

Transparent photovoltaics

Organic Salts as a Route to Energy Level Control in Low Bandgap, High Open-Circuit Voltage Organic and Transparent Solar Cells that Approach the Excitonic Voltage Limit

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Transparent Luminescent Solar Concentrators for Large-Area Solar Windows Enabled by Massive Stokes-Shift Nanocluster Phosphors

Authors: Yimu Zhao and Richard R. Lunt, *Adv. Energy Mater.* **2013**, 3, 1143–1148.

Recommended and Commentary by Albert Migliori, Los Alamos National Laboratory

You know right away, if you think about it, that for this to work the system cannot absorb or use visible light. So what's left? Turns out there is lots of solar energy just the red side of where humans can see. In fact, something like half is left in the near infrared [1,2]. So the challenges that Lunt and team had to overcome include reasonable capture of photons near and below 1 eV, and then the same challenges as the perovskite photovoltaics must overcome, namely traps, photoluminescence lifetime, environmental endurance, toxicity, and, of course, the issues with the levelized cost of electricity (my commentary at <http://www.condmatjournalclub.org/?p=2650>). Mitigating this is the fabulous unobtrusiveness that transparency brings, plus the application to multiple gap systems. Let's consider that for the moment. The bottom line is the levelized cost of electricity (LCOE), an attempt to measure the present monetary value of the total cost of a generating facility over its full lifetime against the total electrical energy ever generated by the facility. Today, with Si photovoltaics so cheap, a powerful motivation for photovoltaics (PV) is to reduce the cost of the support structures because with cheap Si, this has become a much more important component of LCOE. This can be done by either increasing total PV efficiency, or reducing or eliminating the support structures. One route that seems promising for maybe perovskite but certainly transparent PVs is to coat the already pretty good Si PV system with another PV that does not absorb the photons Si needs to work. If the coating is easy, then a few percent additional energy capture may reduce the size and cost of the PV plant by nearly the same amount. And no additional infrastructure is needed for such a tandem cell device.

Now consider a conventional band semiconductor with a gap below the band gap of Si. Its bandwidth will still extend to energies above its gap, albeit with reduced density of states, so that it will absorb some photons that Si might use. But with a smaller gap, those higher energy photons are less effective in driving photocurrents than if Si were to catch them. So the ideal coating PV would produce voltages near the excitonic limit (the PV output voltage is near the photon energy per carrier). The approach described here builds on the use of ionic inorganic salts of the polymethines or cyanines (exact composition in first recommended article). The first advantage is that these are big molecules so that their energy landscape does not look like a band semiconductor, but more like isolated resonant absorbers. Thus they are resistant to absorbing higher energy photons than the design target, and therefore the absorption can be tuned away

from visible light, as the authors have done. Another advantage is that the charge-carrying anion can be changed. By adjusting this anion's mass upward, the exciton diffusion length is increased, the effect of (non radiative) traps is reduced, and the external quantum efficiency (number of carriers per incident photon) rises. Reaching values near 20% (Si is nearer 60%), such systems become usable. The other surprise from this work is the open circuit voltage. Though the authors do not have a solid microscopic picture of what is going on, a systematic substitution of anions resulted in gains of 70% on the excitonic limit open circuit voltage, to near 75% of the maximum possible.

So how does one use these? One way is to coat Si PVs. The environmental issues remain, but recent results show 3-year survivability, much like the improvements in that area for perovskite PVs. But another approach is to make special window glass with nanoclusters in it. Here, a very nice trick is implemented, described in the second recommended article. The idea is to capture UV light through a window and down-convert it to near IR using a large Stokes shift obtained through tailoring of metal halide clusters. The absorption in the visible is essentially zero, and the authors were able to get near-unity quantum yields. That is, nearly every UV photon is Stokes shifted to near IR. In the usual spontaneous Raman effect, the polarizability (not polarization) is modulated at the system's phonon frequencies. The phonons have energy (not much) and momentum (lots). Thus the incoming high energy (visible) photon with low momentum combines via a weak anharmonicity in the polarizability so that the incoming photon gives up energy to excite the phonon and also momentum. The momentum makes the slightly red-shifted (it lost energy to the phonon) photon (Stokes shift) come out at an angle to the incident one that is large because the phonon momentum is large. The nanostructures here don't have momentum conservation to affect the outgoing photon, so a UV photon and a vibrational mode in the molecule that is not IR active but does modulate the polarizability produces an IR photon and leaves behind the rest of the incident photon energy, no momentum conservation restriction required, upping the probability of the event.

It wouldn't work if the shift was only to visible because the windows would fluoresce visible light, and people would not like that. Once the IR photon is emitted, the window glass acts as a light pipe, carrying nearly all the IR photons to the edges. The tuning comes in the way the nanoclusters, and ligands they are embedded in, work together ($\text{K}_2\text{Mo}_6\text{Cl}_{14}$ and $(\text{tetrabutylammonium})_2\text{Mo}_6\text{Cl}_{14}$ in acetonitrile). The whole system acts as a "solar" concentrator, so all that needs done is to coat the edges of the window with the IR photovoltaics described above. This area of organic salts, excitons, and giant Stokes shifts is rich in unanswered questions, and important for renewable energy.

References:

1. **Theoretical limits for visibly transparent photovoltaics**, Richard Lunt, Applied Physics Letters **101**, 043902 (2012).
2. **Transparent, near-infrared organic photovoltaic solar cells for window and energy-scavenging applications**, Richard R. Lunt, and Vladimir Bulovic, Applied Physics Letters **98**, 113305 (2011).

