Does mesoporosity enhance thin film properties? A question of electrode material for electrochromism of WO₃†

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Replacing the commonly used indium tin oxide (ITO) with a thin metal layer as a quasi-transparent electrode leads to enhancement and acceleration of the electrochromic response of WO₃, as otherwise there is an electronic activation barrier at the interface between WO₃ and the ITO electrode, impeding fast electron transfer.

1. Introduction

In recent years, the use of sol–gel-derived metal oxide thin films with nanoscale porosity for diverse electrochemical applications, *e.g.* Li-based batteries, super-capacitors, *etc.* has become a subject of growing interest. Such devices are based on reversible oxidation/reduction, especially using the intercalation/decalation of Li⁺. It is generally believed that the partitioning of crystalline metal oxides into mesostructures could result in improved charge capacity, faster electrochemical response and other advantages. Electrochromism represents a suitable model system to study the general influence of nanostructures on electrochemical properties; it involves reversible coloration upon applying an external potential, with tungsten oxide (WO₃) being one of the most promising and best-studied materials since the discovery of its electrochromism in thin films by Deb *et al.*[1] The phenomenon has been studied for several decades, and electrochromic WO₃ films have been prepared by various techniques, including sputtering, thermal evaporation and sol–gel processes.[2] The latter offers the possibility of creating mesoporous WO₃ films with enhanced kinetics[3,4] due to their porosity when those films are amorphous. However, upon repeated counter-ion insertion and extraction, the redox stability of most sol–gel-derived amorphous films is rather low. The use of Li⁺ in anhydrous organic solvents instead of protons in acidic aqueous solutions slows down not only this degradation, but also the electrochromic response due to the lower diffusion coefficient of Li⁺ compared to H⁺. Furthermore, it requires an inert atmosphere and therefore special sealing to avoid contact with ambient humidity in later applications.

WO₃ is an ideal model system to study the influence of well-ordered mesoporosity (pores between 2 nm and 50 nm in size) on the electrochemical properties of nanoscale metal oxides, since the degree and speed of coloration/decoloration can be accurately measured and is directly related to the corresponding electrochemical processes. Recently, our group discovered that fully crystalline mesoporous WO₃ films prepared by sol–gel

templating exhibit good redox stability.[5] It was expected that the presence of nanoscale porosity would substantially improve the coloration and decoloration by means of several effects: Firstly, a high surface area and thus a large interface between WO₃ and the electrolyte can improve the diffusion of Li⁺ to and from WO₃. Secondly, the ordered mesopore structure in turn partitions WO₃ into small crystallites, thus decreasing the diffusion length inside the solid. Thus, the mesoporosity should facilitate Li⁺ insertion and desertion, but it was found that the coloration/decoloration kinetics were not substantially improved.[5] Since the films were crack-free and showed excellent overall homogeneity, these results pointed to a further parameter governing the electrochromic response, namely the interface between tungsten oxide and transparent conducting oxides (TCOs) such as indium tin oxide (ITO) and fluorine-doped tin oxide (FTO).

For opto-electronic applications TCO materials like ITO or FTO are widely used as transparent electrode materials. Only recently, several studies showed that TCOs are not very suitable for organic photovoltaics[6] due to a band mismatch which causes poor electron injection from p-type polymers to the ITO electrode. This behavior has been exploited in OLEDs (organic light-emitting diodes) by using a thin layer of wide-band-gap metal oxides like WO₃ as a buffer layer thus increasing OLED efficiency. Measurements by Kelvin probe show that the work function increases from 4.7 eV (ITO) to 6.4 eV for WO₃-covered ITO, in this case improving the hole injection from ITO–WO₃ and limiting leakage currents.[7,8]

In the present study we have investigated the influence of TCO electrodes on the kinetics of Li⁺ insertion into WO₃. It is shown that the interface between WO₃ and TCO has a strong impact on the coloration kinetics, thus masking the effect of defined mesoporosity on Li⁺ insertion. As a potential alternative, it is demonstrated that the use of thin metal films instead of TCOs as transparent electrodes improves the electrochromic response of mesoporous or non-templated tungsten oxide thin films and demonstrates that defined mesopores indeed enhance these properties, especially with regard to kinetics.

