

Tunable Transmittance of Near-infrared and Visible Light in Reconstructed Nanocrystal-in-Glass Composite Films

The bonding arrangement in amorphous materials plays a dominant role in determining their electrochemical, optical and transport properties. However, it remains a challenge to manipulate amorphous structures in a controlled manner. Recently, scientists at the Molecular Foundry at Lawrence Berkeley National Laboratory (LBNL) developed synthetic protocols for incorporating well-defined nanocrystals into amorphous materials [1,2]. This “nanocrystal-in-glass” approach not only allows combining two functional components in one material, but it could also provide a handle, by virtue of the interfacial covalent bond, for manipulating the glass structure and deliberately changing its properties.

Now, researchers from LBNL and the Institute of Materials Science of Barcelona (ICMAB, Spain) have demonstrated the power of this approach by introducing tin-doped indium oxide nanocrystals (ITO NCs) into niobium oxide glass (NbO_x) and showing that a new amorphous structure is created as a consequence of linking the glass to the nanocrystals (Figure 1).

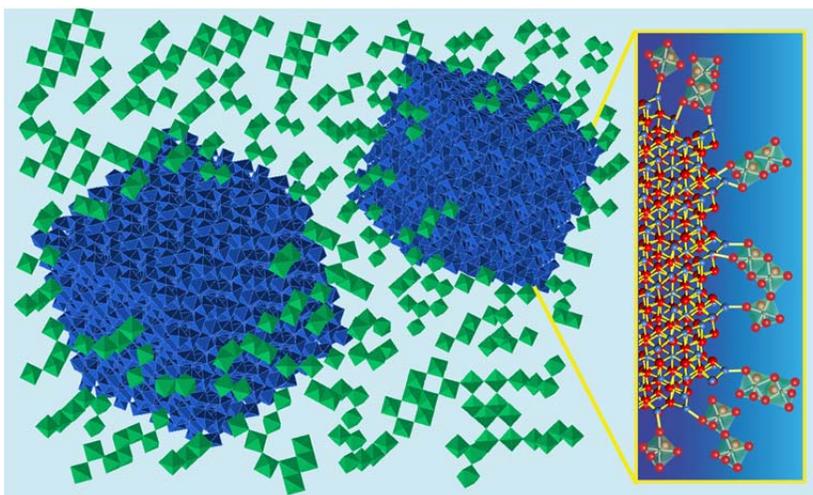


Figure 1: ITO nanocrystals covalently linked to amorphous NbO_x . $[\text{NbO}_6]$ octahedral units are shown in green, ITO nanocrystals in blue. In the inset, the niobium atoms are located at the center of the green octahedra, oxygen atoms are red and indium atoms are blue.

The two components of the composite, ITO NCs and NbO_x , were selected for their different spectral-selective electrochromic properties. When electrochemically reduced, ITO NCs block near-infrared (NIR) light through a plasmonic electrochromic effect [3], while NbO_x mostly blocks visible light. By linking these functional components, a previously unrealized optical switching behavior is achieved. Namely, these transparent ITO-in- NbO_x films (Figure 2b) are capable of selectively blocking NIR and visible light by varying the applied electrochemical voltage over a range of 2.5 V (Figure 2c). In addition, the reconstructed NbO_x glass has superior properties – its optical contrast is enhanced five-fold (Figure 2d) and it has excellent electrochemical cyclability, with 96% of charge capacity retained after 2,000 cycles. Window coatings with such a unique optical switch could reduce energy consumption in buildings by dynamically and independently modulating daylight and solar heat.

