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PII: S2468-2179(17)30062-X

DOI: [10.1016/j.jsamd.2017.08.005](https://doi.org/10.1016/j.jsamd.2017.08.005)

Reference: JSAMD 119

To appear in: *Journal of Science: Advanced Materials and Devices*

Received Date: 29 May 2017

Revised Date: 10 August 2017

Accepted Date: 14 August 2017

Please cite this article as: P. Jittiarporn, S. Badilescu, M.N. Al Sawafta, L. Sikong, V.-V. Truong, Electrochromic Properties of Sol-Gel Prepared Hybrid Transition Metal Oxides A Short Review, *Journal of Science: Advanced Materials and Devices* (2017), doi: 10.1016/j.jsamd.2017.08.005.

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**Electrochromic Properties of Sol-Gel Prepared Hybrid Transition Metal
Oxides.**

A Short Review

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**Electrochromic Properties of Sol-Gel Prepared Hybrid Transition Metal Oxides.
A Short Review**

Abstract

This short review paper revisits the progress achieved in the last 10-15 years in the field of hybrid electrochromic materials, synthesized through sol-gel methods. During the recent decade, new avenues have been opened, exploring new concepts and particularly interesting applications of electrochromism. In this paper, we will discuss some of the new research directions in the field of electrochromism, together with novel applications of many electrochromic hybrid oxides. The most important incentive for enhanced properties of traditional materials has been the advent of nanotechnology. The discoveries in the field of synthesis of nanomaterials enabled to expand the materials and connect the morphological features of nanoparticles to the electrochromic properties at the macro level. This was possible because of the emergence of the new and more elaborate characterization methods, enabling to unveil hitherto unknown structural and morphological properties of electrochromic materials. It is important to mention the development of novel hybrid materials with significantly improved EC properties, where tungsten oxide is associated with carbonaceous materials such as MWCNT or graphene. These hybrid materials with enhanced EC properties, compared to the inorganic hybrids, will be remarkable in the future, for a series of novel applications. Retracing briefly the history of EC hybrid materials and summarizing the principal achievements will be useful not only for researchers in the field but for a wider readership as well.

Keywords: Hybrid electrochromic materials, sol-gel methods, electrochromism, hybrid oxides, nanomaterials

1. Introduction

Electrochromism is a reversible change in the optical properties (color, transparency) of a material, in response to an applied voltage. Since its discovery (Debye called electrochromism (EC) a “novel electrophotographic system”)[1, 2], substantial efforts have been made to study the electrochromic (EC) materials, their properties and applications in devices, principally, in smart windows. In the beginning, the electrochromic materials were mostly transition metal oxides and their thin films were prepared by costly physical vapor deposition methods [3, 4].

Later on, hybrid materials consisting of two transition metal oxides, a transition metal oxide and organic molecules, or conducting polymers, often displaying multi-electrochromism, have been developed. At the same time, the fabrication methods have been diversified and new, less costly methods have been discovered and, among them, a prominent place is occupied by the sol-gel methods.

EC characteristics of transition metal oxides arise from the reversible redox reactions of the transition metal ions, that is, the electron-ion double injection/extraction, under the applied voltage. In the inorganic materials, the EC performances are mainly governed by the redox reaction characteristics, that is, the amount of reduced/oxidized metal ion (i.e. coloration center) and the switching kinetics [5, 6]. During the recent decade, new avenues have been opened, exploring new concepts and particularly interesting applications of electrochromism.

Tremendous progress has been achieved in the last 10-15 years. Not only that many new materials have been developed, by using a great variety of methods, but, somehow, the applications of EC materials shifted, from “smart windows” applications to entirely new fields. There are a number of invaluable research and review papers well worth to revisit in order to have a better idea about the developments in the field [7-15]. It is felt that it is worth summarizing some of the new research directions in the field of electrochromism such as, for example, tungsten oxide – graphene (and derivatives) nanocomposites, tungsten oxide – multi-walled carbon nanotube hybrids, described in section 4 of this review. In this short review paper, we will discuss these, together with some of the better known properties and applications

of EC hybrid oxides. Retracing briefly the history of EC hybrid materials and summarizing the principal achievements will be useful for researchers in the field.

As this review is focused on electrochromic materials prepared through sol-gel methods, a short introduction to sol-gel chemistry it is believed to be useful.

The sol-gel chemistry was developed more than forty years ago and the new technology gradually replaced the tedious, high-temperature processes used for thousands of years for the fabrication of ceramic and glassy materials. A number of very good review papers [16-18] cover the science of the sol-gel process as well as the most important aspects of its development, starting with the sol-gel fabrication of silicon oxide and transition metal oxides and hybrids, and the discovery of inorganic-organic hybrids, having today extremely important applications.

In the present paper, dedicated to hybrid metal oxide electrochromic materials, only short background information on the sol-gel process will be given. The interested reader can gather more information by consulting the review papers [16-18].

2. Synthesis of transition metal oxides and hybrids by the sol-gel process

The sol-gel process is based on the hydrolysis and condensation of molecular precursors, performed under mild conditions. Two chemical ways are presently used to form the solid phase network: the metal-organic route, using metal alkoxides in organic solvents and the inorganic route, using metal salts (chlorides, nitrates, sulfides, etc.) in aqueous solutions. The route using alkoxide precursors appears as the most versatile one. Mixed inorganic and organic precursors can also be used to fabricate hybrid materials. The sol-gel process starts generally with the alcoholic solution of a metal alkoxide precursor, $M(OR)_n$, where R is an alkyl group. Hydrolysis of metal alkoxides produces hydroxyl groups, and by their poly-condensation a three-dimensional network is formed. The two reactions – hydrolysis and poly-condensation occur simultaneously and generate low molecular weight by-products such as alcohol and water. Both reactions occur by nucleophilic substitution (S_N) which involves three steps: nucleophilic addition (A_N), proton transfer within the transition states, and removal of the protonated species (alcohol, water). The process ends with the formation of a tetrahedral SiO_2 or MO_x network [19]

Due to their high reactivity, the sol-gel process in the case of metal alkoxides can be carried out without using a catalyst. The condensed species are forming oligomers, oxo polymers, colloids, gels or precipitates. Oxo polymers and colloidal particles give rise to sols which can be gelled, dried and densified in order to get powders, films or monolithic glasses. A schematic of the sol-gel process, leading to the different end products is shown in Figure 1. The figure shows the different products that can be obtained through the sol-gel process. Once the sol is formed by hydrolysis and poly-condensation of the starting material, depending on the intermediate processes (coating, gelling, precipitating, etc.), a variety of end product can be obtained. The rate of condensation (poly-condensation or polymerization) of inorganic precursors can be controlled via the chemical modification of alkoxides with complexing ligands such as, for example, acetylacetonate. Using complexing ligands is very important in the sol-gel process as they can moderate the rate of the hydrolysis and condensation reactions. Drying under normal conditions gives a xerogel that have a high surface area and porosity and can be densified. Depending on the post-processing, monoliths, films, fibers or powders can be obtained directly from the gel state.

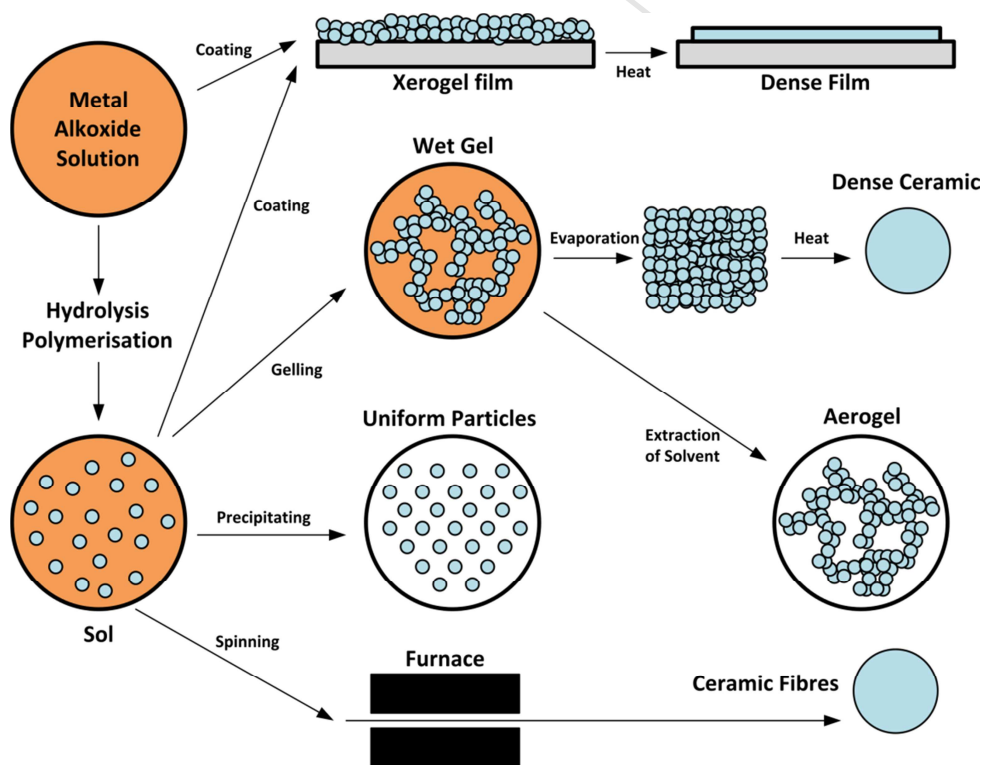


Fig. 1. Possible end products of the sol-gel processes (Reproduced with permission from reference [16]).

