Nanoelectrochromics for Smart Windows: Materials and Methodologies

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ABSTRACT

Electrochromic (EC) materials can change their optical properties under an external electrical voltage, forming the basis of "smart windows" – an optical switching device that can optimize its solar-gain characteristics according to ambient conditions and user preferences, offering great energy-saving potential and user comfort, especially for highly glazed buildings. Recent research on nanomaterials and nanoassemblies for high performance EC devices (denoted henceforth as nanoelectrochromics) has revealed significant improvement on coloration efficiency, switching time, and cycling durability; therefore showing promsing potential for smart window applications. We address here the scientific and technical issues of nanoelectrochromics, emphasizing the material preparation and device assembly for large-area window applications. A perspective showing the opportunities and challenges in nanoelectrochromics is also presented.

Keywords: smart window, electrochromism, nanomaterials, nanoelectrochromics

1 INTRODUCTION

Over the past several decades, there has been an ever increasing interest in dynamic glazing technologies, i.e., smart windows, for building applications [1-3]. A smart window is in principle an optical switching device integrated in or attached to a window glazing and offers adjustable control of the solar radiation (both the visible and the near infrared (NIR) part) that transfers through it. The application of smart windows can provide a huge potential of energy savings by reducing a certain amount of heating, cooling, and lighting loads [1-3].

The key to smart windows is a material/system that can change reversibly and persistently its optical properties (e.g., transmission or reflection) in a controllable way. Electrochromic (EC) materials [1-3, 4] that exhibit a reversible color change induced by an externally applied electric voltage are of particular interest and show several distinguished advantages for smart windows. For example, EC materials only require a small voltage (typically 1–3V) for switching, and they exhibit good open circuit memory in both bleached and colored state. More importantly, EC smart windows are an active glazing technology and can respond in a controllable way to the ambient environment and/or the user preferences, hence contributing both to the energy efficiency and the user comfort of buildings.

Considering the worldwide production of window glazings for both residential and industrial applications, it is not surprising that the EC smart windows have been experiencing a pronounced market pull [3]. Many industrial institutions have been investigating EC smart windows, where commercial products are starting to emerge. However, the benefits of EC smart windows have yet to be realized at scale, as conventional EC smart windows suffer from significant drawbacks related to cost, durability, and functionality [3, 5, 6]. Thanks to the rapid development of nanotechnology, the possibility of designing high performance EC devices by using nanostructured EC materials or nanoassemblies (denoted hereafter as nanoelectrochromics [7]) has attracted great attention [6-10]. The application of nanoelectrochromics has revealed high coloration efficiency, high color contrast, fast switching, and longer cycling durability, thus showing promsing potential for large-area smart window applications. More importantly, nanoelectrochromics have provided the field with new functionalities such as NIR selective optical modulation for independent control over visible and NIR transmittance [6, 11, 12].

It is no doubt that the control of chemcial composition, size, and morphology at nanometer scale can lead to a myriad of possibilities for nanoelectrochromics towards high perforamcne EC smart windows. However, it may also results in a certain complexity in understanding the involved mechanisms and kinetics that may lead the fundamental research to practical applications. In this work, we discuss the scientific and technical issues of nanoelectrochromics, emphasizing the material processing and device assembly for large-area window applications.

2 ELECTROCHROMIC SMART WINDOWS

Being an active optical switching device, EC smart windows can be achieved by several different device configurations [1, 2]. Figure 1 illustrates schematically an extensively studied EC smart window architecture [7], which is a battery-like device and consists of several different functional components, i.e., transparent conductor, EC layer, electrolyte, and ion storage layer (or a complementary EC layer). Each material and component contribute greatly to the overall performance of the EC smart windows.

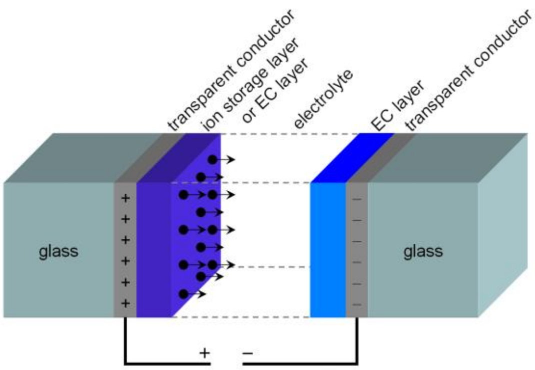

Figure 1: Architecture of an EC smart window, showing the transport of cations under an external electrical field.

