LOW COST VOLTAGE-CONTROLLED WINDOW CAN BE TUNED TO BLOCK VISIBLE AND/OR INFRARED LIGHT

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PROJECT TITLE: Low Cost Solution Processed Universal Smart Window Coatings
PROGRAM: OPEN 2012
AWARD: $4,730,970
PROJECT TEAM: University of Texas, Austin (Lead); Heliotrope, Inc.; LBNL
PROJECT TERM: March 2013 – September 2016
PRINCIPAL INVESTIGATOR (PI): Dr. Delia Milliron

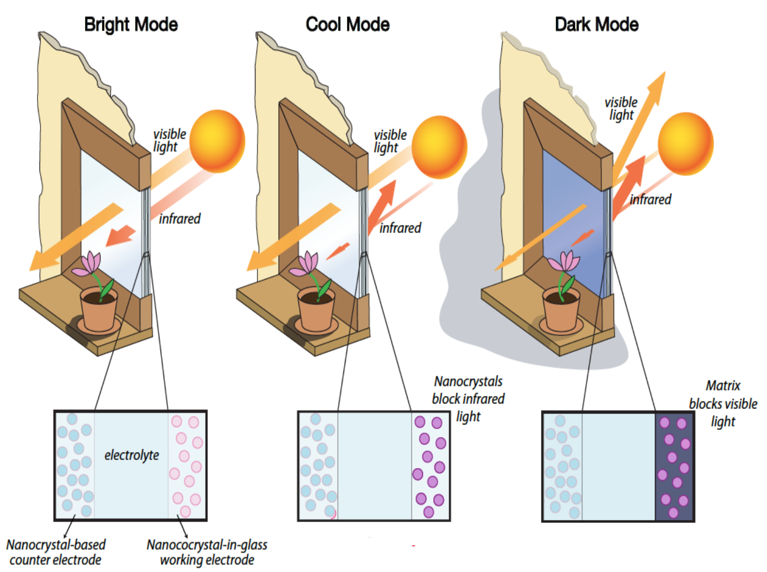
TECHNICAL CHALLENGE

Each year about 2.5 quads of primary energy is expended for air conditioning to counteract the heat entering through windows from sunlight. Electrochromic (EC) windows, that can be tuned to block light transmission using an applied voltage, are now available commercially as options in sealed double pane window units. However they have not reached significant market implementation due in large part to high cost, typically around $50/ft^2. These window panes are typically manufactured via vacuum deposition techniques, and modulate the broad spectrum of sunlight from the visible through the near-infrared (NIR). Realistic operation of these devices in the highest-value applications is expected to save 0.6 quads annually over baseline static windows. In addition to the high cost, a barrier to the use of these windows is the reduction of useful visible light (daylighting) when they are darkened to block heat transmission. Newer technologies are needed that can demonstrate a marked improvement in optical performance, cycling stability, switching speed, and a significant reduction of manufacturing cost to be competitive with inexpensive static coatings (~$3-5/ft^2 for the coating alone).

TECHNICAL OPPORTUNITY

Advances in materials science have created new approaches to the fabrication of coating with EC properties. Switching to nanostructured composite EC materials opens up solution-based deposition techniques that could lower the cost of electrochromic window fabrication by about 40% compared to conventional ECs. Furthermore, the recent discovery of a plasmonic EC effect present in some novel nanocomposites allows for independent management of NIR and visible light transmittance. This could enable independent control of visible and IR light carrying heat into building spaces and could save up to an additional 0.1 quads.

Figure 1: Dual-band electrochromics employing nanocrystals embedded in a polyoxometalate (POM)-derived glass. NIR transmission is modulated via capacitive charging of the plasmonic nanocrystals whereas visible light transmission is independently controlled via polaronic absorption in the glass matrix



INNOVATION DEMONSTRATION

Prior to ARPA-E support, the project team had demonstrated a prototype "dual-band" EC material, able to independently modulate visible and NIR light transmission[1,2]. Early experiments combined indium tin oxide (ITO) nanocrystals within a Nb_2O_5

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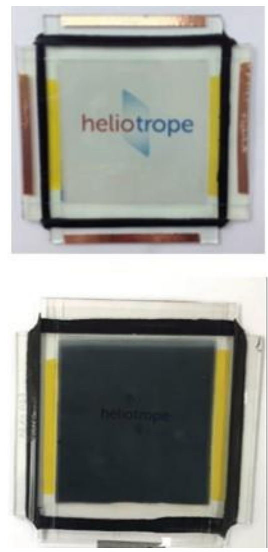
[1] Nb-Doped Colloidal TiO_2 Nanocrystals with Tunable Infrared Absorption, L. De Trizio, R. Buonsanti, A. M. Schimpf, A. Llordes, D. R. Gamelin, R. Simonutti, and D. J. Milliron, *Chem. Mater.*, **2013**, *25* , pp 3383–3390

[2] Tunable near-infrared and visible-light transmittance in nanocrystal-in-glass composites, A. Llordés, G. Garcia, J. Gazquez & D. J. Milliron, *Nature* **2013,** 500, 323–326

polyoxometalate (POM) cluster-derived matrix. The device (Figure 1) could transition to a "cool" state via the application of modestly negative voltages, resulting in a ~65% decrease in NIR transmission (T_{NIR}) while maintaining visible light transmission (T_{VIS}) at ~96%, reducing solar heat gain but allowing daylighting. Applying a more negative voltage decreases the T_{VIS}, transitioning the window into a "dark" state much like a traditional EC window. These states are end points on a continuum of optical states accessible via intermediate voltages.