In addition to the fabrication of electrochromic materials, sol-gel methods have today numerous applications such as the synthesis of ferroelectric coatings for condensers, waveguides, the fabrication of optical fibers for optical telecommunication, ceramic superconductors, protection of metals, etc. A fascinating new field of research in materials science is the sol-gel fabrications of hybrid structures such as ormosils, a new type of nanocrystalline material, containing luminescent dyes and SiO₂ for self-tuning lasers, solar collectors, elements for nonlinear optics, sensors, biological markers, etc. More applications are included in Figure 2.

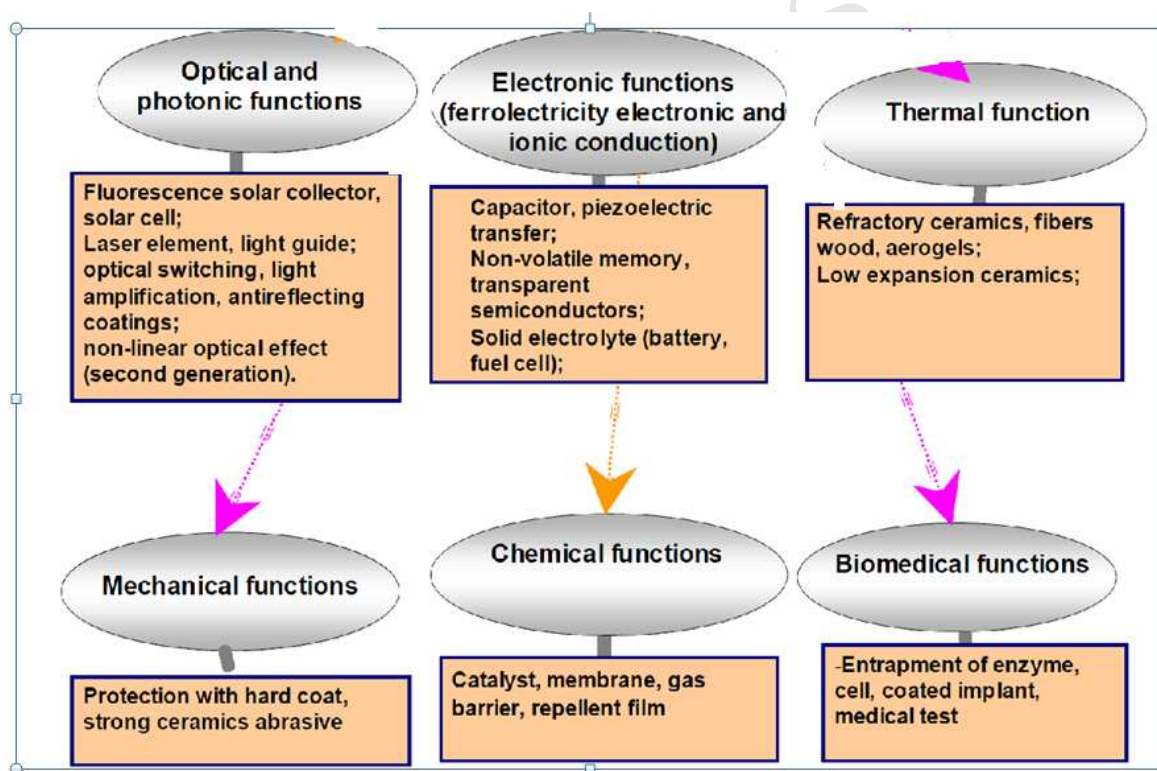


Fig.2. Applications of sol-gel method according to Sakka (Reproduced with permission from ref. [17]).

Mixed metal alkoxide systems are of great interest because of the potential properties and applications they provide. The structure and morphology of the resulting network depend on the relative chemical reactivity of the two metal alkoxides that is a function of degree of

unsaturation. The extent of unsaturation is given as $(N-Z)$ where N is the coordination number of the atom in the stable oxide network and Z is the oxidation state [18].

Elements such as Ti, Zr, Al and B with high unsaturation have much higher reactivities. The sequence of reactivity is as follows:



Chelating additives such as glycols, acetic acid, etc. have been used to slow down the rate of the hydrolysis and condensation reactions.

Inorganic precursors in aqueous solution are less expensive than metal alkoxides and more appropriate for industrial applications.

In the following section, the most important hybrid (composite) electrochromic oxides, their preparation through a sol-gel process, and their most important properties are described.

3. Hybrid electrochromic inorganic oxides

3.1 Hybrid electrochromic materials based on tungsten oxide

The transition metals whose oxides display electrochromic properties are shown in the periodic table of elements below.

ELECTROCHROMIC OXIDES:

H																				He
Li	Be											B	C	N	O	F	Ne			
Na	Mg											Al	Si	P	S	Cl	Ar			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr			
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe			
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn			
Fr	Ra	Ac																		



Cathodic coloration

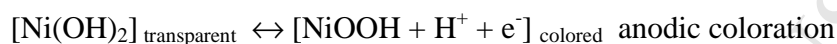
Anodic coloration

Fig 3. Electrochromic oxides showing both cathodic and anodic coloration (Reproduced with permission from Ref. [20]).

EC oxides are classified as cathodically and anodically coloring, depending whether they are colored (or transparent) in their reduced (or oxidized) states as shown below. The most representative cathodically coloring oxide is WO_3 , while NiO is the most used anodically coloring material [20]:



and:



Many other inorganic materials have been studied for their electrochromic properties such as Prussian Blue, oxides of V, Mo, Nb, and Ti (cathodically coloring), and oxides of Ni, Co, and Ir (anodically coloring) The most commonly used oxides are based on tungsten and nickel, which exhibit cathodic and anodic electrochromism, respectively, according to the highly schematic reactions for the case of proton insertion/extraction.

Tungsten oxide is still the best electrochromic material, the most studied for devices such as smart windows, rear and side view mirrors, sunroofs, etc., and most hybrid materials were, and still are prepared by doping WO_3 with other transition metals. This section is devoted to hybrid transition metal oxides based on WO_3 . Hybrid materials can be designated in two ways, either by showing the main component, for example WO_3 and separately the dopant, $\text{WO}_3 : \text{X}$ (X = doping transition metal), or, showing, distinctly, the two transition metal oxides, for example $\text{WO}_3.\text{XO}$. Sometimes, hybrid oxides are called composite oxides or binary combination of oxides as well.

Transition metal oxides have similar electronic structures, with empty d bands that will be populated when cathodic charge injection takes place. The color change happens by inter-band transitions [21].

The first comprehensive review on inorganic electrochromic materials, prepared through a sol-gel process, was published in 1997 by Aegerter et al [22] and it is today still a good reference for

the hybrid materials known at the end of the last century. In order to show the progress in this field, a table that contains the pure and hybrid materials known at that time, is reproduced here.

Table 1 Electrochromic materials prepared through a sol-gel process (Reproduced with permission from reference [22]).