2. Experimental

Synthesis

All chemicals were reagent grade (Sigma-Aldrich) and used as received. The quasi-transparent gold electrodes were prepared on

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thoroughly cleaned glass by thermal evaporation of 1–2 nm chromium as an adhesion layer and 20 nm of gold. The conductivity of about 70 Ω cm^{-1} for these thin quasi-transparent gold electrodes was slightly lower than for the commercial ITO-coated glass (hallerglas, Germany) 30 Ω cm^{-1}. Thin WO_3 films with a thickness of 50–150 nm were prepared on both types of substrate by thermal evaporation (PVD) from WO_3 powder (Aldrich). A quartz microbalance was used to monitor the rate of deposition (1–2 nm s^{-1}) and thickness. The substrate temperature was initially 20 °C and rose to 60 °C after deposition. The amorphous films were heated to 550 °C at a ramp of 5 °C to crystallize the films.

For mesoporous WO_3 layers, a dip-coating solution was prepared from 207 mg of the block copolymer $H(CH_2CH_2CH_2(CH)CH_2CH_3)_{89}(OCH_2CH_2)_{79}OH$ (referred to as 'KLE') dissolved in 6 mL of EtOH. To this solution 750 mg WCl_6 dissolved in 4.5 mL EtOH and 3 mL THF was added and the resulting solution was stirred for 2 h. The solution was filtered with a 200 nm syringe filter and films were deposited on various substrates (Si wafers, ITO-coated glass slides, gold-coated glass slides). The relative humidity in the dip-coating chamber was adjusted to 5–10% and the withdrawal speed was 48 cm min^{-1}. After dip-coating, the samples were kept at constant humidity for 2 min and then transferred into an oven at 80 °C. For further stabilization the samples were heated to 300 °C at a ramp of 5 °C and kept for 1 h at 300 °C. Thereby, the inorganic matrix was stabilized sufficiently without destroying the KLE template. Finally, the samples were calcined with a ramp of 5 °C min^{-1} to 550 °C, resulting in template removal and full crystallization of the inorganic matrix.

Characterization

Two-dimensional small-angle X-ray scattering (2D SAXS) measurements were carried out using a Nonius rotating anode (Cu Kα radiation, λ = 0.154 nm) with pinhole collimation and a MAR CCD area detector (sample detector distance of 750 mm). The film thickness was measured with a profilometer (Alpha-Step IQ from KLA-Tencor). The morphology (Fig. S3 of the ESI†) of the electrodes was examined with a LEO Gemini 982. Absorbance spectra and *in situ* absorbance measurements at 630 nm were recorded on a UVIKON Kontron 960 spectrophotometer (Kontron AG, Eching, Germany). Electrochemical measurements were performed using Autolab 12 potentiostat/galvanostat (Eco Chemie, Netherlands). WO_3 films on gold and ITO-covered glass were utilized as working electrodes; a Pt wire was taken as the counter electrode, and an Ag wire served as a pseudoreference electrode.

3. Results and discussion

In our previous studies of mesoporous crystalline WO_3 films deposited on ITO substrates, a pronounced dependence of the electrochromic response on the temperature was found, *i.e.* with higher temperature more charge could be inserted and thus the coloration was increased.[5] Here, as a structure-directing agent, we used the same KLE block copolymer template previously applied to WO_3. Fig. 1 shows that the difference in optical density (ΔOD), *i.e.* the difference in absorbance between colored and bleached states, increases reversibly from 0.075 at 20 °C to 0.125 at 70 °C, reverting to 0.075 at 20 °C upon subsequent cooling. This behavior and the accelerated kinetics were previously solely attributed to faster ion diffusion into the film. These experiments again confirm the excellent electrochemical and temperature stability of the fully crystalline mesoporous WO_3 films.[5] However, taking into account the results from studies on OLEDs, some electronic activation barrier is expected to be present in the electrochromic films as well.

