Dye–Sensitized Nanostructured Crystalline Mesoporous Tindoped Indium Oxide Films with Tunable Thickness for Photoelectrochemical Applications


1Laboratoire de Chimie de la Matière Condensée de Paris-UMR7574, CNRS, Université Paris 6, Collège de France, 11 place Marcelin Berthelot 75005 Paris
2Laboratoire de Chimie et Biologie des Métaux, Université Grenoble 1, CNRS, CEA, 17 rue des Martyrs 38054 Grenoble cedex 9
3Department of Technology for Biology and Health, CEA LETI-MINATEC, 17 rue des Martyrs, F-38054 Grenoble CEDEX 9, France
4Collège de France, 11 Place Marcelin Berthelot, 75005 Paris

Abstract

A simple route towards nanostructured mesoporous Indium–Tin Oxide (templated nano–ITO) electrodes exhibiting both high conductivities and optimized bicontinuous pore–solid network is reported. The ITO films are first produced as an X-ray–amorphous, high surface area material, by adapting recently established template–directed sol–gel methods using Sn(IV) and In(III) salts. Carefully controlled temperature/atmosphere treatments convert the as–synthesized ITO films into nano-crystalline coatings with the cubic bixbyite structure. Specially, a multi-layered synthesis was successfully undertaken for tuning the film thickness. In order to evaluate the performances of templated nano–ITO as an electrode substrate for photoelectrochemical applications, photoelectrodes were prepared by covalent grafting of a redox–active dye, the complex [Ru(bpy)_2(4,4′-(CH_2PO_3H_2)2-bpy)]Cl_2 (bpy=bipyridine). Surface coverage was shown to increase with the film thickness, from 0.7 × 10^{-9} mol.cm^{-2} (one layer, 45 nm) to 3.5 × 10^{-9} mol.cm^{-2} (ten layers, 470 nm), the latter value being ~ 100 times larger than that for commercially available planar ITO. In the presence of an electron mediator, photocurrents up to 50 μA.cm^{-2} have been measured under visible light irradiation, demonstrating the potential of this new templated nano–ITO preparation for the construction of efficient photoelectrochemical devices.

Keywords

ITO; Mesoporous; Sol-gel Process; Multi-layered; Ruthenium dye; Photocurrents

INTRODUCTION

In the context of increasing global energy demand, the development of photoelectrochemical (PEC) devices for H_2 evolution through water splitting is a highly active field of research.1-3

Electronic Supporting Information available. FE–SEM images of films heat treated under various atmosphere, EDX analyses, cyclic voltammograms of the various non–functionalized and functionalized electrodes, absorption spectrum of a functionalized 10–layers templated nano–ITO film and peak–to–peak potential difference versus the scan rate curves are available in supporting information.
This technology is indeed recognized as a promising and sustainable solution to store sunlight energy under a chemical form that can then be used on request. Specially, the construction of PEC devices by the dye-sensitized approach requires combining efficient molecular photosensitizers or photocatalysts with a suitable electrode material. The latter should be produced via low-cost processes and display specific features such as optical transparency in the visible region, high electrical conductivity as well as a large surface area allowing a high grafting density of the catalytically active species. To gather all these properties, materials displaying a defined porosity are of interest.