Material	State	Color
WO ₃	a, c	Blue
WO ₃ -TiO ₂	a	Blue
WO ₃ -MoO ₃		
MoO ₃	a, c	
CeO ₂		UV
CeO ₂ -SnO ₂		
CeO ₂ -TiO ₂	c, *	UV
TiO ₂		Grey
TiO ₂ -Al ₂ O ₃		Blue
TiO ₂ -Cr ₂ O ₃		Blue
TiO ₂ -WO ₃		
TiO ₂ -viologen		
Nb ₂ O ₅	a, c	a-brown, c-blue
Fe ₂ O ₃		
Fe ₂ O ₃ -TiO ₂		
SnO ₂		
V ₂ O ₅	c	Green, yellow, red
V ₂ O ₅ -Na ₂ O		
V ₂ O ₅ -Ta ₂ O ₅	Powder	Grey
V ₂ O ₅ -Nb ₂ O ₅	Powder	Grey
V ₂ O ₅ -TiO ₂	a	Blue, green, yellow, reddish-brown

a-amorphous, c-crystalline, * - material used for counter-electrode

In the 80s, the sol-gel routes for the fabrication of WO₃ were based on sodium tungstate as a precursor material, but there is today a plethora of precursor molecules both organic and inorganic, and, generally, the chemistry of the reactions is well established. [23,24]. Very soon, new precursors have been tested such as peroxopolytungstic acid, in the beginning, prepared from metallic tungsten and tungsten carbide, dissolved in a solution of hydrogen peroxide [25,26] and later, from tungsten, hydrogen peroxide solution and acetic or propionic acid [27,28]. The method based on peroxopolytungstic acid (PTA) remains one of the best methods to prepare tungsten oxide and hybrid oxides, as PTA can easily be mixed with the ethanolic

solutions of alkoxides of different transition metals. The ease of doping and the facile control of the chemical composition are among the most important advantages of the sol-gel technique. Sodium tungstate was also used as a precursor, by preparing first the tungstic acid and stabilizing it with oxalic acid [29]. This quite recent work is interesting as, for the first time, the sol-gel method for the preparation of tungsten oxide was combined with a physical method, thermal evaporation, used for the deposition of MoO_3 . In this case, the mixing and formation of hybrid oxide, happens during the annealing process. The improved coloration efficiency and the short response time were accounted for by the disorder created by mixing. The authors don't discuss the possible role of the MoO_3 nanorods.

It is interesting to note that, from the very beginning, the sol-gel method was associated with nanotechnology [30]. This idea was validated by the varying synthetic methods that led to a diversity of morphologies of electrochromic nano-materials. Generally, it has been shown that transition metal oxides in a nanomaterial form exhibit shorter response times and, sometimes, enhanced coloration efficiency. However, some authors argue that nanostructuring doesn't bring new functionalities, compared to their bulk counterparts [31- 35]. In the opinion of Wang et al. the ideal nanostructures for EC materials may include ultrathin crystalline nanorods, nanowires or nanotubes, crystalline mesoporous structures, etc. These nanostructures with large specific surface areas are expected to possess fast and stable EC switching. Different kinds of materials have to be combined in order to exhibit multi-colors and to enhance the coloration efficiency and the stability of devices.

The connection of electrochromism to the nanostructural features will be emphasized in the case of specific examples. In the case of hybrid oxides, the shape of the nanoparticles, corresponding to the two materials may be pivotal for determining the EC properties.

In this section, instead of describing the individual procedures utilized to fabricate the WO_3 -based hybrid EC materials, we will show some of the emerging general tendencies, by focusing on the mechanisms accounting for improved, or, on the contrary, deteriorated EC properties by doping. The mechanisms became more comprehensible as novel data became available, after the introduction in the field of new characterization methods. We should note here that the emergence of new characterization methods such as XRD, XPS, SEM, EDX, AFM, DTA etc., brought about the major advancement in the field of EC materials during the last decades.

Many of the studies on hybrid EC materials have shown that, generally, the EC properties of tungsten oxide are improved only when doping is carried out by small amounts of dopant (5-10%) and, when the ionic radii of the two metals are close. It is thought that the improvement is the result of the preserving of the amorphous phase of WO_3 in the hybrid material, even at annealing temperatures when it would, normally, crystallize. For example, when investigating the optical and EC properties of sol-gel made anti-reflective $\text{WO}_3\text{-TiO}_2$ films, Zayim, by using XRD and XPS, found that even small titania contents can delay the crystallization of WO_3 and can lead to important structural changes in the tungsten oxide films [36]. Heat-treated sample of $\text{WO}_3\text{-TiO}_2$ films (1 and 5 mol %) are crystalline at 400°C , while samples with 10 and 15 mol% remain amorphous up to 400°C as shown in Fig. 4.

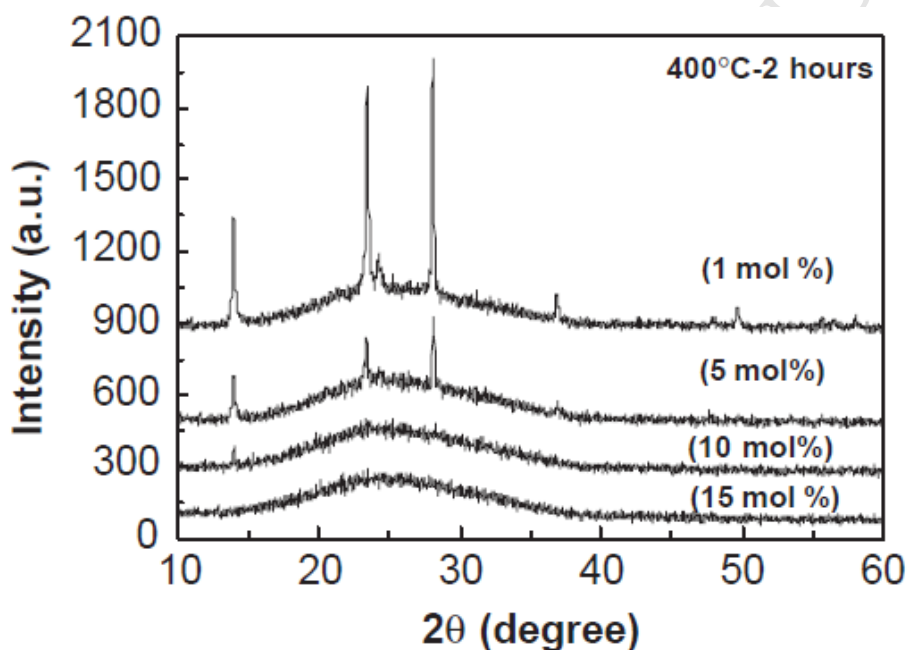


Fig.4. $\text{WO}_3\text{-TiO}_2$ thin films, heat treated at 400°C for 2 h (Reproduced with permission from Ref.36)].

It was found that the higher the percentage of titanium, the larger the disorder, which leads to a delay of the crystallization. [36,37]. For the same hybrid material ($\text{WO}_3\text{-TiO}_2$), it has been suggested that, in the presence of TiO_2 , the polymerization of polytungstate polyanion is delayed. The authors believe that replacing the WO_6 octahedron by the TiO_6 one, led to an increased disorder [38]. However, the ionic radius of Ti^{+4} (0.62\AA) is very close to that of W^{6+} (0.60\AA) and

the monoclinic structure of WO_3 should be preserved by doping [39]. In the case of mixed films, SEM images show an increase in porosity [40]. The same general observations can be made in the case of WO_3 films doped with Mo. Indeed, hybrid amorphous WO_3 - MoO_3 films with 5-10% MoO_3 have been prepared via a sol-gel dip coating method [41]. It is believed that MoO_3 inhibits the growth of the WO_3 crystal grains from the solid solution as the ionic radius of the Mo^{6+} (0.59 Å) is very close to that of the W^{6+} ions (0.60 Å). Moreover, the surface morphologies of the hybrid 5-10% MoO_3 in the WO_3 films studied by SEM illustrated the high roughness, compared with the pure WO_3 film, leading to a high interface between the electrochromic hybrid film and Li-based electrolyte. However, when the spray pyrolysis method was used for the deposition, the WO_3 films with 2% molybdenum oxide exhibited the maximum optical density at 633 nm and showed high coloration efficiency and short response time, compared to the pure WO_3 film. The results were explained in terms of the defects in the two metals [42].

Ternary hybrid films based on WO_3 have also been prepared and tested. Luo et al. prepared TiO_2 , and MoO_3 -doped WO_3 films by a sol-gel method. The optimum molar ratio of the components was found to be WO_3 : MoO_3 : TiO_2 93:7:5. This particular hybrid oxide has shown high coloration efficiency, short response time, and high cyclic stability [43].

Gold-doped tungsten oxide films have been included in this class of hybrid oxides for their interesting electrochromic properties as well as because of a novel mechanism of coloration due to the plasmonic properties of gold nanoparticles.

A special case of hybrid oxides is that of gold-doped WO_3 . More recently, preliminary results regarding the effect of gold nanoparticles on the electrochromic properties have been reported by two groups [44, 45]. Gold was added in the form of a gold precursor (hydrogen chloroauric acid) on the surface of the film and, in some cases, the coloration efficiency was found improved; however, the mechanism of the involvement of gold is still unclear.

Macro-porous gold-doped tungsten oxide films have been prepared by our group by a sol-gel method [46]. The results have shown that the properties of the gold – WO_3 composite films depend significantly on the doping method. The films having gold nanoparticles on the surface of the film, have shown the best electrochromic behavior, especially regarding the coloration

efficiency. The macro-porous films, with, or without gold, show higher coloration efficiencies than the compact films, fabricated without a template.