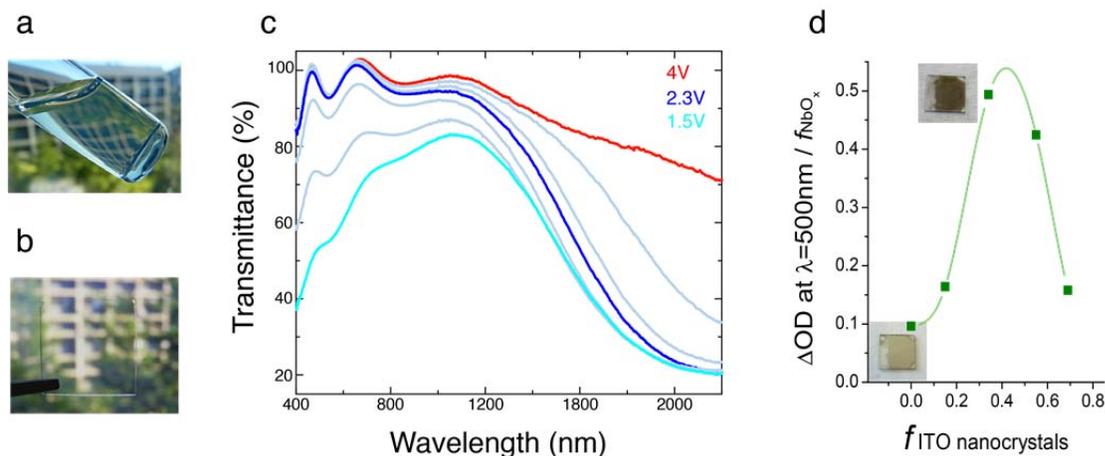


Figure 2: a) Polyniobate clusters (POM)-stabilized ITO aqueous dispersion, POM; $[N(CH_3)_4]_6Nb_{10}O_{28}$. b) ITO-in- NbO_x film (thickness ≈ 150 nm) on glass substrate. c) Transmittance spectra under applied electrochemical voltage (versus Li/Li^+) of an ITO-in- NbO_x composite film. Intermediate voltages are shown in gray. d) Change in optical density at 500 nm between 1.5 V and 4 V vs volume fraction of ITO nanocrystals (f_{ITO}). Photographs of charged films with $f_{ITO}=0$ and $f_{ITO}=0.34$ are shown as insets.

A key aspect of the research study was to control the composite structure at different length scales that govern the macroscopic electrochromic properties – from the atomic scale (bonding and crystal structure) to the mesoscale (crystallite sizes, interface densities and connectivity). The LBNL researchers controlled these characteristics by using a building-block colloidal approach, where nanocrystals and glass-forming molecules are synthesized separately and then linked together. In their colloidal approach, interfacial chemical bonds were made by combining ligand-stripped ITO NCs and polyniobate clusters (POMs) in aqueous solution. This process resulted in POM-stabilized nanocrystal dispersions, from which films were deposited and then thermally annealed.

Grazing incidence x-ray diffraction (XRD) measurements, performed at SSRL's Beam Line 11-3, enabled studies of the composite film structure (Figure 3). XRD patterns of films annealed at 400-500°C show that the molecular POMs thermally condense, leading to an interconnected amorphous NbO_x matrix that remains bonded to the crystalline ITO nanocrystals (Figure 3 a,b). Profile-fitting analysis enabled quantification of the broadening of the ITO Bragg peaks following thermal processing at different temperatures. The integral breadth monotonically increased with increasing temperature (Figure 3c), pointing to progressive interfacial dissolution of ITO in the adjacent NbO_x matrix. At higher temperatures ion mobility increases and eventually a crystalline ternary $InNbO_4$ phase is formed at 650°C (Figure 3 d, e). This observation further supports that, at lower temperatures, indium and likely tin can locally diffuse into the amorphous NbO_x matrix and disrupt its bonding arrangement.