Transparent conducting oxides (TCO) such as tin–doped indium oxide (ITO) are substrates of choice for the construction of optoelectronic devices. Various methods based on both physical or chemical deposition have been explored to synthesize ITO as thin or thick films. Such films exhibit different microstructures and they are either dense or porous, depending on the process used and the targeted application. Recently, nanostructured ITO has been reported and used for grafting catalysts, organic dyes or for adsorbing metalloproteins. In these studies, the substrates were prepared either by a vacuum–based glancing angle deposition technique, by a sol–gel process or by spin–coating of ITO nanoparticles. With the latter technique, mesoporous ITO films with uncontrolled pores network were synthesized. These films exhibit high specific surface area and an adjustable thickness. After grafting a water oxidation catalyst, current densities were enhanced by two orders of magnitude by comparison with a planar electrode, due to the increase in the surface coverage. ITO films with an ordered mesoporous structure could be prepared from molecular tin and indium precursors and synthesized block copolymer templates, by the sol–gel process. It nevertheless resulted in amorphous insulating hybrid organic–inorganic films, which required an appropriate treatment at high temperature under a suitable atmosphere to reach suitable electrical conductivities. This treatment allowed the crystallization of the pore walls, the formation of the porous network and of defects into the inorganic network. The influence of the pore walls thickness and of the defect concentration onto the conductivity of very thin films (~ 100 nm) has been studied. The best specific resistance obtained after optimizing the microstructure of the film (thickness, pore wall and pore size, defects) was 0.5 Ω·cm. However, it should be highlighted that these properties were achieved onto conductive substrates (ITO or FTO); little attention has been paid to the synthesis of transparent, mesoporous, conductive thin films onto non–conductive substrates. Moreover, a better control of the thickness of the films, the doping level and the size of particles and pores is still highly desirable to optimize the properties required for the development of efficient molecular-based PEC devices.

Herein, we report for the first time the synthesis of nanostructured mesoporous ITO, called templated nano–ITO, by a template–directed sol–gel based technique onto non–conductive glass substrate. The procedure was successfully applied to obtain optically transparent multi-layered films with tunable thickness and high electrical conductivity. Furthermore, these sol–gel–derived mesostructured TCO films have a significantly high specific surface, allowing an efficient sensitization by a ruthenium-based redox-active dye. The resulting films were shown to display interesting photoelectrochemical properties under visible light irradiation.

RESULTS AND DISCUSSION

Synthesis of templated nano-ITO films

The ITO films described in this study were synthesized by a template–directed sol–gel synthesis coupled with the dip–coating process onto glass substrates (Figure 1). Dip–coating of a MeOH/acetone solution of In(acac)₃, SnCl₄ and the PIB–b–PEO polymer as the template resulted in an initial hybrid, transparent and homogeneous film. However, at this
stage, X–ray diffraction and electrical measurements indicated that the film was amorphous (Figure S1) and not conductive. A thermal treatment at 450°C in air for 1 hour was necessary to form a poorly conducting nanostructured, mesoporous hybrid organic–inorganic film of templated nano–ITO with an open porous network. Top–down (Figure 1) and cross–section (Figure 2) Field Emission Scanning Electron Microscopy (FE–SEM) images show that after the heating step the films were highly porous and uniform with a thickness of 45 nm. Thermal treatment at a higher temperature (up to 550°C) in air did not change the porosity of the films (Figure S2). The crystallinity of the films was studied through ex–situ X–ray diffraction analyses and the main results are reported in Figure 3. In all cases and in agreement with the literature, the nanostructured ITO films exhibited the cubic bixbyite structure. The size of the ITO nanocrystalline particles was determined using Sherrer equation and the method from Williamson et al. and was shown to vary from 15 nm to 20 nm in diameter depending on the temperature used for the heat–treatment of the films (300°C and 450°C, respectively; see supplementary information, Table S1). These values are confirmed by TEM analyses that showed the presence of nanocrystallites (Figure 3). Indeed, the heat–treated nanoarchitectures exhibit well–defined nanoparticles with edges and steps; 450°C–calcined films contain ~ 20 nm ITO crystallites. The composition of the templated–ITO films was determined by EDX and XPS analyses (Figure S3). We found that Sn was homogeneously distributed into the film with an Sn:In ratio of 10:90 in good agreement with the initial ratio in the sol.

