IN DEVELOPMENT

Lawrence Berkeley Unveils Plasmonic Electrochromic Window Coating

Figure 7. Delia Milliron, Staff Scientist at Lawrence Berkeley National Laboratory's Molecular Foundry. Photo courtesy Delia Milliron.

Lawrence Berkeley National Laboratory's (LBNL) Molecular Foundry announced groundbreaking research on a new transparent electrochromic film that modulates near-infrared (NIR) solar heat gain without affecting visible light transmission. While traditional dynamic window coatings – photochromic, thermochromic, gasochromic, and electrochromic – can provide a range of solar control, they primarily modulate visible light. LBL's prototype plasmonic electrochromic coatings may offer a unique opportunity to selectively control the transmission of NIR without affecting visible transparency.

Initiating the research internally, LBL's Molecular Foundry recently received a Department of Energy (DOE) Advanced Research Projects Agency – Energy (ARPA-E) grant to further develop the technology. The research team, led by the Delia Milliron, Staff Scientist at the Foundry (Figure 7), aims to create a low-cost electrochromic window coating technology, which can respond to changing weather conditions by regulating the visible light and heat entering a building through its windows, reducing energy usage. The Molecular Foundry team is working in partnership with Stephen Selkowitz's Windows Research and Development team and the Energy Analysis Group, both of LBNL's Environmental Energies Technologies Division (EETD), and with Heliotrope Technologies.

Energy Design Update interviewed Milliron to learn more about the new coating, current laboratory results, and the pathway of future testing. "Over the past 2 years we've developed a new electrochromic with functionality. The principle we came up with is to find way to use nanocrystals synthesized chemically to absorb NIR, yet that stay transparent so the coating does not interfere with visible light transmittance (VL). We can thus drive a better solar heat gain coefficient (SHGC) without affecting VL. We are also looking at incorporating the new nanocrystal coating with a more conventional electrochromic to control light, so that a homeowner can tune selectively for NIR transmittance and VL," Milliron said (see Figure 8).

"This research is driven by 3 key factors: the functionality of controlling heat and light; the opportunity to actually manufacture the technology inexpensively, and modeling results," Milliron explained. "Frankly, modeling results are helping guide technology development, such as defining which markets are best for this application. Modeling will also help us predict which of the possible solution process options are best, what are our branch points in the decision to manufacture, and which approach will give us the most cost savings. We need to have a full picture of lifecycle costs, embodied energy, and payback."

Figure 8. West facing windows absorb heat through the sun. The principle behind the proposed technology uses nanocrystals synthesized chemically to absorb near infrared light and inhibit solar heat gain, while staying transparent so that the coating does not interfere with visible light transmittance. Photo courtesy Delia Milliron and Lawrence Berkeley National Laboratory.

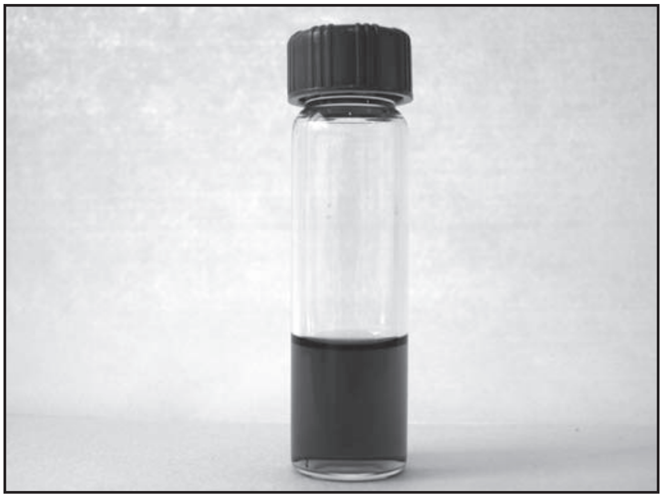

Figure 9. A vial containing the nanocrystal dispersion. Photo courtesy Delia Milliron and Lawrence Berkeley National Laboratory.

