorganic Chemistry Research Advisor: Prof. Mark E. Thompson	Ph.D., 2010
St. Cloud State University	Chemistry	B.S., 2005

Publication/Patent Metrics

Total Publications: 56	Patents: 9 (1 provisional)	h-index: 25
Independent Publications: 20	Citations: 1668	i10-index: 36

Independent Grants/Awards

2016	DOE-EFRC: Center For Actinide Science (PI: Thomas Albrecht-Schmidt)
2015	AAAS Early Career Award for Public Engagement with Science (Top 4 Finalist)
2015	NSF-Major Research Instrumentation Grant
2015	Selected as 1 of 50 "Not to miss" presentations at the Fall 2015 National Meeting of the American chemical Society
2015	C&EN's ChemPics Tumblr Blog Chemistry Photo of the Year
2014	Army Research Office-Young Investigator Program Award
2014	American Chemical Society-Petroleum Research Fund

Five Example Publications

1) Hill, S.P.; Dilbeck, T.; Baduell, E.; Hanson, K. Integrated Photon Upconversion Solar Cell via Molecular Self-Assembly at Hybrid Interfaces. *ACS Energy Lett.* **2016**, 1, 3-8. http://pubs.acs.org/doi/abs/10.1021/acsenergylett.6b00001.

2) Hill, S.P.; Banerjee, T.; Dilbeck, T.; Hanson, K. Photon Upconversion and Photocurrent Generation via Self-Assembly at Hybrid Interfaces. *J. Phys. Chem. Lett.* **2015**, 6, 4510-4517. http://pubs.acs.org/doi/abs/10.1021/acs.jpclett.5b02120.

3) Ogunsolu, O.O.; Murphy, I.A.; Wang, J.C.; Das, A.; Hanson, K. Energy and Electron Transfer Cascade Self-Assembled Bilayers for Application in Dye-Sensitized Solar Cells. *ACS Appl. Mater. Interfaces* **2015**, 7, 27730-27734. http://pubs.acs.org/doi/abs/10.1021/acsami.6b09955.

4) Das, A.; Ayad, S.; Hanson, K., Enantioselective Protonation of Silyl Enol Ether Using Excited State Proton Transfer Dyes. *Org. Lett.* **2016**, 18, 5416–5419. http://pubs.acs.org/doi/abs/10.1021/acs.orglett.6b02820.

5) Das, A.; Banerjee, T.; Hanson, K., Protonation of Silylenol Ether via Excited State Proton Transfer Catalysis. *Chem. Comm.* **2015**, 52, 1350-1353. http://pubs.rsc.org/en/content/articlelanding/2015/cc/c5cc08081a#!divAbstract.

Synergistic Activities

1) Reviewer: *Journal of the American Chemical Society, Journal of Physical Chemistry, ACS Photonics, Advanced Materials Interfaces, Sensors, Chemistry of Materials, Physical Chemistry Chemical Physics, ACS Applied Materials & Interfaces, Inorganic Chemistry, Journal of Graphics and Modeling, Inorganic Chemistry, Polymer Chemistry, Langmuir, Dalton Transactions, Chemical Sciences, ACS Nano, Angewandte Chemie, Materials Technology: Advanced Performance Materials, Applied Surface Science, Journal of Materials Chemistry A.*
2) Panelist for SCIENCE 2034 Live (Washington, DC): A United State Senate and House Congressional briefings on the importance of funding basic science and its implications for life in the future. (Hosted by the Science Coalition)
3) Founder and Organizer of the monthly First Friday, *Ask a Scientist* event in Railroad Square, Tallahassee
4) Regular contributor of scientific content to www.chemistry-blog.com, twitter.com and www.reddit.com/r/chemistry/.

Students/Postdocs

Postdoctoral Associates: Tanmay Bannerjee(2014-2016), Anjan Das (2014-current), Sahan Salpage (2016-current)

Graduate Students: Jamie Wang (2013-current), Sean Hill (2013-current), Omotola Ogunsolu (2014-current), Tristan Dilbeck (2014-current), Suliman Ayad (2016-current), Yan Zhou (2016-current)

Undergraduate Students: Ian Murphy (2013-2016),Enric Baduell (2014-2016), Bryan Casale (2014-2016), Catherine Kent (2014-current), Kyle Violette (2015-current), Victoria Posey (2016-current), Justin Silver (2016-current), Alex Braun (2016-current)

Awards and Honors Received by Students

2016	Tristan Dilbeck, 2nd place graduate poster, Florida Inorganic/Material Symposium
2016	Kyle Violette, 1st place undergraduate poster, ACS Florida Meeting and Exposition
2016	Tristan Dilbeck, Ford Foundation Fellowship (honorable mentioned)
2015	Omotola Ogunsolu, FSU Art in Stem Competition (runner-up)
2015	Jamie C. Wang, NSF-Graduate Research Fellow
2015	Omotola Ogunsolu, P.E.O. International Peace Scholarship
2015	Ian Murphy, 1st place undergraduate poster, ACS Florida Annual Meeting and Exposition
2015	Sean Hill, 2nd place graduate poster, ACS Florida Annual Meeting and Exposition
2015	Jamie C. Wang, 1st place graduate poster, Florida Inorganic/Material Symposium
2015	Sean Hill, 3rd place graduate poster, Florida Inorganic/Material Symposium
2015	Ian Murphy, 1st place undergraduate poster, Florida Inorganic/Material Symposium
2015	Catherine Ken, 2nd place undergraduate poster, Florida Inorganic/Material Symposium
2014	Omotola Ogunsolu, Reverie Innovation Scholarship
2014	Jamie C. Wang, 2nd place graduate poster, Florida Inorganic/Material Symposium