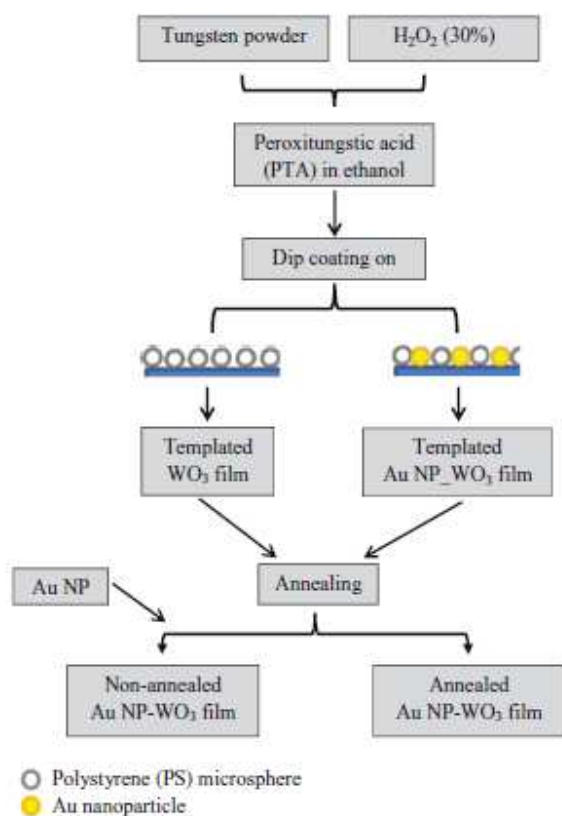


Fig.5. Flow-chart showing the fabrication of the Au – doped WO_3 film (Reproduced with permission from Ref. [46]).

Recently, very small gold nanoparticles were synthesized and added to the tungsten oxide precursor solution [47]. The EC performance obtained with very small gold nanoparticles (3-5 nm) was found much improved compared to pure WO_3 specifically, in terms of the response time. The authors attributed the improved electrochromic properties to an increase in conductivity due to gold nanoparticles as well as to Surface Plasmon Resonance (SPR) - based absorption.

Hybrid EC oxides with tungsten oxide used as a dopant, have been prepared as well. For example, Pehlivan et al. prepared the niobium oxide-tungsten oxide hybrid film, using niobium ethoxide and tungsten chloride as precursors [48]. The authors were interested to see the effect of

W doping (5 and 10%, respectively), on the EC properties of Nb_2O_5 . Doping with WO_3 was found to increase the smoothness of the film surface, that is, the grain size of niobium oxide decreases when WO_3 is introduced in the film. The total charge injection in Nb_2O_5 films was found improved by WO_3 doping. It was also observed that crystallized films showed faster coloring kinetics than the amorphous films. Larger amounts of tungsten oxide were introduced in niobium oxide by Mujawar et al. [49]. The authors found that, with the increase in the percentage of tungsten oxide, the negative effect on the crystallization of composite $\text{WO}_3\text{-Nb}_2\text{O}_5$ thin film has been observed. Preservation of amorphous structure improves the EC properties of the composite $\text{WO}_3\text{-Nb}_2\text{O}_5$, by offering more conducive channels for the intercalation–de-intercalation of H^+ ions in the thin films.

It should be reiterated that in the case of all WO_3 – based hybrid films, preserving the amorphous structure, by using small amounts of dopants, results in improved EC properties.

3.2 Hybrid materials based on vanadium pentoxide

Due to the large lithium intercalation capacity, sol-gel derived vanadium pentoxide (V_2O_5) has generated a significant research interest. V_2O_5 gels can be used in energy storage/conversion devices such as electrochromic (EC) devices, rechargeable lithium ion battery technologies, and pseudo capacitor applications. In addition, vanadium pentoxide showed good sensing and catalytic properties. Among the different nanostructures for lithium intercalation applications, vanadium pentoxide nanotubes and nanorods have been found to be the most promising, especially as electrode material for lithium ion batteries. V_2O_5 shows both anodic and cathodic EC properties. However, there are many disadvantages such as poor cycle reversibility and quite narrow optical modulation and low coloration efficiency.

Aiming to improve the low conductivity and the narrow optical modulation of vanadium pentoxide and, at the same time, to take advantage of its layered structure, Jin et al. prepared Mo-doped V_2O_5 thin films by a combined sol-gel and hydrothermal method [50]. In this work, the V_2O_5 sol was prepared by quenching the melted material in deionized water, while the Mo sol was prepared from a peroxopolymolybdate solution and the hybrid sols through a hydrothermal reaction. The results have shown that the partial replacement of V by Mo having a larger ionic radius, results in an increase in the interlayer distance. The change in the structure of the hybrid material was confirmed by FTIR and Raman spectroscopy by small shifts of the vanadium

pentoxide bands, as the doping level is too low to see the spectrum of MoO_3 . The results reveal that Mo incorporation remarkably increases the current density and the inserted/extracted charge capacity of Li^+ ions. The best EC properties correspond to a 5 mole% doping level and in this case, multi-electrochromism has been observed (orange \rightarrow green \rightarrow blue). The authors explain the improved EC properties by the donor defects introduced by doping.

By doping with TiO_2 , the doping level of vanadium pentoxide can be increased substantially. As shown in Figure 6, the doping level of V_2O_5 could be increased up to 30% [51,52].

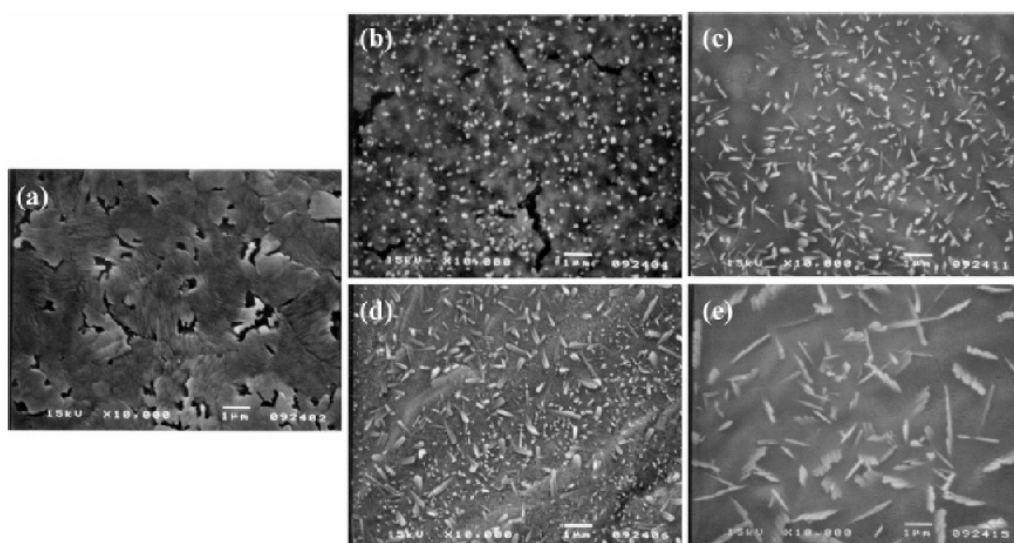


Fig.6. SEM micrographs showing the surface morphology of mixed V_2O_5 - TiO_2 system with various V/Ti mol ratios, after heat treatment at 500°C for 1 h. (a) V/Ti) 100:0, (b) V/Ti) 95:5, (c) V/Ti) 90:10, (d) V/Ti) 80:20, and (e) V/Ti) 70:30, respectively (The scale bar on all the images is $1\ \mu\text{m}$) (Reproduced with permission from ref.[51]).

The authors found the presence of randomly oriented rod-like particles in the hybrid films. Ti-doped V_2O_5 films were found very strong mechanically. They were found to be amorphous with a uniform surface texture. Most importantly, they had a very high coloration efficiency ($76\ \text{cm}^2/\text{C}$) at $550\ \text{nm}$ [52].

The enhanced intercalation properties (100% corresponding to a 20% doping level) of the hybrid is explained by a reduced Li^+ diffusion distance as well as by the reduced crystallinity. When V_2O_5 is added to TiO_2 or ZrO_2 (10% doping level) thin films, the authors found a slight decrease

in transmission, increased refractive indices, and improved EC properties. The increase in the refractive index can be used to make antireflective and reflective filters. For some of the mixed films, the contrast between the colored and bleached states was found improved [53].