For tuning the thickness and, as a consequence, the electrical properties of these mesoporous films, a multi–layered synthesis has then been undertaken. Multi–layered films were obtained by performing several (one to nine) cycles of dip-coating and thermal treatment at 450 °C for 5 min (flash treatment) to stabilize the layer, before a final thermal treatment at 450°C for 1h in air. The thickness of the films was evaluated from cross-section FE–SEM images and found to vary linearly from 45 (1 layer) to 470 nm (10 layers) (Figure 2f, left). Figure 2f right shows that the 10–layers films are transparent, as the transmittance is above 80 % from 450 to 850 nm. Small–angle X–ray scattering (Small–Angle X–ray diffraction) onto templated nano-ITO films heat–treated at 450°C indicates the presence of a well–ordered pores network within the film (Figure S4). The porosity of the film is homogeneous and connected as seen on FE-SEM images (Figure 6a.). The variation of the electrical conductivity, measured by using a two–probe set–up, as a function of the thickness of the film is presented in Figure 4.

As expected, the electrical conductivity increases as a linear function of the thickness of the film, varying from 5 S.cm⁻¹ (70 nm; 2 layers) to 40 S.cm⁻¹ (470 nm; 10 layers). The value obtained for the thickest film is quite remarkable when compared to values previously reported by Smarsly and coll. for mesoporous mono–layered ITO films deposited onto planar ITO commercial substrates (σ = 0.6 and 1.9 S.cm⁻¹ for thicknesses of 110 and 145 nm, respectively). We note that the latter were deposited onto conductive substrates while the films prepared in our study were directly deposited onto simple non-conductive glass substrates. Consequently, the conductivity we measured did only characterize the templated nano–ITO films, without any contribution from the substrate. Thus, this property is likely to reflect an excellent particle–particle contact between the ITO nanocrystals in the 3–D network. To reach such interesting conductivity values, we found that the temperature of the flash thermal treatment between the deposition of two layers (450°C for 5 min) has a significant importance: it allows the nucleation of small particles and also a partial decomposition of the template. By contrast, a flash thermal treatment performed at 200°C only generated amorphous hybrid organic–inorganic films with a poor electrical conductivity. In that case, the final treatment at 450°C for 1 h induced stresses in the films due to the formation of large amount of gazes (CO, CO₂) from the decomposition of the
Film sensitization with a redox–active dye

To further characterize these templated nano-ITO films, dye sensitization by covalent grafting of a redox–active dye was undertaken and the electro– and photo–electrochemical properties of the resulting functionalized electrodes were evaluated. The photoactive ruthenium complex \([\text{Ru(bpy)}_2(4,4'-(\text{CH}_2\text{PO}_3\text{H}_2)_2\text{-bpy})]\)Cl_2 1,27 bearing the 4,4’–bis(methylphosphonic acid) 2,2’–bipyridine ligand, has been employed. Phosphonic acids are indeed well-known to form robust monolayers onto transparent conductive oxides such as ITO by covalent reaction with surface hydroxyl groups.28, 29 A 10–layer templated nano–ITO film was soaked for 24 hours in a 10^{-4} M methanolic solution of 1. The cyclic voltammograms (CVs) recorded on the resulting functionalized substrate as a working electrode displayed a quasi–reversible system assigned to the Ru^{III/II} couple, at E_{1/2} = + 1.3 V vs NHE (Figure 5). The linear variation of the cathodic and anodic peak current densities with scan rates ranging from 10 to 100 mV.s^{-1} unambiguously confirms the presence of the ruthenium complex at the surface of the electrode. For comparison, the CVs of a similar redox–active species, the complex \([\text{Ru(bpy)}_3]^{2+}\), recorded in solution on a non–functionalized 10–layer templated nano–ITO electrode have been recorded. In that case, the peak current densities varied linearly with the square root of the scan rate as expected for a diffusion controlled process (Figure S5). The grafting density was determined through the integration of the peak area and conversion of the resulting charge to a number of moles per square centimeters. With a 10–layer templated nano–ITO film, grafting densities of 3.5 10^{-9} mol.cm^{-2} were obtained. Increasing the soaking time from 24 hours to 72 hours did not increase the grafting density. A quasi–linear variation of the grafting density as a function of the film thickness was observed (Figure S6), in good agreement with the increase of the active surface due to the 3D network. For comparison, the same procedure was applied to commercially available planar ITO electrodes. Cyclic voltammetry analysis of this modified electrode (Figure S7) confirmed the presence of surface–bound ruthenium complexes, however with a grafting density of only 3.10^{-11} mol.cm^{-2}. The design of a multi–layered templated nano–ITO electrode displaying a three dimensional network thus resulted in a 100-fold increase of the grafting density of 1.