The sandwich configuration of EC smart windows allows a reversible electrochemical reaction to cycle between the EC layer and the ion storage media as the external voltage is applied; the overall transparency of the EC layer is then changed due to the formation of color centers (or defect complexes) or to an electrochemical reaction that produces a colored compound [13]; a voltage pulse with opposite polarity makes the device regain its original properties. The overall coloration process can be described as the simultaneous injection of electrons/holes and cations/anions into the EC layer during the reduction/oxidization step, depending on the coloration reaction (i.e., cathodic or anodic coloration) of the EC materials. Taking the most popular WO_3 material as an example, the involved electrochromism can briefly be interpreted in terms of a double-charge-injection model that describes the formation of tungsten bronze (M_xWO_3) as a consequence of injection of electrons and positively charged ions ($M = H^+$, Li^+, etc.) into the transparent WO_3:

$$\underset{\text{(transparent)}}{WO_3 + xe^- + xM^+} \leftrightarrow \underset{\text{(colored)}}{M_xWO_3}. \quad (1)$$

Although the involved ion insertion/extraction processes may be different with the cathodic EC materials (e.g., WO_3) and the anodic EC materials (e.g., NiO), there are some general considerations. For example, The ion insertion or extraction reaction is limited both by the diffusion coefficient and by the length of the diffusion path: the former depends primarily on the chemical structure and crystal structure of the material; whereas the latter is determined by the material microstructures, such as morphology and size. In case of nanomaterials, the diffusion path length is represented by the smallest dimension of the particles [6-10]. Obviously, designing an EC nanomaterial with the proper composition and crystal structure is important to achieve fast kinetics.

3 NANOELECTROCHROMICS

The nomenclature of nanoelectrochromics here denotes an active EC component consisting of pre-synthesized, nanoscale building blocks, such as nanoparticles, nanowires and nanotubes [7]. Although well functional EC devices can be achieved in traditional EC thin films that are relatively dense, they are in general not considered as nanoelectrochromics unless distinct nanoscale features such as ultrahigh porosities are clearly presented.

3.1 Materials

A number of EC nanomaterials and nanoassemblies have been reported in literature [7-10]. Among these, WO_3 represents probably the most studied compound. Other EC nanomaterials showing interesting properties include, among others, TiO_2, MoO_3, Nb_2O_5, V_2O_5, NiO, and Prussian blue (PB). There are also organic compounds such as viologens and pyridines exhibiting interesting and useful EC properties; hence, forming an organic-inorganic hybrid system enrichs also the content of nanoelectrochromics.

Apart from the difference in chemical compositions, EC nanomaterials can also be prepared with different morphologies or dimensionalities (Figure 2), such as zero-dimensional (0D) clusters or particles, one-dimensional (1D) rods, wires, belts, or tubes, two-dimensional (2D) thin films or sheets, and three-dimensional (3D) mesoporous solids; within each class, there are differences in surface-related properties such as exposed crystallography planes and related surface reactivities. EC nanomaterials may have different structural forms and consequently different properties, for example, TiO_2 existing as anatase, rutile and brookite. Apparently, a combination of chemical composition, crystal structure, size, and dimensionality at nanometer scale will result in not only a myriad of possibilities towards high performance EC smart windows, but also a certain complexity in understanding the involved mechanisms and kinetics.

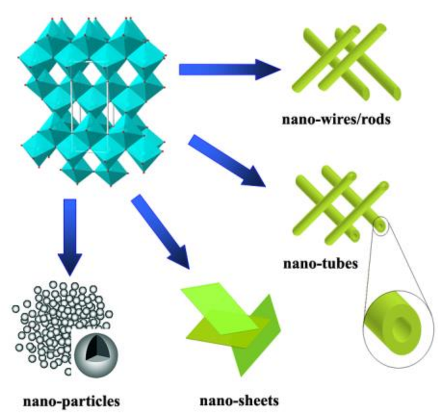

Figure 2: Dimensionality control of nanomaterials (The polyhedral representation is anatase TiO_2).

In general, nanoelectrochromics offer the possibilities of improved switching times, higher coloration efficiency, and most importantly, improved stability/durability against electrochemical cycling [6-10]. For example, crystalline WO_3 films usually exhibit good structural stability but poor EC performance; whereas the best EC performance is usually achieved in amorphous WO_3 films with poor structural stability. Lee *et al*. have prepared WO_3 films with high porosity by electrophoresis deposition of pre-synthesized WO_3 nanoparticles (diameter: 10–20 nm, Figure 3a) [14]. The WO_3 nanoparticle films exhibited a high charge insertion density (Figure 3c), which is about 10 times higher than the crystalline WO_3 films. Such improvement can be attributed to large active surface area of the nanoparticle film (Figure 3b), which provides direct and sufficient contact between electrolyte and electrodes. The WO_3 nanoparticle films showed also excellent cycling stability due to the improved crystallinity. For example, the WO_3 nanoparticle films had no obvious changes over 3000 cycles in acidic electrolyte (Figure 3d), whereas the amorphous WO_3 films degraded significantly after only 500 cycles.

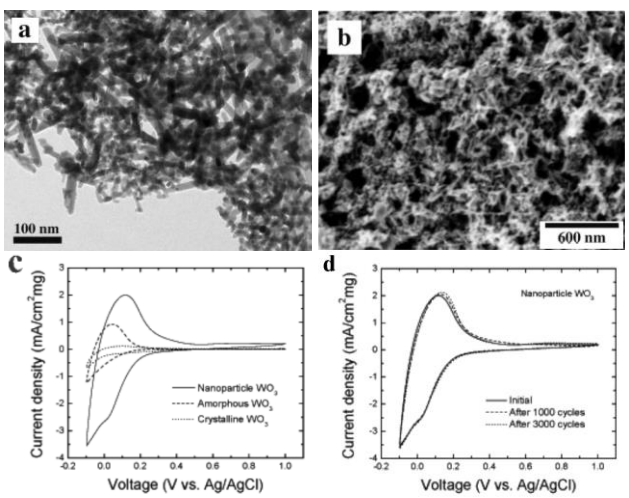

Figure 3: (a) Transmission electron microscopy (TEM) image of crystalline WO_3 nanoparticles; (b) scanning electron microscopy (SEM) image of the WO_3 film by electrophoresis deposition; (c) cyclic voltammograms (CV) of the three different WO_3 films; and (d) CV of the WO_3 nanoparticle film after different cycles in 1 M H_2SO_4 [14].