The project team goals were to develop devices based on these materials approaches, with improved optical properties, switching speed, and durability. Most significantly, the project focused on scaling up fabrication of devices from 4 cm^2 to 25 cm^2 using a lower-cost, higher-throughput solution-processable technique (such as spray coating) to fabricate all three major components of the device: the elctrochromic electrode, the counter electrode, and the electrolyte. The targets for these films included demonstrating +/-5% film uniformity, <15 min switching time, 30% T_{NIR} modulation while maintaining T_{VIS} at >50%, and cycling the transitions at least 100 times. Accomplishing these challenging targets required rethinking the materials set at the beginning of the project to allow the use of scalable solution-processessable techniques.

Figure 2: Solution-deposited visible-light-modulating electrochromic prototype in transmitting (top) and blocking (bottom) states



The team found the maximum achievable T_{NIR} with the original ITO/Nb_2O_5 materials set to be fundamentally limited. They identified a new materials set, CsWOx/ITO, and demonstrated substantially improved T_{NIR} and T_{VIS} values and switching speeds. When coupled with the team's parallel work on the counter electrode and electrolyte, the EC devices demonstrated performance that surpassed the end-of-project solid-state device targets including the reduced switching time.

Simultaneous efforts at Heliotrope focused on translating the materials and devices to solution-processed manufacturing techniques. The team overcame two significant challenges. First, they were able to reliably charge the devices at the outset via a built-in electrochemical reaction. Second, they were able to fabricate ~100 cm^2 devices with blade coating. It is expected that either this manufacturing technique or curtain coating will readily transfer to a pilot production line or larger.

Having achieved many of the original technical targets, the team began working to ensure durability against UV degradation, long-term cycle life, and reduce the slightly off-neutral coloration observed in some of the states. Mixtures of the tungsten oxide with niobium oxide materials were found to be significantly more color neutral than pure WO_3 or Nb_2O_5 devices. Further improvements in coloration, switching speed, durability, and spectral transmission of the three states were realized by fabricating a templated mesoscale architecture of WO_x nanocrystals and infilling the pores with NbO_x.

PATHWAY TO ECONOMIC IMPACT

The promise of the project team's technology has been recognized through investment by Prelude Ventures, receipt of an R&D 100 award in 2013, selection for $1M in Small Business Innovation Research (SBIR) funding in 2014, and selection for $250k of funding through the Wells Fargo Innovation Incubator program.

The team is now working on transitioning the the dual-band window technology to a commercial product. The window market is highly sensitive to coloration and requires long-term durability. The team is currently experimenting with variants of their successful chemistries to achieve improved coloration and durability, and is also carrying out environmental stress testing to identify and mitigate the deleterious effects of long-term aging.

In parallel, the team is using the new solution-processed techniques to manufacture single-band EC windows that have the potential to be fabricated at a significantly lower cost than incumbent vacuum deposition technologies. The Heliotrope team estimates an installed actual selling price significantly less than the ~50/ft^2 for competing products, and a near 7x reduction in capital costs for manufacturing equipment. The team has established agreements with window fabricators to produce or sell EC panes rather than competing directly with full insulated glazing unit (IGU) window assembly manufacturers.

The Heliotrope team plans to establish itself in the EC window market with a single band product while work continues to improve the coloration, speed, and durability of the dual-band window. The first market for the dual band window may be in higher value "stepping-stone" product offerings such as vehicular windows, skylights, or sunroofs.

LONG-TERM IMPACTS

The teams work has demonstrated the commercial promise of an entirely new approach to creating controllable window coatings, with a resulting cost reduction that has the potential to enable the projected U.S. energy savings of up to 0.6 quads using electrochromic windows in certain climate areas. Further advances based on this new approach may yield significantly improved control of optical properties with expanded applications and associated further energy savings.

INTELLECTUAL PROPERTY AND PUBLICATIONS

As of September 2016, the Heliotrope team's project has generated three invention disclosures to ARPA-E, three U.S. Patent and Trademark Office (PTO) patent applications and two issued patents:

Patents

"*Conductive Transition Metal Oxide Nanostructured Electrochromic Material and Optical Switching Devices Constructed Thereof*," (2015), Patent No US2015/0277202 A1, T.M. Mattox, B. Koo, G. Garcia, D.J. Milliron, L.De Trizio, C. Dahlman.

"Nanocrystal polymer composite electrochromic device" (2015), Patent No US9207513, D.J. Milliron, E.L. Runnerstrom, B.A. Helms, A. Llordes, R. Buonsanti, G. Garcia.