In fact, using a thin gold layer as a transparent electrode, the KLE-templated mesoporous WO_3 films exhibit a pronounced
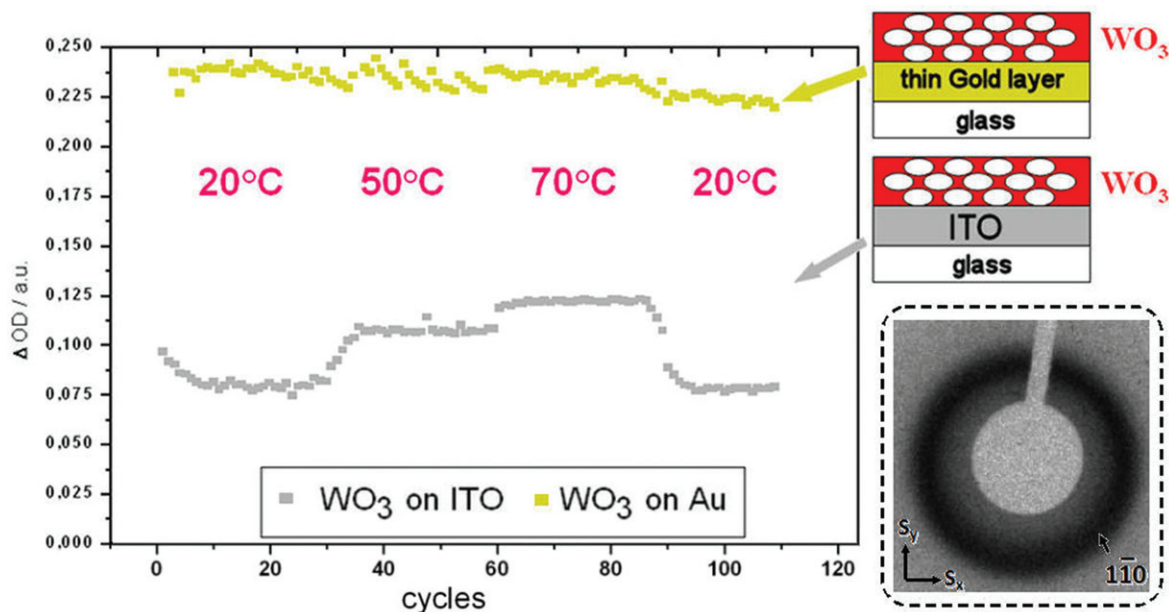
Fig. 1 ΔOD for mesoporous WO_3 films (thickness = 120 nm) on gold and ITO with electrode schematics. Inset (bottom right): 2D SAXS pattern in transmission mode for WO_3 on metal with well-defined first-order maximum, *i.e.* mesoporosity.

enhancement of the electrochromic response compared to similarly prepared films on ITO-coated glass (Fig. 1). In particular, ΔOD is markedly increased, although the thickness of about 120 nm and the mesostructure of the films deposited on gold and ITO are almost identical, as both WO_3 films were deposited by dip-coating using the same solution. The thickness was measured by profilometry and the 2D SAXS pattern in transmission geometry, (measured by using ultrathin Si substrates, see inset Fig. 1), *i.e.* with an angle of incidence of 90° between the X-ray beam and the film. The 2D SAXS pattern exhibits a well-defined first-order maximum, independent of the substrate (ultrathin Si substrate with and without metal layer). Similar to our previous studies, the structure corresponds to a bcc arrangement of ellipsoidally distorted spherical mesopores. Thus, the mesostructure is identical to the mesoporous WO_3 films prepared on ITO or Si wafers and structure effects can be excluded as the origin of the differences in ΔOD. Surprisingly, no temperature dependence is observed for mesoporous WO_3 films deposited on gold, proving that the temperature factor for the corresponding films on ITO has to be attributed to an activation barrier for electronic transfer at the ITO–WO_3 interface. This electronic barrier is apparently negligible at the Au–WO_3 interface. Similar observations are made when other metals (Pd, Pt) are used as electrodes; gold was chosen because it possesses the highest transparency and a thermal stability suitable for calcining the film at 550 °C. Such a high temperature is required to remove the block copolymer template and to crystallize WO_3. Replacing ITO with other TCO materials like antimony-doped tin oxide (ATO) or FTO, *i.e.* using ATO- or FTO-coated glass as the substrate, did not produce better performances. This result is consistent with the explanation presented before, since the work functions (ATO: 4.8 eV, FTO: 4.4 eV) are similar to that of ITO (4.3–4.7 eV, the work function of ITO is altered by the heat treatments due to a decrease in oxygen vacancies). By contrast, the work function of gold is 5.2 eV, closer to the 6.4 eV observed for $W(VI)O_3$ and 5.3 eV for $W(V)O_3$. To further investigate whether the better performance of mesoporous WO_3 on gold is only due to the sol–gel preparation method and the mesoporosity, WO_3 films were also thermally evaporated on ITO and gold, and calcined afterwards in air at 550 °C to fully crystallize tungsten oxide and to ensure comparability with the mesoporous films treated under these conditions. The thickness and morphology of thermally evaporated films depend only to