The amount of ruthenium complex grafted on a 10–layer templated nano–ITO film was also independently determined by UV–visible absorption spectroscopy. The spectrum of 1-sensitized templated nano–ITO displays a metal–to–ligand charge transfer absorption band located at 450 nm and characteristic of complex 1 (Figure S8). The absorbance value allows to estimate a grafting density of 6 10^{-9} mol.cm^{-2}. Comparison with the grafting density value obtained by cyclic voltammetry (see above) indicates that roughly 60 % of the grafted molecules were electroactive. This value is significantly lower than the 90 % reported by T. J. Meyer and coll. for thicker (2.5 μm) non templated nano–ITO films prepared by spin–coating of ITO nanoparticles onto planar ITO.24 However, the general difficulty to obtain a good signal–to–noise ratio yields some inconsistency in the determination of surface coverages by UV–vis absorption spectroscopy, as already underlined by Limoges and coll.21 Thus, the grafting densities discussed in the following refer to electrochemical measurements and thus to electroactive grafted complex 1.

A transparent 10–layer ITO film called dense nano–ITO was also prepared by a similar sol–gel process, however in the absence of any PIB–b–PEO template (see Figure 1 and Figure S9). We first verified that the film exhibited the bixbyite structure (not shown). The film was about 280 nm thick for 10 layers and found to contain micropores, due to the contact between the ITO nanoparticles (Figure S10). After film sensitization by 1, a grafting density
of $1.3 \times 10^{-9}$ mol.cm$^{-2}$ was determined from the CVs analysis (Figure S11), thus a value three times lower than the one obtained with the 10–layer templated nano–ITO. This difference can be explained by the absence of mesoporosity in the dense nano–ITO (see the FE-SEM characterization in Figure 1). This result highlights the role played by the 3–D network in the optimization of the grafting density of a functional molecule.

**H$_2$–treated templated nano–ITO films**

It is commonly observed that the electrical conductivity of TCO films can be increased by thermal treatment under a reducing atmosphere. In–situ electrical conductivity measurements were performed at a constant temperature of 200°C, under a 5% H$_2$/Ar atmosphere, on a 10–layer templated nano–ITO film. A slight increase of the conductivity value, from 130 S.cm$^{-1}$ to ~160 S.cm$^{-1}$, was observed over 30 min (Figure S12). After cooling down the film to 25°C under the same reducing atmosphere, the conductivity of the resulting H$_2$–treated templated nano-ITO film is superior to its initial one (95 S.cm$^{-1}$ versus 40 S.cm$^{-1}$ at 25°C). The optical transmission of the film was found to be unchanged.

Scanning electron microscopy (SEM) studies confirmed that the H$_2$–treated templated nano-ITO films remain homogeneous and that the aperiodic pore structure of the native nanostructured film (Figure 6) is not changed. By contrast with other reported preparations of nanostructured ITO films for which the reductive treatment was required for electrical conductivity of the films, its benefit in the present case – a two-fold increase of the electrical conductivity – is moderate. This is due to the fact that the electrical conductivity was already quite high at the end of the synthesis. The thermal treatment at 450°C for one hour thus appears sufficient to establish a well–connected ITO network, with a good particle-particle contact between the ITO nanocrystals, as observed by scanning electron microscopy (Figures 6a, 6b).