3.2 Assembly

Nanoelectrochromics may also provide economic benefits. Unlike the traditional EC thin films made by processes such as sputtering and chemical vapor deposition, EC nanomaterials can be prepared as well as assembled via solution-based methods that are usually less costly and easily scalable.

There are several methods for assembly of EC nanomaterials into large-scale devices, such as spin coating, dip coating, and layer-by-layer (LBL) self-assembly. Spin coating, for example, is a cheap and fast method to prepare homogeneous thin films, which can be adjusted to achieve structurally uniform thin films containing tiny EC nanoparticles, Figure 4. The thickness of the resulting films can be adjusted by controlling a variety of parameters, such as the rotation speed. Moreover, the nanoparticle films are usually porous due to the incompact aggregation of individual EC nanoparticles.

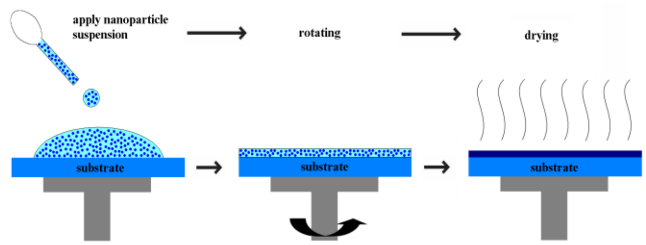

Figure 4: Schematic representation of the principle of spin coating process for assembly of EC nanoparticle films.

It is worth noticing that the interaction between EC nanoparticles and the substrate need to be strong enough to keep the produced films from peeling off. The LBL self-assembly in this regard has some advantages, as shown in Figure 5. In a typical LBL process, a charged substrate is exposed alternately to dilute aqueous solutions of polycations and polyanions, enabling the deposition of a polyelectrolyte complex as a thin film with controlled thickness and composition [15]. The LBL process has been widely used to assemble nanoparticle films and allows also a combination of different materials [16]. The EC nanoparticle of interest usually need to be pretreated with a suitable surfactant before the LBL process, it is therefore of particular interest in designing or selecting polycations or polyanions with desirable properties, e.g., ionic conductivity [17]. The LBL method is also ideal for the preparation of organic-inorganic hybrid EC materials.

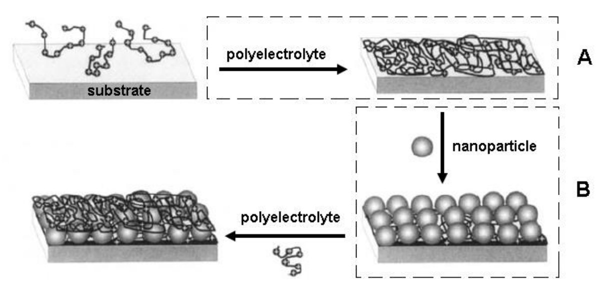

Figure 5: Schematic representation of the principle of electrostatic LBL self-assembly. The process consists of treating substrate and nanoparticle with oppositely charged polyelectrolytes and then depositing them alternately. Repeating the A and B process gives a nanoparticle film with controlled thickness.

4 CONCLUSIONS AND OUTLOOK

Electrochromism has captured the attention of academic and industrial researchers for the past several decades, though the promise of EC devices such as smart windows and displays has yet to be fully realized.

Nanostructured EC materials usually exhibit specific size-dependent and/or surface-dependent properties, which are very important for high performance EC devices with fast kinetics and improved thermodynamics. Thus, the application of nanotechnology in EC smart windows represents a myriad of opportunities and challenges. At this point, one may say that the development of new EC nanomaterials or systems with new or improved EC performance will still be the focus of the research. More investigations will still be necessary to understand the fundamentals such as the relationship between crystal structures of EC materials and their cycling stabilities, optical modulations, coloration efficiencies, and so on.

Wet chemical approaches can result in high-quality EC nanomaterials with controlled size, shape, surface and stoichiometry. The wet chemical methods are favourable with respect to reduced material and manufacturing costs and for large-scale production. Moreover, the surface of EC nanomaterials may readily be modified with surfactants, forming colloidal materials that are ideal for large-area deposition, such as spin coating and LBL assembly. This means that inexpensive EC smart windows with a large-area may be developed at large-scale by employing mainly the wet chemical approaches.

Nanoelectrochromics are indeed an interesting and complex subject and require therefore substantial research effort. We hope this work may inspire new material design or processing strategies for nanoelectrochromics.

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