MATERIALS SCIENCE

Composite for smarter windows

Glass has been prepared that selectively absorbs visible and near-infrared light when an electrochemical voltage is applied. This opens the way to 'smart' windows that block heat on demand, with or without optical transparency. SEE LETTER P.323

BRIAN A. KORGEL

Residential and commercial buildings account for about 40% of energy use and about 30% of energy-related carbon emissions in the United States[1]. To decrease this energy demand, materials are needed that help to regulate the heating and lighting requirements of buildings by responding to environmental changes. In particular, electrochromic window materials, which change colour and/or transparency when subjected to an electric field, could significantly reduce energy consumption in buildings[2]. On page 323 of this issue, Llordés *et al.*[3] report a great advance in the development of such materials. They have made a composite in which nanometre-scale crystals of indium tin oxide are embedded in a niobium oxide glass, with high control of nanocrystal loading and dispersion. The electrochromic performance of the composite is much better than expected from a simple sum of the optical absorption of its two separate components, because of both the nanostructure of the material and synergistic interactions that occur at the interface between the components.

Inorganic nanocrystals are typically synthesized chemically with organic capping groups attached to aid the crystals' dispersibility in solvents and to prevent aggregation or undesired particle growth. Unfortunately for many applications, the organic groups do not have useful electrical or optical properties. There has thus been much effort to replace the organic groups with inorganic groups that either add to the capabilities of the crystals or can be converted into an electrically or optically active material. This approach has been used to make nanocrystal assemblies with greatly improved electrical properties[4] and to convert nanocrystals capped with inorganic complexes into a more useful photovoltaic material[5] (a material that converts light into electricity).

Llordés *et al.* have used this strategy to create their nanoparticle-in-glass materials. The authors first stripped indium tin oxide (ITO) nanocrystals of their organic caps and replaced them with niobium-containing polyatomic ions known as polyoxometalate (POM) clusters. These clusters attach covalently to the ITO surface to create a shell around the nanocrystal. The researchers then condensed the modified nanocrystals into a film, simply by evaporating the solvent from a dispersion of the crystals. Finally, they converted the POM between the densely packed ITO nanocrystals into a niobium oxide (NbO_x) glass matrix by heating the film to 400 °C. Compared with previously reported synthetic routes for making nanoparticle-in-glass materials, in which inorganic crystals are grown within a glass[6], Llordés and co-workers' method provides rigorous control over the nanocrystals' size distribution and volume fraction. And, by adding more POM to the dispersion of POM-stabilized ITO nanocrystals, the authors could increase the volume fraction of the NbO_x glass matrix.

One of the key features of the ITO nanocrystal–NbO_x glass material is that the glass is covalently bonded to the nanocrystals. This restricts the molecular orientations available to the octahedral NbO_6 units found in the glass, and leads to remarkable structural ordering that differs from that of pure NbO_x. It turns out that this ordering improves the electrochromic properties of the glass matrix: NbO_x in the composite is five times darker than the bulk material when a similar voltage is applied.

ITO nanocrystals are also electrochromic, but in a different wavelength region from NbO_x: they undergo reversible electrochemical