a small extent on the substrate, and the thickness can therefore be finely tuned.

Closer inspection of the absorbance during the redox cycles reveals that the kinetics of the electrochromic response of thermally evaporated WO_3 on ITO also vary significantly with temperature, as can be seen in Fig. 2. For convenience, we present only the evolution of the absorbance during redox cycles (±1 V *vs.* Ag), since the evolution of the charge inserted/extracted is very similar to this curve (see Fig. S1 of the ESI†).

In the case of thermally evaporated WO_3 deposited on ITO (blue curve) the amount of charge inserted at 20 °C and therefore the coloration (increase in absorbance) is low and only gradually achieved, whereas at higher temperatures both kinetics and overall coloration improve. Likewise the oxidation and bleaching process is even slower. Therefore the reduction at −1 V *vs.* Ag was carried out for 1 min to reach about 95% of the film's maximum coloration (after which the rate of charge insertion became very small). The oxidation/bleaching at +1 V *vs.* Ag took as long as 2 min at low temperatures, but was significantly accelerated at 70 °C.

In contrast to the poor performance of thermally evaporated WO_3 on ITO, such WO_3 films prepared on gold (red curve) basically exhibit no temperature dependence and very fast kinetics, especially for the bleaching which was completed in a few seconds. This allows very fast switching times for applications.

Obviously, the transparency of the gold-coated glass was lower (85% compared to 95%), thus the absorbance curve is shifted to higher values (as if a constant filter had been applied), yet the crucial difference in absorbance remains unchanged. It is also worth noting that for the thermally evaporated films the maximum difference in absorbance was about 0.29 (and therefore the maximum charge capacity was about 9 mC cm^{-2}, *i.e.* a coloration efficiency of 31–33 cm^2 C^{-1}) independent of the electrode. However, for WO_3 this value was only reached at 70 °C on ITO, but on gold at all temperatures. Moreover, on gold surfaces the kinetics are always very fast, whereas on ITO high temperatures were needed to accelerate the electrochromic response. The thickness of the films also influences the response: for a layer of up to 125 nm of WO_3 the electrochromic response is still accelerated on gold, whereas the kinetics on thicker WO_3 films increasingly resemble those on ITO (see 250 nm of WO_3 Fig. S2 of the ESI†). As only the electrode material (ITO or Au)
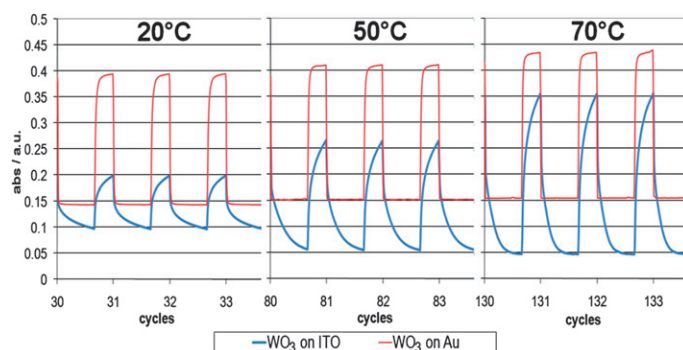
Fig. 2 Variation of absorbance at 630 nm during redox cycles (±1 V *vs.* Ag in 1 M LiClO$_4$ in propylenecarbonate) at different temperatures for thermally evaporated 50 nm WO_3 films prepared on ITO-(blue) and Au-(red) coated glass.