Because this approach can reduce solar gain without inhibiting daylighting, Milliron feels this technology may be better positioned against competing, traditional window glazings. By separately tuning the incoming NIR, which generates heat, and VL, which can provide daylighting, LBL hopes this technology will improve the energy efficiency of buildings by reducing the need for both air conditioning, heating, and electric lighting, and by enhancing the comfort of occupants, by managing the visible light that enters. LBL's breakthrough electrochromic nanotechnology is based on a plasmonic electrochromic effect that dynamically modulates the localized surface plasmon of doped semiconducting nanocrystals. An applied voltage is used to alter the optical properties of the glazing. In a dynamic window construction, voltage control strategies could be tied to HVAC setpoints to ensure effective operation. Based upon current laboratory testing results, the prototype phase technology can modulate up to 60% of solar NIR (Figure 9).

"We did a lot of materials development; these test units are all coated using a solution processing, making their eventual manufacturing process a lot cheaper, so that we can bring this technology into reach of the average consumer," Milliron clarified. "We are at the stage now where our team is building the materials into a complete prototype. Modeling will help us define the target dynamic range for NIR and VL modulation and to predict how dark and clear the tints can be. This development will take place over the next 3 years, funded by ARPA-E. Our goals will be to optimize optical and switching performance. We will be asking how much infrared we can manipulate, and maintain VL? These initial stages will also help us develop a scalable manufacturing approach. Techniques like spray coating – how do they translate to the large scale, and how can we bring manufacturing costs down?"

Milliron used degenerately doped semiconductor nanocrystals (NCs), such as tin doped indium oxide (ITO), that have a well defined localized surface plasmon resonance (LSPR) in the NIR region of the solar spectrum. When activated by an applied voltage, ITO NCs show a large spectral shift in their NIR LSPR due to electrochemical doping (Figure 10).

"The nanocrystals are synthesized using the standard chemical technique of colloidal chemistry; using a flask of solvent, we bring the components of the nanocrystals to a chemical reaction, and after growth in an organic solution, we isolate them with a standard purification technique to got a stable solution. Related procedures have been used for large area coatings and devices like static optical films, displays, or photovoltaic cells."

"I've always been interested in electrochromics as a nanomaterials chemist," Milliron said. "It was really through talking with my colleagues in window development that my perspective was informed, and I understood the need. One of the things that's really needed is a way to control IR transmittance. 10 years ago the community took a preliminary look at electrochromic properties of nanocrystals, but it was not suitable for windows. I figured that we had made a lot of progress in the last 10 years, and that maybe with a twist on chemistry and composition, we could move the spectral features into the wavelength range that really matters for solar radiation."

According to initial laboratory research (Refer to Guillermo Garcia, Raffaella Buonsanti, Evan L.

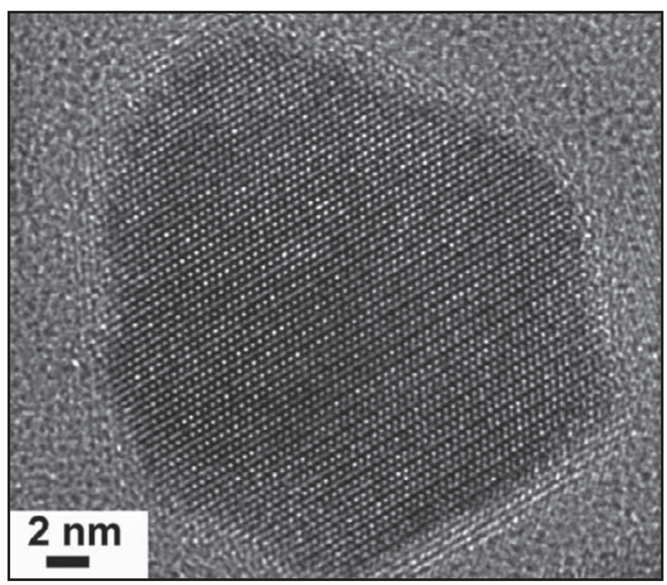

Figure 10. High-resolution transmission electron microscopy image of an electrochromic nanocrystal. Photo courtesy Delia Milliron and Lawrence Berkeley National Laboratory.