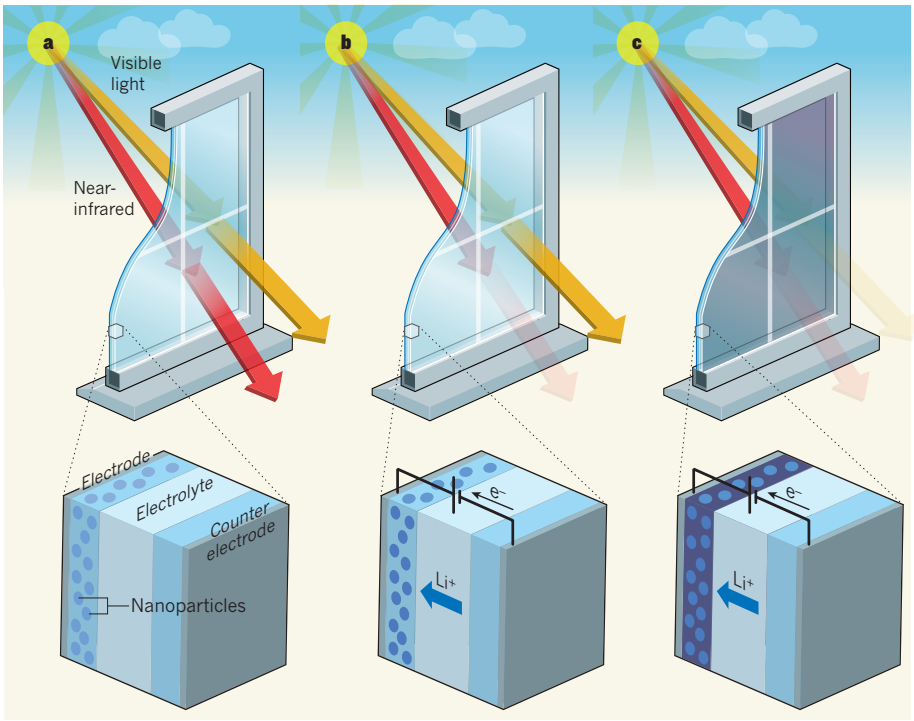

Figure 1 | Electrochromic window design. Llordés *et al.*[3] propose that their nanoparticle-in-glass composite material could be used to make windows that controllably and selectively absorb visible light and near-infrared light (heat). **a**, In the design, the window is an electrochemical cell in which two conducting glass panes are separated by a solid electrolyte material. The authors' material is deposited on one pane, forming an electrode; a counter electrode is deposited on the other pane. In the absence of an electrical load, the window is transparent to visible and near-infrared light. **b**, When an intermediate voltage is applied, charge carriers (lithium ions, Li^+, and electrons, e^-) move through the circuit. The nanoparticles in the composite become chemically reduced, whereupon they block most incoming near-infrared light. **c**, At lower voltages, the glass matrix of the composite also becomes reduced and blocks most incoming visible light.

redox reactions and absorb near-infrared light in the reduced state, but are transparent to this part of the spectrum when oxidized[7]. The combination of ITO nanocrystals with a NbO_x glass matrix therefore yields a material in which both visible and near-infrared light absorption can be electrochemically modulated. This material could thus be used in smart windows, to control the amount of both heat (near-infrared) and light passing through them (Fig. 1). What's more, the optical transparency can be tuned independently of the near-infrared transparency.

Llordés and colleagues' approach for making composite materials of inorganic nanocrystals in glass opens the way to a range of new material properties and applications, not just in electrochromics. The challenge for each application is to identify the best combinations of nanocrystal composition and modifiable inorganic capping groups.

More specifically, several issues must still be addressed before the material can be used in windows. The authors used lithium metal as a counter electrode to test the performance of their material, but this is not acceptable for commercial applications because of safety concerns. A suitable counter electrode must be identified. Additionally, the researchers performed their photoelectrochemical tests using a liquid electrolyte as a charge-carrying material, whereas a solid electrolyte is probably more appropriate for buildings applications. The materials needed to build an electrochromic window will be more expensive than conventional window materials, so the extra expense will need to be balanced by the energy and cost savings that can be achieved through their use. Ideally, no power input will be needed to maintain transparency or opacity, but this ability remains to be explored.

Nevertheless, Llordés and co-workers' results are promising. With appropriate counter electrodes and a solid-state electrolyte, and if long-term stability of the composite can be demonstrated, windows that have multispectral band transparency may be just around the corner, potentially enabling buildings that offer unprecedented energy efficiency and comfort. ■

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1. Richter, B. *et al. Rev. Mod. Phys.* **80,** S1–S109 (2008).
2. Li, S.-Y., Niklasson, G. A. & Granqvist, C. G. *J. Appl. Phys.* **108,** 063525 (2010).
3. Llordés, A., Garcia, G., Gazquez, J. & Milliron, D. J. *Nature* **500,** 323–326 (2013).
4. Panthani, M. G. & Korgel, B. A. *Annu. Rev. Chem. Biomol. Eng.* **3,** 287–311 (2012).
5. Jiang, C., Lee, J.-S. & Talapin, D. V. *J. Am. Chem. Soc.* **134,** 5010–5013 (2012).
6. Sakamoto, A., Yamamoto, S. *Int. J. Appl. Glass Sci.* **1,** 237–247 (2010).
7. Garcia, G. *et al. Nano Lett.* **11,** 4415–4420 (2011).