was changed, the electrolyte and therefore the Li^+ insertion seem to exert little influence on the process, while the electronic transfer *via* the electrode–WO_3 interface appears to be the rate-limiting factor. A complete interpretation of these findings is rather difficult, yet a mismatch of the band structures of ITO and WO_3 is evidently one of the key factors. In agreement with the observations from OLED studies[7,8] electron injection from WO_3 into ITO is not favorable and oxidation/bleaching in electrochromism also requires this electron transfer. On gold the barrier for electronic transfer to and from the film is much smaller, thus allowing fast and complete reduction and oxidation, while on ITO the equilibrium, *i.e.* full coloration, is only attained at high temperatures. This line of argument is corroborated by cyclic voltammetry. Fig. 3a shows an almost reversible redox couple of WO_3 on gold, while the reduction and oxidation peaks are separated by about 1 V on ITO. This overpotential is possibly due to the band mismatch between WO_3 and ITO. The reduction peak around -0.8 V *vs.* Ag is followed by the oxidation peak at -0.7 V for WO_3 on gold, whereas on ITO the oxidation only takes place around $+0.2$ V *vs.* Ag. Moreover, the temperature dependence on ITO is clearly seen.

A similar enhancement in kinetics was reported in other electrochromic systems like $Ni(OH)_2$ on metallic Ni[9] or mostly amorphous WO_3 on ITO, but with a thin gold overlayer onto which additional potentials can be applied.[10] Hence, while the effect seems to be most pronounced for crystalline WO_3, further experiments are needed to test amorphous WO_3 and other electrochromic systems and thereby elucidate the underlying mechanisms. Because of recent advances in novel transparent electrodes like ZnO–Ag–ZnO[11] with similar transparency to ITO and better conductivities, an application in a multilayer system

might be feasible. Indeed, ZnS–Ag–ZnS has already been investigated by Leftheriotis *et al.* showing the feasibility of replacing TCO electrodes in electrochromic systems.[12–14] Unfortunately, no data on the kinetics and crystallinity of these ZnS–Ag–ZnS–WO_3 electrodes are provided, yet interestingly in the cyclic voltammogram the separation of oxidation and reduction peaks is reduced by 400–500 mV on ZnS–Ag–ZnS compared to a TCO electrode, in this case FTO.[14]

Based on the findings of this work it is evident that in previous studies, including our studies, the influence of mesoporosity on electro-optical properties was masked by the electronic activation barrier between the WO_3 and the ITO electrode, impeding fast electron transfer. This effect obscured the advantages of mesoporous organization, such as high surface area and good accessibility of the film for the electrolyte, but also the well-defined pore walls with the maximum thickness of 10–15 nm which represents the maximum diffusion path of the Li^+ ions. Thus, the preparation of mesoporous WO_3 on thin metal layers allows the unmasked influence of mesoporosity and nanoscaled crystallinity on electrochromism to be addressed. For this purpose, three types of samples were compared: WO_3 with ordered mesopores ('meso-WO_3') was templated by evaporation-induced self-assembly using a block copolymer, yielding deformed spherical mesopores placed on a distorted bcc lattice, with a diameter of *ca.* 14 nm parallel to the plane and *ca.* 8 nm perpendicular to the substrate. The treatment at 550 °C resulted in a highly crystalline WO_3 matrix. A second type of sol–gel template material, *i.e.* a weakly porous WO_3 film ('low meso-WO_3'), was obtained by using only 1/10 of the template, with otherwise identical conditions. These two sol–gel derived films were compared with a thermally evaporated WO_3 film ('evap-WO_3').