For a given thickness (see Table 1), the capacitive current of a H$_2$–treated templated nano–ITO electrode (Figure S13) is slightly higher than in the absence of the reductive treatment (58 vs 39 μA.cm$^{-2}$ at 1.3 V vs NHE and at a scan rate of 100 mV.s$^{-1}$), in agreement with its improved electrical conductivity. Grafting of redox–active complex 1 (grafting density of $4.4 \times 10^{-9}$ mol.cm$^{-2}$) resulted in current densities as high as 287 μA.cm$^{-2}$ (capacitive current subtracted; Figure S14), to be compared with 192 μA.cm$^{-2}$ the value obtained with films that were not submitted to the reductive treatment (Figure 5).

**Electrochemical features of the various ITO films described in this study**

Characteristic values for the various films are summarized in Table 1. The peak–to–peak potential difference ($\Delta$E) between the cathodic and anodic waves of grafted complex 1 have been measured, at various scan rates (Figure S15), for the three following ITO films: a 10–layer dense nano–ITO and a 10–layer templated nano–ITO with or without H$_2$ treatment. The $\Delta$E value indeed allows for a qualitative comparison of the efficiency of the heterogeneous electron transfer between 1 and the different ITO films. The $\Delta$E value for a commercially available planar ITO electrode is also reported for comparison. As expected, a quasi-ideal response was obtained for the latter, with $\Delta$E being roughly equal to zero and not varying with the scan rate. For all the films reported here, the $\Delta$E values were lower than 200 mV at the highest scan rate (Table 1). Increasing the scan rate from 10 to 100 mV.s$^{-1}$ indeed resulted in an increase of $\Delta$E from 40 mV to 116 mV on the 10–layer dense nano–ITO, and from 72 mV to 189 mV on the 10–layer templated nano-ITO, respectively. The heat treatment under reducing conditions allowed for a slight improvement of the reversibility of the process. This quasi–reversibility of the redox process indicates that the heterogeneous electron transfer from the ITO framework to the redox probe is not rate–limiting.
Photo–electrochemical measurements

We investigated the photoelectrochemical properties of a 10-layer templated nano-ITO substrate functionalized by the photoactive complex 1 in the presence of [Co(NH$_3$)$_5$Cl]Cl$_2$ as an electron acceptor. At 0 V vs Ag/AgCl in a phosphate–buffered aqueous solution, visible–light irradiation led to the establishment of a photocurrent with a photocurrent density of 50 μA.cm$^{-2}$ (Figure 7). This current enhancement under light irradiation is attributed to the establishment of a photo–induced electron transfer from the photo–excited ruthenium dye to the Co(III) acceptor in solution, the Ru(II) ground state of the dye being subsequently regenerated by electron transfer from the ITO electrode. No photocurrent was observed either in the absence of the acceptor in solution or in the absence of 1 on the nanostructured ITO surface. By comparison, when a planar commercial ITO substrate functionalized with 1 was employed in place of the templated nano–ITO one under the same experimental conditions, a 150–fold lower photocurrent (330 nA.cm$^{-2}$) was measured (Figure 7). The establishment of a photocurrent density as high as 50 μA.cm$^{-2}$ is quite remarkable by comparison with values reported in the literature for related ruthenium–based photocathodes based on TCO or nanostructured carbon-based materials.$^{30-32}$ That nicely shows the advantage of such novel high surface transparent conducting oxides as the 3D networked templated nano–ITO films described in this study, in view of the development of efficient photo–electrocatalytic devices. This has also been recently demonstrated for quantum dot–sensitized mesoporous TiO$_2$ films prepared by a similar multi-layered process.$^{33}$

CONCLUSION

We have successfully employed a multi-layered template–directed sol–gel technique for the synthesis of mesoporous nanostructured ITO films with tunable thickness. These films are constituted of well-defined ITO nanoparticles, with small size of 20 nm and a narrow size distribution, organized in a 3-D interconnected network of pores. These films, available at a low cost and through a highly controllable process, display the qualities required for photoelectrochemical applications: optical transparency in the visible region, high conductivity, and high surface area to reach high grafting densities of electro- and/or photoactive components. As a proof of concept, the covalent grafting of a redox–active ruthenium-based dye was successfully achieved and cathodic photocurrents were established under visible–light irradiation in the presence of an electron mediator in solution. Templated nano–ITO film thus represents a promising electrode material for the development of new technologies in the field of artificial photosynthesis and water splitting.