STRUCTURAL BIOLOGY

RNA exerts self-control

A crystal structure of two bound RNA molecules not only provides insight into how regulatory riboswitch sequences affect messenger RNA expression, but also expands our understanding of RNA structure and architecture. SEE LETTER P.363

BHASKAR CHETNANI & ALFONSO MONDRAGÓN

Over the past three decades, our knowledge of the role of RNA in cellular processes has expanded enormously[1]. For example, the structures of various regulatory RNA sequences called riboswitches have revealed how they affect the transcription or translation of their downstream messenger RNA sequences through the recognition and binding of specific ligands[2]. On page 363 of this issue, Zhang and Ferré-D'Amaré[3] provide another structural insight — this time, into a bacterial riboswitch, called a T-box, in complex with a transfer RNA molecule. Their data elucidate how one RNA molecule recognizes another RNA of similar size and regulates its own transcription through a simple switching mechanism*.

To support the process of protein synthesis, cells must regulate the pool of tRNAs that become charged with (covalently bound to) specific amino-acid residues and deliver them to the growing protein chain. Enzymes known as aminoacyl-tRNA synthetases carry out tRNA charging. In Gram-positive bacteria, a T-box riboswitch located upstream of the coding region of the mRNA of each aminoacyl-tRNA synthetase negatively regulates synthesis of the mRNA[4].

The T-box RNA consists of at least two independently folded domains: a sensory 'aptamer' domain that forms a long stem called stem I and that binds to specific tRNAs; and a second domain, which can switch between two alternative conformations depending on whether the bound tRNA is charged or uncharged[5]. Whereas binding of a charged tRNA leads to termination of transcription of the aminoacyl-tRNA coding sequence (Fig. 1a), an uncharged tRNA stabilizes an antiterminator conformation of the T-box, leading to transcription of the mRNA and subsequent protein synthesis (Fig. 1b).

Stem I is a mostly double-helical RNA domain roughly 100 nucleotides long and is studded with several phylogenetically conserved structural motifs along its length[4]. Previous work has implicated most of these motifs in tRNA recognition and binding[4], yet atomic-level details of this process have remained largely unknown. Zhang and Ferré-D'Amaré provide the first glimpse into this mechanism by describing the crystal structure of a complex between stem I of the T-box of tRNA synthetase for the amino acid glycine and an uncharged glycyl-tRNA. The authors' co-crystal structure also explains the precise role of the stem I motifs, delivers intriguing

*This article and the paper under discussion[3] were published online on 28 July 2013.

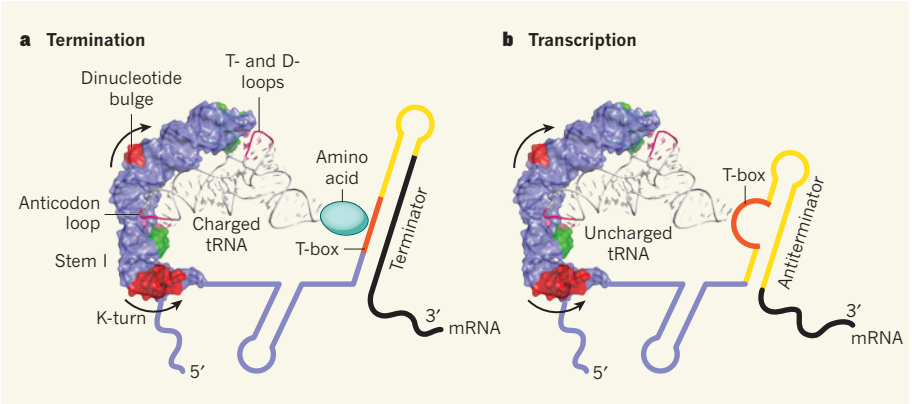

Figure 1 | RNA meets RNA. Zhang and Ferré-D'Amaré[3] present the structure of the stem I domain of a T-box riboswitch in complex with an uncharged tRNA. Stem I bends at the dinucleotide bulge and the K-turn to recognize tRNA by binding to its anticodon loop and the T- and D-loops. **a**, The amino acid present in a charged tRNA is thought to prevent interaction between the T-box sequence motif downstream of stem I and the acceptor end of the tRNA, favouring formation of a terminator loop that stops transcription of the mRNA downstream of the T-box. **b**, By contrast, the free acceptor end of an uncharged tRNA interacts directly with the T-box sequence and leads to the formation of an antitermination loop, allowing transcription of the mRNA and its subsequent translation into a protein.