In a recent paper, He et al. suggested the preparation of the hybrid V_2O_5 - TiO_2 by electrodeposition of vanadium pentoxide on TiO_2 nanorod arrays [54]. The authors combined the electrochemical deposition of vanadium pentoxide with a hydrothermal method for the fabrication of nanorod arrays of TiO_2 using titanium n-butoxide as a precursor (method reported in [55]). TiO_2 nanorod arrays uniformly covered the surface of the substrate. The array consisted of a large collection of one-dimensional nanorods, growing vertically on the substrate. The result shows that the hybrid films have a more stable electrochemical response up to 500 cycles and good cyclic stability, which suggests the improved performance of V_2O_5 as an electrochromic material in a hybrid structure. The authors explain the improved electrochromic properties by the TiO_2 nanorod array structure, which contributes to improve the structural stability of the V_2O_5 and the intercalation/de-intercalation process of Li^+ ions within the V_2O_5 film.

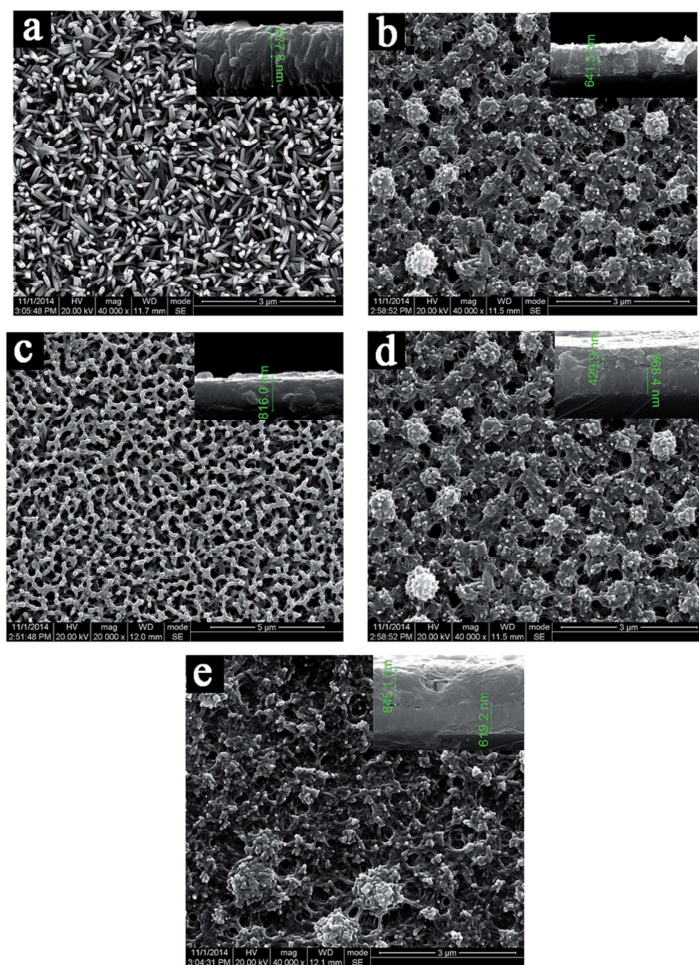


Fig.7. Surface and cross-section SEM images of (a) V₂O₅, (b) TiO₂, (c) TiO₂/1cir-V₂O₅, (d) TiO₂/4cir-V₂O₅, and (e) TiO₂/8-cirV₂O₅ (Reproduced with permission from Ref.[54]).

Layered silver vanadium oxide nanowires have been synthesized by the hydrothermal polycondensation of ammonium metavanadate [56]. Figure 8 shows the SEM images of silver vanadium oxide nanowires at different magnifications. The top view scanning electron SEM images (Figure 2a, b) of the SVO film on ITO glass show that the film is formed by entangled nanowires. The film was 500 nm thick, as shown in the image of the cross section in Figure 2c.

The authors attributed the improved EC properties to the increased electrical conductivity as well as to the enlarged interlayer spacing.

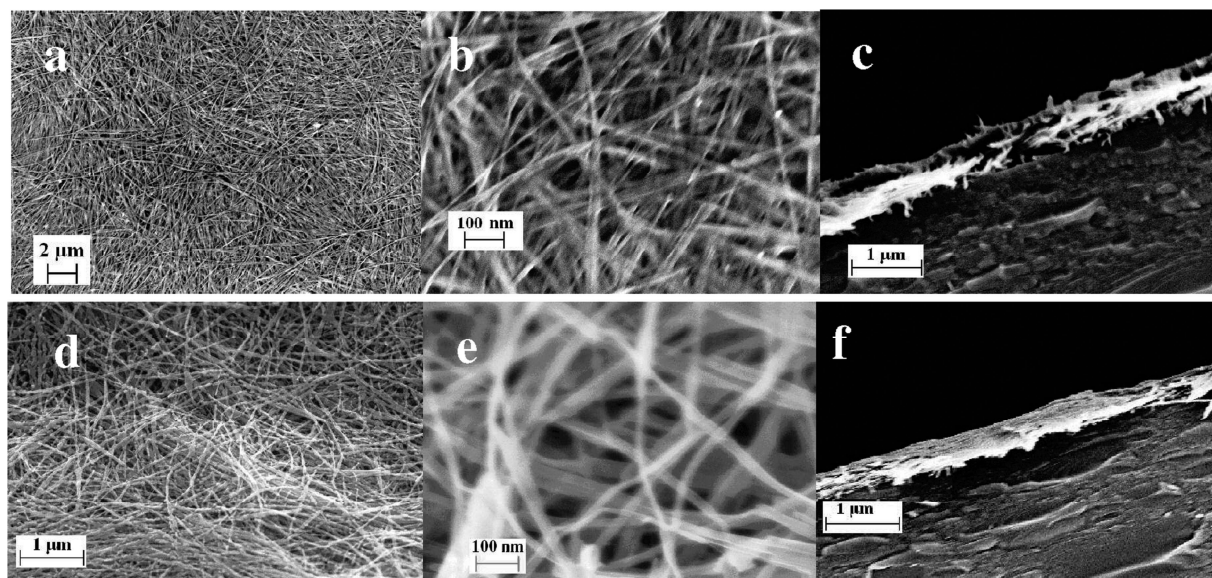


Fig.8 (a,b)Top-view SEM images of a SVO nanowire thin film on ITO glass. (c) SEM image of a cross section of the SVO nanowire thin film on glass. (d,e) Top-view SEM images of a V_2O_5 nanowire thin film on ITO glass. (f) SEM image of a cross section of the V_2O_5 nanowire thin film on glass (Reproduced with permission from Ref. [56]).

The fast response time in the Ag-doped vanadium oxide is accounted for by the faster diffusion of Li ion in the film.

3.3. Other hybrid oxides.

Among other hybrid systems, $CeO_2 - TiO_2$ films have been prepared early in the 90s and suggested to be used as a passive transparent counter electrode material in electrochromic devices [57- 60]. The highest charge intercalation capacity (10 mC/cm^2) was found when the hybrid oxide had a CeO_2 - TiO_2 ratio of 1:1 [60]. The precursors used for the fabrication of the mixed oxides were based, either on cerium and titanium alkoxides, or titanium alkoxide combined with inorganic precursors for CeO_2 such as ceric ammonium nitrate and the deposition of the films was done by spin- or dip-coating. Generally, it was found that the microstructure of the hybrid films for low contents of CeO_2 consisted of small CeO_2 crystallites embedded in a TiO_2 matrix. For compositions with more than 50% CeO_2 in the film, the size of crystallite was found much larger (10 to 50 Å). This hybrid oxide appears to be very attractive as a transparent counter-electrode in a device using lithium conductors.

The $\text{CeO}_2 - \text{TiO}_2$ counter electrode was used in an EC device, in conjunction with WO_3 /Prussian blue and a gel polymer electrolyte [61]. The device revealed a good optical modulation and faster coloration/bleaching kinetics of the primary EC electrode than the CeO_2 films.

Plasmonic transparent conductive oxide nanocrystals for selective optical modulation in the near-infrared region of the solar spectrum have recently emerged as a new type of electrochromic materials. Among these non-conventional EC materials that use capacitive charge injection in nanocrystals, are antimony-doped tin dioxide (Sb: SnO_2 , ATO) on conductive substrates, tin-doped indium oxide (ITO) and aluminium-doped zinc oxide (AZO) having plasma frequencies in the NIR (1600 nm to 4000 nm) [62].

The operation of a nanocrystal-based plasmonic EC film and the capacitive nature of the EC effect are shown in Figure 9.