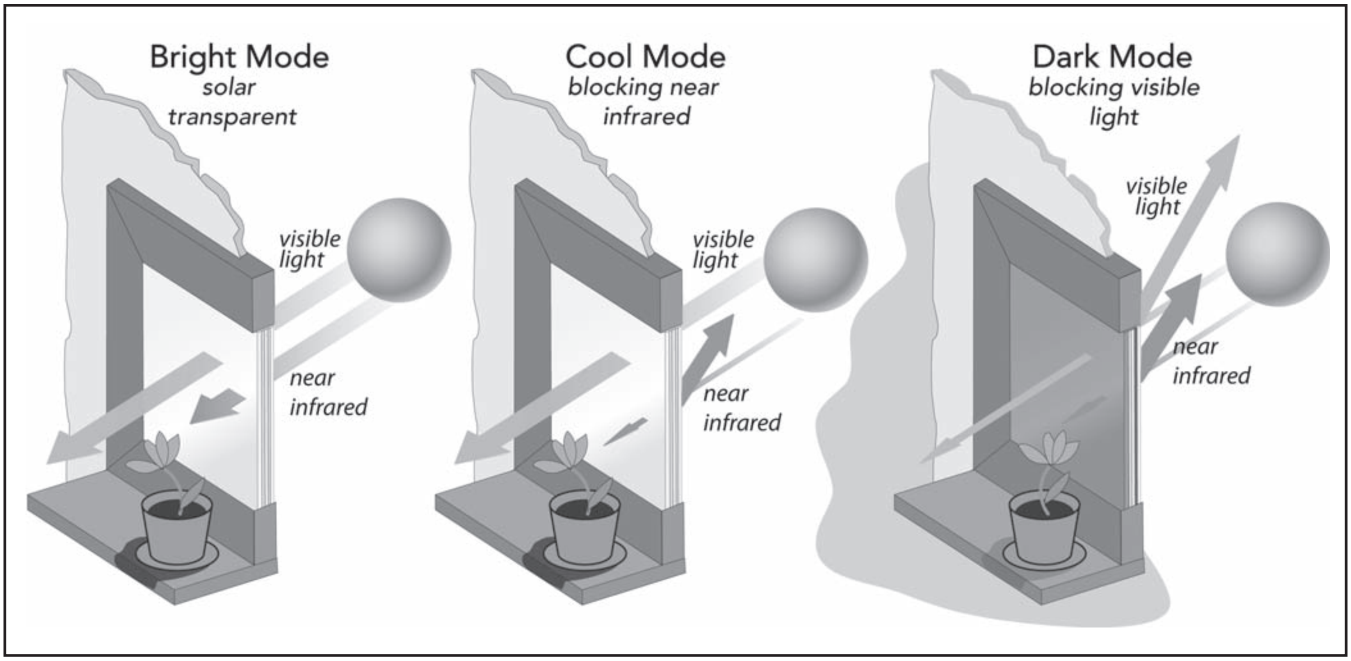

Figure 11. Milliron's team will also investigate coatings that combine the near infrared-selective plasmonic electrochromic effect with conventional electrochromic materials that can also modulate visible light, on demand. Photo courtesy Delia Milliron and Lawrence Berkeley National Laboratory.

Runnerstrom, Rueben J. Mendelsberg, Anna Llordes, Andre Anders,Thomas J. Richardson, and Delia J. Milliron, "Dynamically Modulating the Surface Plasmon Resonance of Doped Semiconductor Nanocrystals," Nano Letters, *http://pubs.acs.org/NanoLett*) by utilizing capacitive charging, plasmonic electrochromic coatings can achieve larger optical contrast with minimal charge requirements. Optimization of nanocrystal size, chemical doping level, and film thickness may enhance these results. VL was preserved in the tests, with over 92% of light transmittance preserved during the product's colored state to inhibit solar heat gain. The plasmonic electrochromic coatings also appear to maintain stability, with positive implications for the device's lifecycle. Durability test performance resulted in an 11% reduction in charge capacity after cycling 20,000 times between the applied voltage extremes. Nevertheless, this slight loss in charge did not seem to affect the optical performance. Milliron postulated that charge may have dropped due to solvent evaporation in the cell.

"We built some initial small-scale prototypes, about 1" square, to show that the coatings can switch, and carry out fundamental predicted properties. From there, we have collaborated with the energy analysis team, to get some initial modeling of possible energy savings," Milliron stated.

Actual savings from these technologies will depend heavily upon their performance in diverse climate and operational conditions. LBL used COMFEN 4 software, an EnergyPlus interface, to simulate a broad range of performance levels for commercial and residential buildings in 16 climate-representative reference cities. The software also models window to wall ratios, internal floorspace, and heating and cooling loads. The results will gauge performance of the prototype technology against existing static technologies.