EXPERIMENTAL SECTION

Chemicals

Indium acetylacetonate (In(acac)$_3$; 99.99 % purity), tin tetrachloride (99 %), triflic acid and solvents were purchased from Sigma Aldrich, polyisobutylene-polyethyleneoxide (PIB-b-PEO ; reference P4973-ibEO: MWPIB = 7000 g.mol$^{-1}$, MWPEO = 8500 g.mol$^{-1}$) was purchased from Polymer source. All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification. The ruthenium complex [Ru(bpy)$_2$(4,4′-(CH$_2$PO$_3$H$_2$)$_2$-bpy)]Cl$_2$ 1 was prepared according to a described procedure.$^{27}$ Glass substrates were purchased from TechLab (ref: T29201318R). Planar ITO substrates were purchased from SOLEMS and sequentially cleaned by sonicating in acetone, ethanol and deionized water before use.
Synthesis of templated nano–ITO and dense nano–ITO films

Preparation of the sol—0.882 g of In(acac)₃ was dissolved in a mixture of 2.5 g MeOH and 2.5 g acetone at 70 °C. After cooling for several minutes, 0.06 g of SnCl₄ was added dropwise. To obtain the desirable solution, 1.4 g of PIB–b–PEO block-co–polymer (template) was added and dissolved by careful heating in oven at 70 °C for 1 hour. The resulting clear solution was dip–coated at a low relative humidity (≤20%) and at ambient temperature.

Monolayer synthesis—All films were prepared by using a homemade dip–coater. In this setup, the substrate is fixed by a clamp at the top of a transparent plastic room with the following dimensions: 20 cm width, 35 cm length and 50 cm height. The glass substrate is moved down into the ITO precursor solution by a motor equipped with a withdrawing–speed controller. The glass substrate was dipped into the precursor solutions and then removed at 2.5 mm/s; the films were placed for 60 min in a furnace preheated 450°C in air to induce crystallization.

Multi–layer synthesis—the glass substrate was dipped into the sol solution and removed at 2.5 mm/s and then the film is placed 5 min at 450°C to stabilize the hybrid organic–inorganic layer. After cooling, dip–coating and flash thermal treatments were repeated several times to prepare samples with desirable thickness. Then, the multilayer films were treated at 450 °C for 60 min.

Dense nano–ITO films were synthesized by the same procedure, but from a sol deprived from the block–co–polymer.

H₂–treated templated nano–ITO films were obtained by annealing under reducing atmosphere (5% H₂ in Ar) at 200°C the corresponding templated nano–ITO substrates.

Films sensitization by covalent grafting of 1

The variously prepared ITO electrodes were soaked into a 10⁻⁴ M methanolic solution of complex 1 for 24 hours on an orbital stirring table. The electrodes were sequentially rinsed with methanol, acetone and deionized water and dried in air before electrochemical characterization.

Characterization

The microstructure of the films obtained after different heat treatments were observed by Field Emission (FE) Gun Scanning Electron Microscopy (FE-SEM, Hitachi) and by Transmission Electron Microscopy (TEM, Hitachi). For TEM analyses, the films were scratched from the silica substrates and the resulting powders were deposited onto coated carbon–copper grids. Energy Dispersive X–ray cartographies (Oxford X-Max 50 mm²) were measured on templated-nano ITO films.