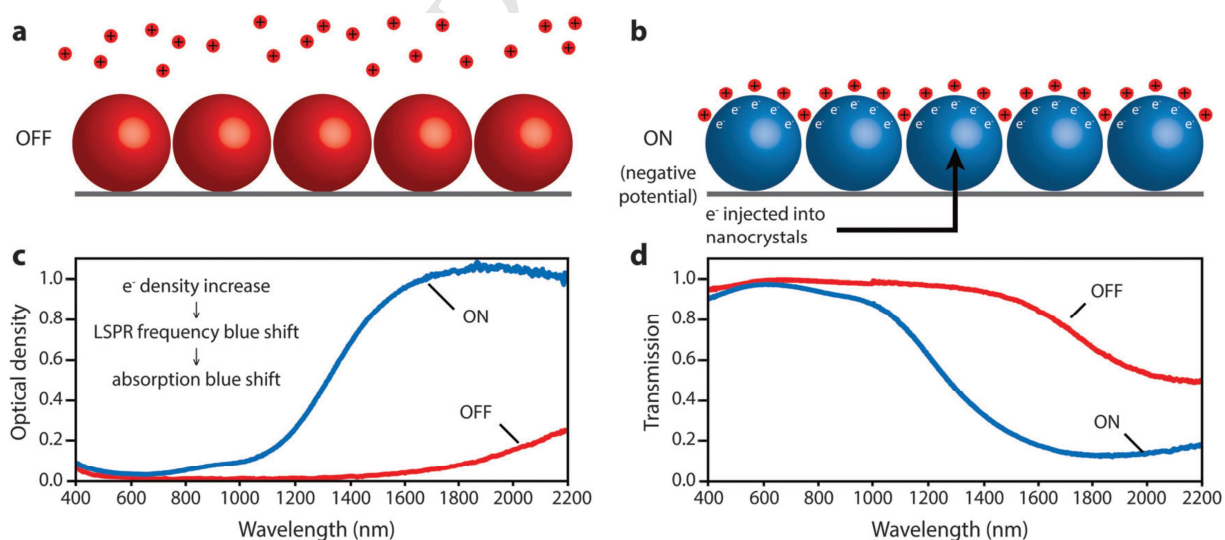


Fig.9. Depiction of the microscopic operation of a nanocrystal-based plasmonic electrochromic film, along with the associated optical changes. (a) In the OFF state, positive potential is applied to the nanocrystals, which are depleted of electrons and lithium ions are repelled. (b) In the ON state, a negative potential is applied to the nanocrystals, which injects electrons. Lithium ions are

attracted to the nanocrystal surface to compensate the injected charge capacitively. (c) Optical density changes resulting from electron injection. The increase in carrier density causes a blue shift in the LSPR and absorption. (d) Corresponding changes in transmission of the film. Parts (c) and (d) adapted with permission from Ref. [63].

4. Novel hybrid EC materials

In this section, some of the novel, advanced hybrid EC materials are shortly reviewed. “Novel” materials are those where traditional EC materials are associated with new materials, discovered more recently, materials with remarkable properties. These materials have improved EC properties, because of the very good electrical and mechanical characteristics of the compounds involved in the hybrids. The novel EC materials represent a new stage in the history of EC materials and it is worthwhile to include them in the present review.

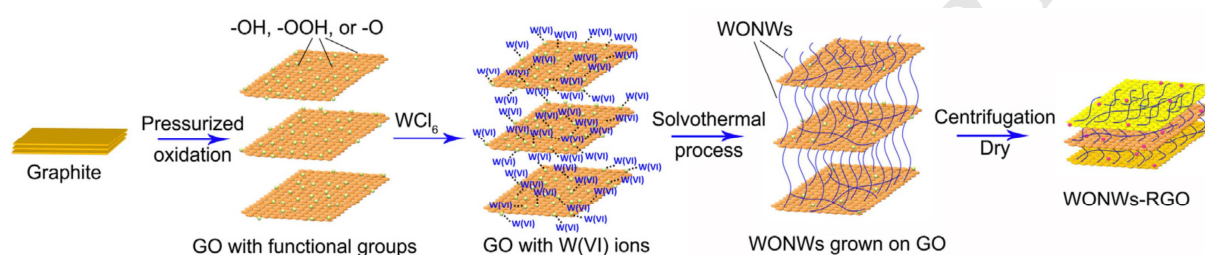
Monolayer graphene has attracted great attention recently due to its high conductivity, good transmittance, excellent mechanical strength, high chemical stability and flexibility. The tradeoff between high contrast ratio and broad spectral response is another challenge. High contrast ratio requires strong optical absorption which limits the efficiency of the bleaching process. The full potential of flexible electrochromic devices is not yet realized. These technologies would benefit from a material which is mechanically flexible, electrically conductive and optically tunable in a broad spectrum. Multilayer graphene (MLG) provides all these requirements and yields a new perspective for optoelectronic device simplicity, high optical contrast and broad band operation.

4.1 Tungsten oxide – graphene (and derivatives) nanocomposites.

Novel hybrid electrochromic composites, based on graphene and its derivatives such as graphene oxide (GO) and chemically reduced graphene oxide (RGO) with very good electrochromic performance, have been synthesized by using different approaches [64-66]. One dimensional tungsten oxide nanomaterials such as nanowires and nanorods and arrays on conductive substrates are especially promising platforms for practical EC applications.

Sandwich-structured tungsten oxide-reduced graphene oxide composites have been obtained by using a simple solvothermal synthesis [64]. The authors show that, in spite of a lower electrical conductivity of the reduced graphene oxide, compared to graphene, the EC properties of the composite have been found considerably enhanced. The fast switching time, good cyclic

stability, and high coloration efficiency are due to the covalent bonding between the tungsten oxide nanowires and the oxygen containing groups on the reduced graphene oxide sheets. Very high coloration efficiency ($96.1 \text{ cm}^2/\text{C}$) and good response time have also been obtained by using an electrochemical deposition method [65]. An advantage of the proposed method is to provide a one step reduction of both the tungsten oxide precursor and the graphene oxide. It has to be noted that all the graphene and derivatives composites can be identified by the two characteristic Raman bands at 1363 cm^{-1} (D band) and 1595 cm^{-1} (G band).



-5

Fig.10. Schematic of formation mechanism of tungsten nanowire-RGO composite (Reproduced with permission from Ref. [64]).

A simple sol-gel method using a mixture of peroxotungstic acid with reduced graphene oxide has been devised by Zhao et al. [67]. The porosity of the material originates from the pyrolysis of ethylene glycol used to reduce the graphene oxide. The composite was deposited on the ITO substrate by spin-coating. Because of the porous structure and the increased conductivity, the EC properties are considerably improved in the composite material. As it can be seen in Figure 11, the optical modulation is increased and the cyclic stability and response times are improved as well.

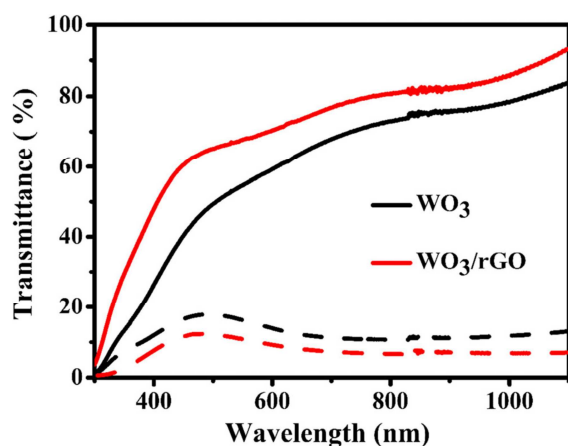


Fig.11. The UV-Vis transmittance spectra of the WO_3 and WO_3/rGO composite films (Reproduced with permission from Ref. [67]).

4.2 Tungsten oxide – Multi-walled carbon nanotube hybrids.

Nanostructured WO_3 thin films have been prepared by a sol-gel method, mixing multiwall carbon nanotubes (MWNTs) with peroxotungstic acid [68]. Lithium dodecyl sulfate (LDS) (1%) was added to the MWCNT suspension and the tubes were dispersed ultrasonically. MWCNTs provided the mechanical reinforcement of electrochromic films, enhancement of electronic conductivity, and a significant improvement of the lithium ions diffusion rate. However, the bleaching time was found long (380 s) because some of the Li ions were entrapped in the WO_3 – MWCNT network as seen in the figure.