Fig. 4 shows the time necessary before a portion of the total bleaching is obtained, thus being more instructive than just comparing the time for 50% bleaching. As can be seen in Fig. 4, sol–gel derived mesoporous WO_3 ('meso-WO_3 on Au') possess the fastest electrochromic response, compared to a less porous WO_3 film ('low meso-WO_3 on Au'), and to thermally evaporated WO_3 ('evap-WO_3'). In fact, completely dense WO_3 films, *i.e.* attaining bulk density, can hardly be prepared by sol–gel processing (even in evaporated films the porosity is about 5–10
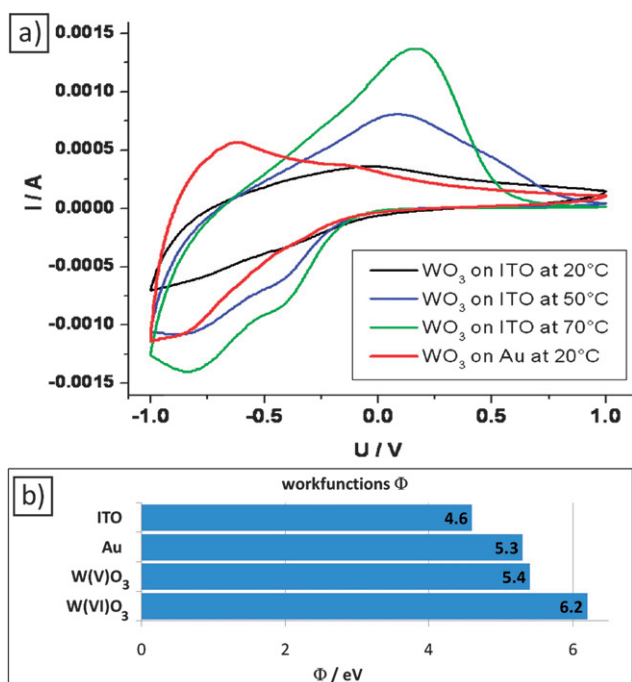
Fig. 3 a) Cyclic voltammograms (*vs.* Ag in 1 M $LiClO_4$ in propylene-carbonate, 20 mV s^{-1}) of thermally evaporated WO_3 films on ITO and Au at different temperatures. b) Work functions for electrode materials.
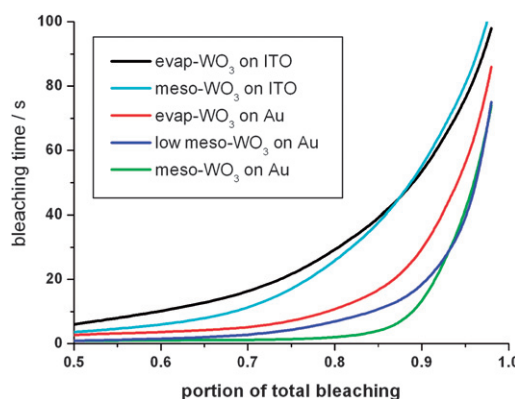
Fig. 4 Bleaching time against portion of total bleaching (*i.e.* the difference between fully colored and bleached state) for different porosities of 100–120 nm WO_3 on Au and ITO (for definitions see text).

vol%). Thus the advantage of the ordered mesoporosity is rather the well-defined pore walls and crystallite sizes and not primarily the higher porosity. A significant improvement in the bleaching time is visible for films with ordered mesoporosity on gold electrodes, but it was completely masked on ITO electrodes. Sputtered films or other materials that can be prepared in dense films should show slower kinetics.

4. Conclusion

In conclusion we have demonstrated that replacing the commonly used indium tin oxide (ITO) with a thin metal layer as a quasi-transparent electrode leads to enhancement and acceleration of the electrochromic and electrochemical response, as otherwise there is an electronic activation barrier at the interface between WO_3 and the ITO electrode, impeding fast electron transfer. This problem can be overcome by the use of thin metal electrodes. We believe that these insights are of general relevance since such hybrid metal–semiconductor electrodes could potentially also enhance other electrochemical systems using nanostructured metal oxides. It should be noted that ITO-coated glass is frequently utilized as an electrode to study nanostructured metal oxides with respect to their electrochemical properties. Our study proves that such data should be interpreted with care. Using lithium insertion for sol–gel-derived mesoporous TiO_2 films we find no significant advantage of a metal electrode compared to ITO, as the kinetics are already fast on ITO, owing to the similar work function (4.6 eV for anatase TiO_2). Nevertheless, our study reveals that it is mandatory to investigate the influence of the electrode for all types of metal oxides, as an optimized oxide–electrode interface could enhance their performance.

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