The team has also published the scientific underpinnings of this technology extensively in the open literature.

Publications

"Linear Topology in Amorphous Metal Oxide Electrochromic Networks Obtained via Low-Temperature Solution Processing," A. Llordés, Y. Wang, A. Fernandez-Martinez, P. Xiao, T. Lee, A. Poulain, O. Zandi, C.A. Saez Cabezas, G. Henkelman, D.J. Milliron, Nature Materials, 2016.

"*The Interplay of Shape and Crystalline Anisotropies in Plasmonic Semiconductor Nanocrystals,*" J. Kim, A. Agrawal, F. Krieg, A. Bergerud, D.J. Milliron, Nano Letters, 16(6), 3879-3884, 2016.

"Defect Engineering in Plasmonic Metal Oxide Nanocrystals," E.L. Runnerstrom, A. Bergerud, A. Agrawal, R.W. Johns, C.J. Dahlman, A. Singh, S.M. Selbach, D.J. Milliron, Nano Letters, 16, 3390-3398, 2016.

"Direct Observation of Narrow mid-Infrared Plasmon Linewidths of Single Metal Oxide Nanocrystals," R.W. Johns, H.A. Bechtel, E.L. Runnerstrom, A. Agrawal, S.D. Lounis, D.J. Milliron, Nature Communications, 7, 11583, 2016.

"*Switchable Materials for Smart Windows,"* Y. Wang, W. Runnerstrom, D.J. Milliron, Annual Review of Chemical and Biomolecular Engineering, 7, 283-304, 2016.

"*United States energy and CO2 savings potential from deployment of near-infrared electrochromic window glazings*," N. DeForest, A. Shehabi, J. O'Dennell, G. Garcia, J. Greenblatt, E. Lee, S. Selkowitz, D.J. Milliron. Building and Environment, 89, 107-117, 2015.

"*Plasmonic Electrochromism of Metal Oxide Nanocrystals*," A. Llordes, E. Runnerstrom, S. Lounis, D.J. Milliron. Electrochromic Materials and Devices, 363-398, 2015.

"*Nanocomposite architecture for rapid, spectrally-selective electrochromic modulation of solar transmittance*," J. Kim, G. Ong, Y. Wang, G. LeBlanc, T. Williams, T. Mattox, B. Helms, D.J. Milliron. Nano Letters, 15(8), 5574-5579, 2015.

"*Redox Chemistries and Plasmon Energies of Photodoped In2O3 and Sn-Doped In2O3 (ITO) Nanocrystals*," A. Schimpf, S. Lounis, E. Runnerstrom, D.J. Milliron, D. Gamelin. Journal of the American Chemical Society, 137(1), 518-524, 2015.

"*Spectroelectrochemical Signatures of Capacitive Charging and Ion Insertion in Doped Anatase Titania Nanocrystals*," C. Dahlman, Y. Tan, M. Marcus, D.J. Milliron. Journal of the American Chemical Society, 137(28), 9160-9166, 2015.

"Low Temperature Synthesis and Surface Plasmon Resonance of Colloidal Lanthanum Hexaboride (LaB6) Nanocrystals," T.M. Mattox, A. Agrawal, D.J. Milliron, Chemistry of Materials, 27, 6620-6624, 2015.

"*Nanostructured electrochromic smart windows: traditional materials and NIR-selective plasmonic nanocrystals*," E. Runnerstrom, A. Llordes, S. Lounis, D. Milliron. Chemical Communications, 50, 10555-10572, 2014.

"*NIR-Selective electrochromic heteromaterial frameworks: a platform to understand mesoscale transport phenomena in solid-state electrochemical devices*," T. Williams, C. Chang, E. Rosen, G. Garcia, E. Runnerstrom, B. Williams, B. Koo, R. Buonsanti, D. Milliron, B. Helms. Journal of Materials Chemistry C, 2, 3328-3335, 2014.

"*Influence of Dopant Distribution on the Plasmonic Properties of Indium Tin Oxide Nanocrystals*," S. Lounis, E. Runnerstrom, A. Bergerud, D. Nordlund, D. Milliron. Journal of the American Chemical Society, 136(19), 7110-7116, 2014.

"*Defect Chemistry and Plasmon Physics of Colloidal Metal Oxide Nanocrystals*," S. Lounis, E. Runnerstrom, A. Llordes, D. Milliron. The Journal of Physical Chemistry Letters, 5(9), 1564-1574, 2014.

"*Tunable near-infrared and visible-light transmittance in nanocrystal-in-glass composites*," A. Llordes, G. Garcia, J. Gazquez, D. Milliron. Nature, 500, 323-326, 2013.

"*Regional performance targets for transparent near-infrared switching electrochromic window glazings*," N. DeForest, A. Shehabi, G. Garcia, J. Greenblatt, E. Masanet, E. Lee, S. Selkowitz, D. Milliron. Building and Environment, 61, 160-168, 2013.