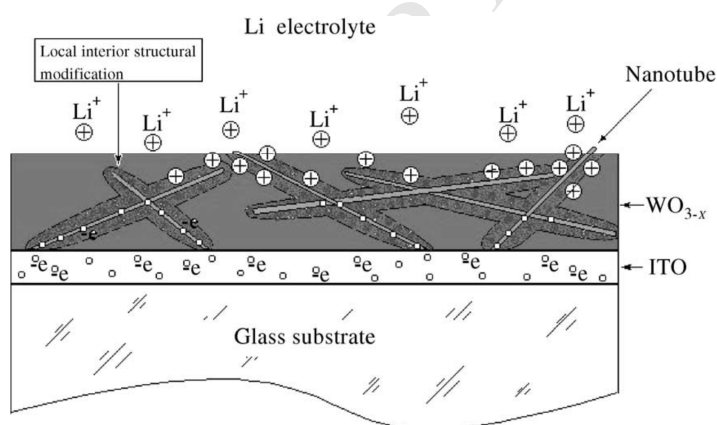


Fig.12. Schematic representation of the combination of carbon nanotubes with electrochromic materials (Reproduced with permission from Ref. [68]).

The quality and EC properties of the WO_3 -MWCNT hybrid were found much improved by using only small amounts (0.1-0.2 wt.%) carbon nanotubes [69]. The authors have demonstrated that the improved properties, especially, the very fast response times, are due to the amorphous, highly porous structure of the composite (see Figure 13).

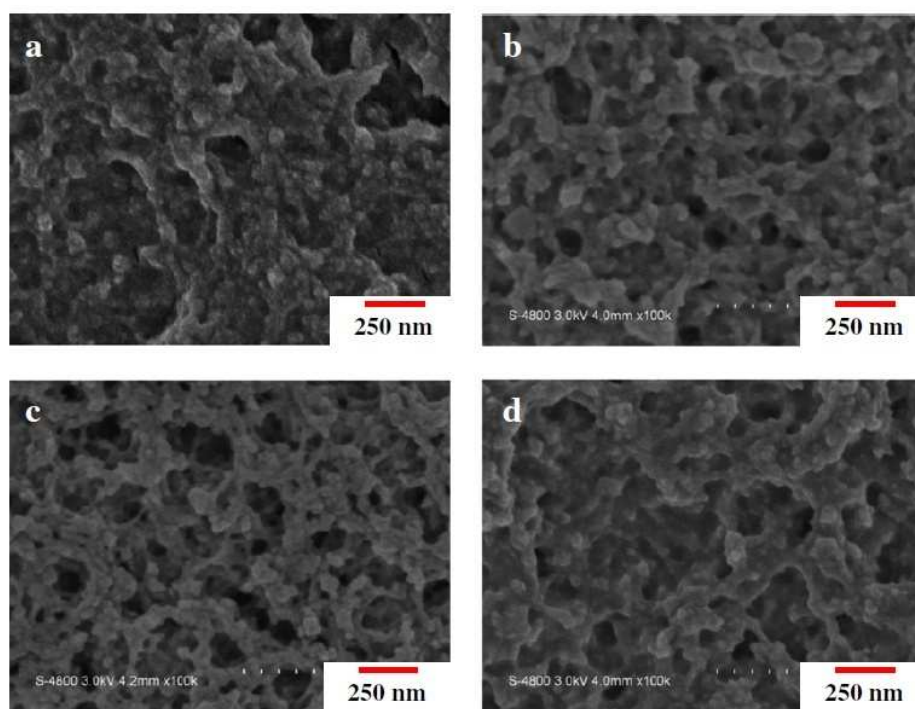


Fig. 13. Surface morphology of as-prepared films. (a) Pristine, (b) 0.05 wt. %, (c) 0.10 wt.%, and (d) 0.20 wt.% MWCNT additions (Reproduced with permission from Ref.[69]).

4.3 Hybrid mesostructured electrochromic materials prepared by a sol-gel method in presence of structure-directing agents.

It can be argued that mesostructured tungsten oxide is not really a composite material. However, as mesoporous (or macro-porous) materials result from composites of tungsten oxide with polymers or amphiphilic block copolymers that would generate the mesoporous structure, including them in the category of composites is justified.

Mesoporous tungsten oxide with pores in the size range of 2 to 20 nm has been prepared by using various structure-directing agents and strategies [70-72].

After the preparation of the composite, solvent extraction and calcination methods are used to remove the templating agent. The TEM images show clearly the mesoporous structure of tungsten oxide:



Fig.14. TEM image of mesoporous tungsten oxide, after ethanol extraction (Reproduced with permission from Ref. [70]).

The improved EC performance, especially, the higher rates of coloring and bleaching, compared to the “standard” sol-gel tungsten oxide, is accounted for by the high surface area of the structure that allows a better access of the electrolyte to the tungsten oxide.

Both amorphous and highly crystalline monoclinic mesoporous tungsten oxide have been prepared by using a novel block copolymer, poly (ethylene-co-butylene)-block-poly (ethylene oxide), possessing superior templating properties [73]. The authors achieved 3D mesoporosity by using the evaporation-induced self-assembly method. They show that a combination of mesoporosity and crystallinity leads to an improved reversibility of the insertion/extraction process, a parameter critical for device application.

Kattouf et al. have integrated the mesoporous tungsten oxide film into a proton-based all-solid-state device [74]. Mesoporosity was created into the tungsten oxide network by using a

commercially available tri-block copolymer, Pluronic P123. Mesoporous WO_3 films were infiltrated with Nafion and a thick Nafion layer on the top of the electrode was used as a proton reservoir for the device. The authors found a dramatic reduction of the switching times (5.9 s for coloring and only 1.6 s for the bleaching time).

Our group has recently reported the preparation of porous vanadium pentoxide nanorods by using templating methods [75, 76]. The effect of meso- and macroporosity on the optical and EC properties of sol-gel prepared V_2O_5 films was examined. Polystyrene microspheres were used for the fabrication of the macroporous film and a tri-block copolymer template for generating mesoporosity. The preparation of the porous films is shown in Figure 15 and the SEM image of the film heat-treated at 500°C is given in Figure 16.

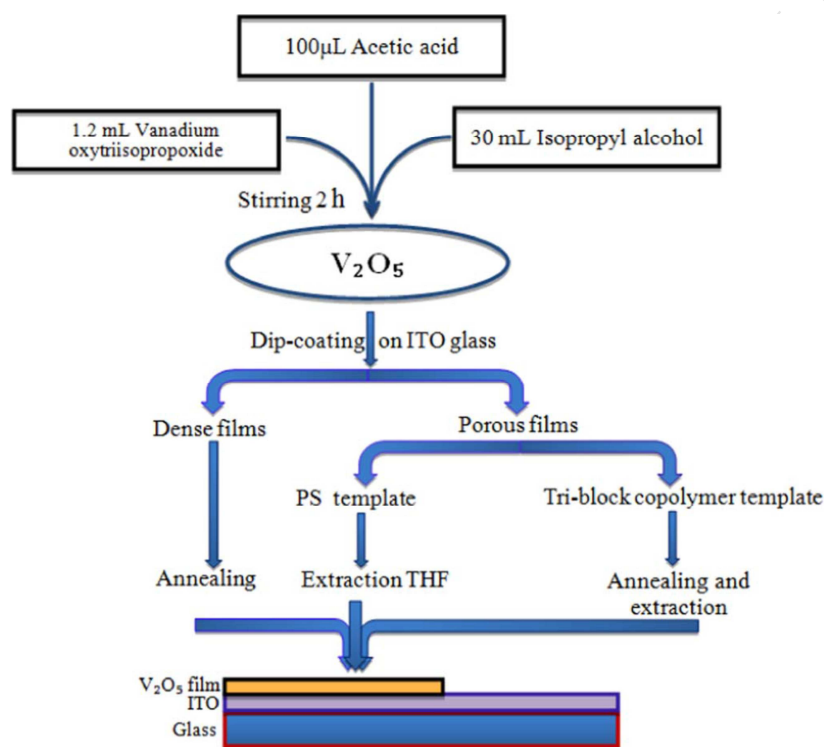


Fig.15. Flow-chart showing the fabrication of the V_2O_5 xerogel and the porous films (Reproduced with permission from Ref. [75]).

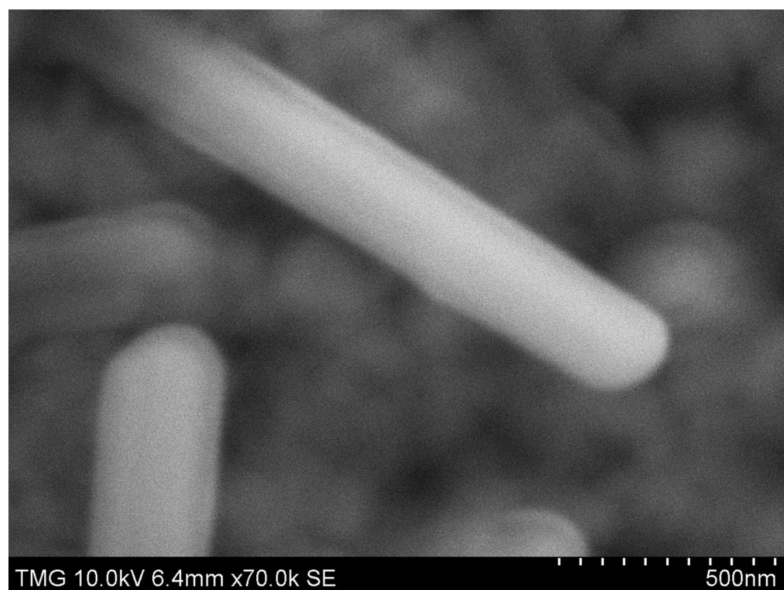


Fig.16. SEM image of one nanorod obtained after annealing the film at 500⁰C (Reproduced with permission from Ref. [75]).