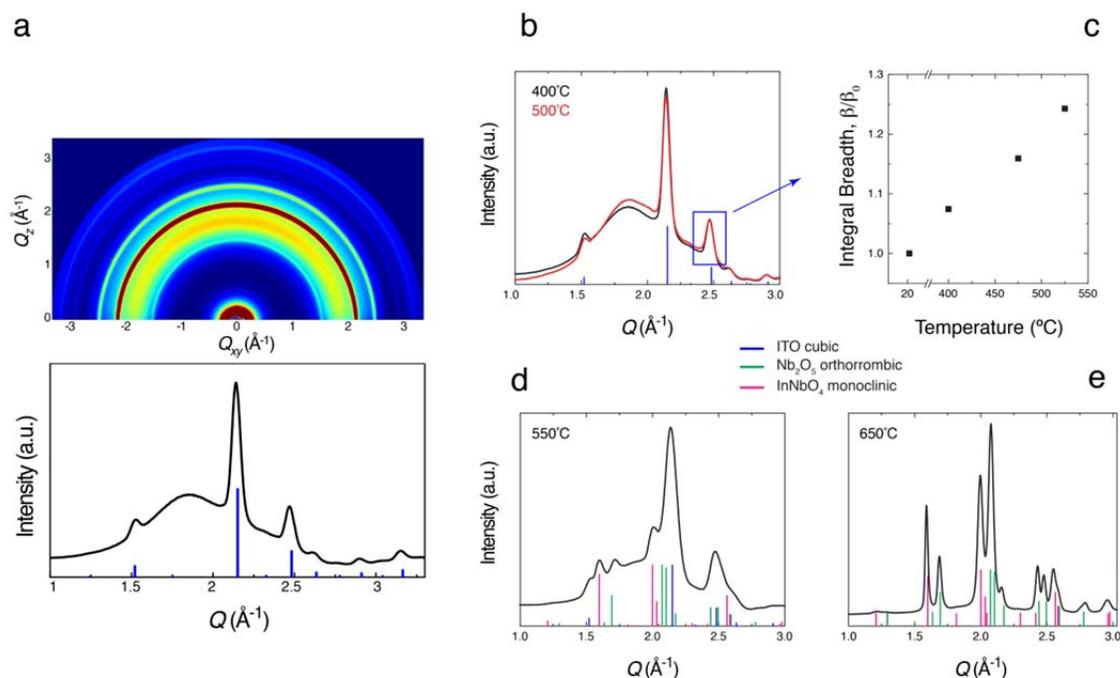


Figure 3: a) Two-dimensional XRD image from an ITO-in-NbO_x film processed at 400°C (top) and XRD pattern obtained after integrating along the out-of-plane scattering direction nominally Q_z (bottom). The indexed diffraction lines result from randomly oriented ITO nanocrystals (cubic In₂O₃ bixbyite structure) whereas the broad peak at $Q=1.85 \text{ \AA}^{-1}$ is assigned to amorphous NbO_x. b) The ITO (400) reflection, highlighted in the blue box, was used to quantify the line broadening evolution upon annealing. c) Normalized integral breadth of the (400) ITO reflection plotted as function of temperature. β_0 correspond to the non-annealed sample. d) and e) show the XRD patterns of composite films annealed at higher temperatures, 550°C and 650°C, respectively.

To identify the structural changes in the NbO_x amorphous network, the authors performed Raman spectroscopy on pure amorphous NbO_x and ITO-in-NbO_x with different nanocrystal–glass interfacial densities. The results showed that the degree of connectivity of the reconstructed NbO_x network is decreased and the topology is dominated by highly distorted edge-sharing [NbO₆] octahedral units as compared to the more regular, vertex-sharing topology observed in pure NbO_x. Hence, the structure of the NbO_x glass is profoundly altered by covalent linking to ITO nanocrystals and it becomes highly distorted, less interconnected and interfacially doped (Figure 1).

This reconstructed amorphous structure plays a crucial role in enhancing the electrochromic properties of NbO_x. The authors suggest that the enhancements in both optical contrast and cyclability are related to the more open network structure, which facilitates ion insertion and extraction and helps relax the stress induced by these electrochemical processes. Consistent with this hypothesis, the charge capacity increased proportionally with the optical contrast.

Beyond electrochromics, this work shows that combining colloidal nanocrystals and glasses in a single heterogeneous composite is a powerful approach to create complex functionalities. Ideally, one could mix and match desired properties by selecting specific compositions. Through the interfacial bonding between the components, one could modify their structure and tune their optical, electrochemical and transport properties.

Primary Citation

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