Best-case results for LBL's new plasmonic electrochromic coating showed an annual heating, ventilation, and air-conditioning (HVAC) energy savings potential as high as 11 kWh/m² a year for commercial buildings, and 15 kWh/m² year for residential, over the highest performing static glazing. Due to schedule of occupancy, lighting and miscellaneous loads, which contribute to internal heat gains, the technology shows the most promise, and greatest energy savings, for residential application.

Among the 16 reference cities, the simulation showed that the technology performed worst in Miami, as increased transmitting functionality is nearly worthless, and even the highest transmitting SHGC enables little discernible performance reduction in the blocking state. Chicago, Boulder, Minneapolis, Helena, Duluth, and Fairbanks showed greatest promised, based on delta ratios between transmitting and blocking performance. San Francisco, while energy-savings favored blocking, was still viable. Energy analysis showed that, outside of a select few hot Southern regions, meaningful savings can be realized from the new glazing prototype. This study finds that outside of the hot, sunny region of the southern US, nanotechnology electrochromic glazings, defined as those that maintain high visible transmittance but switch over a wide range in the NIR, have significant potential to outperform static glazings on the basis of heating and cooling energy. The report concluded that, ultimately, it is the fixed, highly visible transparent nature of the nanotechnology that constrains its applicability, because the highest performing blocking state still transmits approximately 30% of the solar energy in the form of visible light. (To access the full energy analysis report, see "Regional performance targets for transparent near-infrared switching electrochromic window glazings," Nicholas DeForest, Arman Shehabi, Guillermo Garcia, Jeffery Greenblatt, Eric Masanet, Eleanor S. Lee, Stephen Selkowitz, Delia J. Milliron. Building and Environment 61 (2013) 160e168. *http://www.elsevier.com/locate/buildenv*.) For this reason, Milliron's team is currently investigating coatings that combine the NIR-selective plasmonic electrochromic effect with conventional electrochromic materials that can also modulate visible light, on demand (see Figure 11).

"Further improvements are currently being investigated to enhance the glazing performance and establish market deployment opportunities in the next 3 to 5 years," Milliron said. "Ultimately, the potential for success will depend on how effectively this technology performs in reducing building HVAC loads through blocking or transmitting NIR heat, and reducing lighting energy by transmitting visible light."

"Our research is now going to the next step from clear IR transmittance, to darkening the window to also control VL. We are adding a new functionality. Even just for NIR our energy analysis shows a pretty compelling market, with residential energy savings more significant, as the northern markets can really take advantage of solar heating in winter."

Energy Design Update would like to thank Delia Milliron and Lawrence Berkeley National Laboratory for sharing this research with us.

Delia J. Milliron is a Staff Scientist at Lawrence Berkeley National Laboratory, a research center and user facility for nanoscience supported by the U.S. Department of Energy. She received her PhD in Chemistry from the UC-Berkeley, in 2004. From 2004 to 2008 she worked for IBM's research division, investigating opportunities to use nanoparticle materials in next generation data storage technologies. Her current research is motivated by the potential for nanomaterials to introduce new functionality to and reduce manufacturing costs of energy technologies. Her group's activities span from the fundamental chemistry of nanomaterials to device integration and characterization. She is the recent recipient of an R&D 100 Award, an MDV Innovators Award, and a DOE Early Career Research Program grant.

IN BRIEF

Shining the Light on Green Roofs: Data From Photovoltaic Array Interaction

Over a 30 month period, from June 2008 through December 2010, environmental monitoring was conducted in downtown Denver, Colorado, on the Region 8 Environmental Protection Agency (EPA) Headquarter's green roof (20,000 sq ft). The vegetated portion of the green roof covers 20,000 square feet (1,858 m²) of the 33,000 total square ft (3,066 m²) roof. The study was lead by Thomas J. Slabe and former Colorado State University (CSU) doctoral student, (now Dr.) Jennifer Bousselot under the advisement of CSU Professor James E. Klett.

During data collection, the research team noted that shade structures, including photovoltaic arrays, influence the growth of green roof plants (refer to Figure 12).

Figure 12. Part of the photovoltaic structure at the Region 8 Environmental Protection Agency Headquarter's green roof. Photo courtesy Thomas J. Slabe.

Designing with moisture in mind is vital for the success of a green roof, structurally and biologically. For a region such as Metropolitan Denver, moisture may dissipate too rapidly with a thin substrate material

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