The structure of the mesoporous ITO films was measured using a prototype X-ray diffractometer equipped with a curved position sensitive detector (120°) by Inel. A fixed-incidence monochromatic CoKα impinging parallel beam is obtained by reflection on a flat Ge(111) crystal. Cobalt radiation was used instead of more usual copper radiation to avoid sample fluorescence. The beam cross section was 0.05 × 6 mm², producing a rectangular 3 × 6 mm² beam footprint on the sample at fixed incidence 1°. At this incidence, the attenuation length inside the hematite sample is about 0.7 μm. The grazing incidence diffraction patterns (0° < 2θ < 120°, Δ2θ = 0.015°, α =1) were refined using the Rietveld software XND. The broadening components related to finite crystallite size and microstrain were determined.
after taking into account the specific corrections for the instrumental broadening related to the grazing incidence setup.

Small angle X–ray scattering was performed using a Bruker D8 Advance X–ray diffractometer equipped with a Gobel mirror producing a parallel Cu Kalphabeam (40 kV, 40 mA). The beam cross section was 0.1 × 6 mm², producing an almost perfectly square (6 × 6 mm²) beam footprint on the sample at incidence 1°. The diffracted signal was measured using a Vantec position sensitive detector. The grazing incidence diffraction patterns (1° < 2θ < 20 × 10°, α = 1°, 3718 step scans corresponding to an average step size of 0.0349°).

XPS spectra were recorded with a Perkin–Elmer spectrometer operated at 350 W using standard Al radiation. The pressure was below 5 × 10⁻⁸ Pa. the spectrometer was calibrated by assuming the binding energy of the Au4f⁷/₂ line to be at 83.4 eV relative to the Fermi level. The reported BES were corrected to account for the charging effects by assigning the BE value of 284.6 eV to the C1s line of carbon; carbon was present as contamination in the outer layers. Mesoporous films were introduced into the XPS chamber using a fast entry lock system. The peaks were assigner using the NIST XPS database.

**Electrochemical and photo-electrochemical measurements**

Impedance spectroscopy analyses were performed on thin films deposited on glass substrate at ambient and 200°C under air and reducing atmosphere. The resistance of the films was estimated by using homemade cells, where 2 gold wires were applied at the surface of the films. Two Pt electrodes of roughly 200 nm thick, 1 cm length and 1 mm width were sputtered onto the mesoporous films. The distance between both stripes was 7 mm. The sample was then mounted in a sample holder where two gold wires with 0.25 mm of diameter were applied with a mechanical low pressure (Spring system) onto the Pt stripes, thus ensuring electrical contact. The sample holder was then placed in a sealed furnace where temperature as well as gas composition and flow rate are controlled. An impedance analyzer, Solartron 1260 was used to evaluate the evolution of the resistance as a function of the experimental conditions (temperature and atmosphere). Primarily, linearity of the system was checked by modifying AC amplitude from 50 to 350 mV. A 100 mV signal amplitude was applied, without dc polarization.

Electrochemical measurements were performed using a Bio–Logic SP300 bi-potentiostat controlled via the EC-Lab® V9 software. The cyclic voltammetry experiments were carried out in a three-electrode electrochemical cell using the variously prepared ITO films (on glass substrate) as working electrodes. A platinum-grid placed in a separate compartment connected by a glass-frit and filled with the electrolytic solution was used as auxiliary electrode and the reference electrode was based on the Ag/AgCl/KCl 3M couple (Ag/AgCl). A 1 M aqueous solution of triflic acid was used as the electrolyte. External calibration of the reference electrode was performed with the ferricyanide/ferrocyanide redox couple.