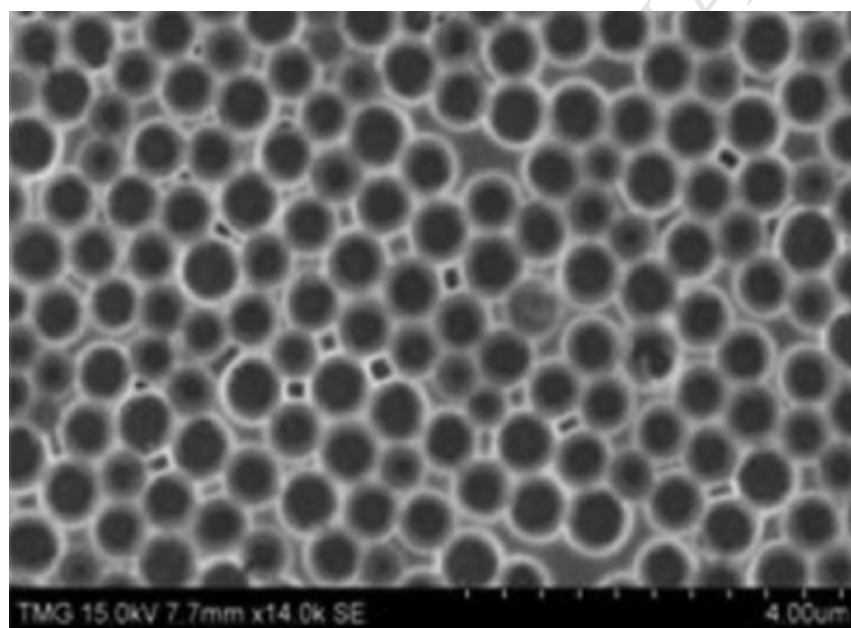


Fig.17. Macroporous structure of the V₂O₅ film (Reproduced with permission from Ref. [75]).

The electrochromic properties of the vanadium oxide nanorods proved to be different from the layered film: the cyclic voltammogram displayed additional redox peaks, the optical modulation was found to be larger in the near-infrared region than in the visible, giving

surprisingly high coloration efficiency. It is believed that the morphological transformation takes place under the effect of a prolonged heating, through a rolling up mechanism, starting with the layer in direct contact with the surface of the substrate.

4.4 Electrochromic “paper-quality” self-supporting displays.

Electrochromic displays with comparable optical qualities to paper-based display media must approach the optical qualities of paper (contrast ratio, high diffusively reflective properties) and meet key requirements in terms of readability, switching speed, and stability.

The structure of these devices is shown below in Fig. 18.

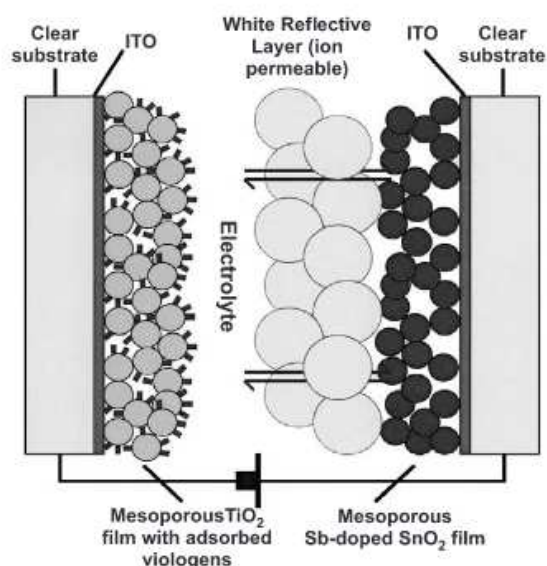


Fig.18. Device cross-section of a Nano Chromick display device (Reproduced with permission from Ref. [77]).

The working electrode is composed of a nanocrystalline n-type metal oxide, modified with electrochromophoric molecular species, usually a redox active viologen derivative, chemically tethered to the surface of the nanocrystalline electrode [78]. It colors when an applied potential causes the accumulation of electrons in the bandgap of the semiconductor and the transfer of the electrons to the adsorbed viologen. The adsorption of the viologens enhances the switching speed.

The general structure of the viologen molecule is shown in Figure 19.

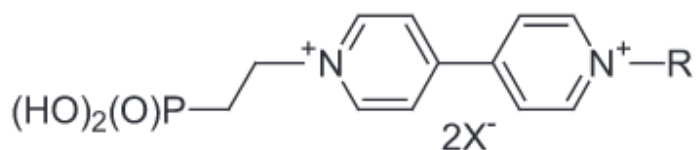


Fig.19.General structure for the viologens modifying the titania surface.

The chromophores diffuse or migrate to the electrode, forming a monolayer on the electrode surface, where they undergo oxidation or reduction with an associated color change.

For paper-quality display applications, a black-on-white contrast would be ideal and can be obtained by synthesizing viologens with different R substituents. The device using a viologen giving the darkest black coloration is shown in Figure 20:



Fig.20.Picture of coloured Nano Chromics device (Reproduced with permission from Ref. [78]).

Such systems exhibit superior reversibility, relative to that of thin film-type devices, because the coloration and decoloration processes occur without ionic intercalation.

Viologen-based ECDs, incorporating ITO nanorods as electrodes exhibited much higher optical contrast ratios than those of devices incorporating only plain ITO electrodes [79]. The ITO nanorods functioned as optical amplifiers in the viologen-based ECDs, increasing the color contrast ΔT (%) from 38% to 61%.

For a review on the different types of EC devices, the interested reader can see the Invited review article for 'Displays' special issue on Organic/Polymeric Displays [80].

In summary, materials such as graphene, reduced graphene oxide, carbon nanotubes as well as composite materials, leading to meso- or macro-porous materials, when associated to tungsten oxide, enhance significantly the EC characteristics. It is extremely important to understand the mechanism by which the EC properties are improved as this will allow to expand and diversify more and more these novel hybrids for a variety of applications.

5. Conclusion and outlook

In summary, the work done for the past two decades had brought many novelties in the field of hybrid EC materials. The most important incentive, for enhanced properties of traditional EC materials, has been the advent of nanotechnology. Indeed, the morphological features of newly discovered nanomaterials, by increasing the surface area and reducing the diffusion path(s) of Li ions, led to increased coloration efficiency, shorter coloration and bleaching times, and increased cyclic stability. The discoveries in the field of synthesis of nanomaterials enabled to expand the EC materials and connect the morphological features of nanoparticles to EC properties at the macro level. This was possible because of the emergence of the new and more elaborate characterization methods, enabling to unveil hitherto unknown structural and morphological properties of electrochromic materials.

Sol-gel methods of synthesis of nanomaterials present many advantages, the preparation of hybrid oxides taking advantage from the ease of doping. However, it has to be mentioned that during the last decade, it has proved beneficial to combine sol-gel synthesis with other solution-based methods, especially the hydrothermal synthesis. Moreover, sol-gel methods have been often used in combination with physical deposition techniques, the formation of the hybrid oxide, occurring during the annealing step.

It is important to mention the development of novel hybrid materials with significantly improved EC properties, where tungsten oxide is associated with carbonaceous materials such as MWCNT or graphene. These hybrid materials with enhanced EC properties, compared to the inorganic hybrids, will be in the future remarkable for a series of novel applications. It can be foreseen that the applications of these novel hybrids will move away from the more traditional energy efficient smart windows. Instead of using the traditional materials for smart windows applications, a new type of electrochromism, based on NIR-selective plasmonic nanocrystals, is advancing the field.

Conflict of interest

The authors confirm that this article content has no conflicts of interest.

Acknowledgments

Financial support from the Thailand Research Fund, through the Royal Golden Jubilee Ph.D. Program (Grant No. PHD/0020/2554) is acknowledged. The author also would like to acknowledge the support from the Department of Mining and Materials Engineering, Faculty of Engineering, Graduated school, Prince of Songkla University and a research internship for P.J. at the Department of Physics, Concordia University.

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