Photocurrent measurements were performed in a specific cell with a flat glass window and three compartments. A three-electrode configuration has been systematically used. The ITO electrode has been connected to a brass wire thanks to a silver conducting paint (Radiospare) and the connection covered by electrolytic tape (polyimide, Hi-bond HB830). This sample is used as the working electrode. A Pt wire counter-electrode and an Ag/AgCl/KCl 3 mol.L⁻¹ (hereafter denoted Ag/AgCl, E⁰ (Ag/AgCl) = + 0.21 V vs NHE) have been used as counter and reference electrodes, respectively, and placed in distinct compartments separated from the main compartment by glass frits. The distances between the electrodes are small, and ohmic losses can be neglected. We used potassium phosphate buffer (0.1 mol.L⁻¹, pH = 7) as electrolyte and [Co(NH₃)₅Cl]Cl₂ (20 mM) as the electron acceptor in solution. The Ag/ AgCl reference electrode has been calibrated in the above described experimental setup.
using the \([\text{Fe(CN)}_6]^{3−}/[\text{Fe(CN)}_6]^{4−}\) couple in phosphate buffer (KPi, 0.1 M, pH 7). \((E(\text{[Fe(CN)}_6]^{3−}/[\text{Fe(CN)}_6]^{4−}) = +0.20 \text{ V vs } \text{Ag/AgCl in KPi buffer at pH = 7}).^{34}\)

The samples were illuminated with a 300 W Xenon lamp (Oriel, ozone free) operated at 280 W coupled to a water-filled Spectra-Physics 6123NS liquid filter for elimination of IR radiation, a Spectra-Physics 59472 UV cut-off filter (\(\lambda > 400 \text{ nm})\). Irradiance at the substrate surface was measured to 600 mW/cm\(^2\) (~6 sun) thanks to a Coherent PowerMax-USB PM150-50C Power Sensor.

**Supplementary Material**

Refer to Web version on PubMed Central for supplementary material.

**Acknowledgments**

This work was supported by the French National Research Agency (ANR) through Labex program (ARCANE, ANR-11-LABX-0003-01) and Carnot funding (Institut Leti) and by the European Research Council under the European Union’s Seventh Framework Programme (FP/2007-2013)/ERC Grant Agreement n°. 306398. W.H. acknowledges the Collège de France for his financial support. We thank Bernard Sartor and Dr Vincent Fourmond for the design and construction of the three-compartment photoelectrochemical cell used in this study.

**REFERENCES**


Figure 1.
Schematic representation of the multi-layered sol-gel process described in this study together with FE-SEM images (top-down views) of the resulting dense nano-ITO and templated nano-ITO films.
Figure 2.
FE–SEM images of multi-layered templated nano–ITO films heat–treated at 450°C for 1 h under air: a) one layer, b) two layers, c) four layers, d) five layers, e) six layers, f) ten layers (left side); Variation of the thickness as a function of the number of layers (bottom left); Transmittance for the 10–layers templated nano–ITO film heat–treated at 450°C for 1 h under air (bottom right).
Figure 3.
Structure and Microstructure of templated nano-ITO nanostructured films heat-treated in air at various temperatures for 1 hour: X–Ray diffraction patterns of nanostructured ITO films heat-treated at 300°C, 450°C and 550°C (left side), Transmission electron micrograph of air-treated nanostructured ITO films at low magnification (right) and high magnification (inset).
Figure 4.
Evolution of the electrical conductivity as a function of the thickness for templated nano-ITO films heat–treated at 450°C for 1 hour in air.
Figure 5.
Top Cyclic voltammograms of complex 1 adsorbed on templated nano–ITO (10 layers, treated at 450°C for 1 hour in air; electrode surface: 1 cm²), recorded in 0.1M aqueous HOTf at scan rates varying from 10 to 100 mV.s⁻¹. Bottom Linear evolution with the scan rate of the cathodic and anodic peak currents (capacitive current substracted; see Fig. S11) related to the RuIII/RuII couple.
Figure 6.
FE–SEM images of 10–layer templated nano–ITO films a) heat–treated at 450°C in air for 1 h and b) heat–treated at 450°C in air for 1 h then at 200°C under H$_2$ for 40 min.
Figure 7.
Top Cathodic photocurrent measurements recorded on a 10-layer templated nano-ITO electrode functionalized with I (electrode surface: 1 cm²) in [Co(NH₃)₅Cl]Cl₂ (20 mM) / KPi buffer (0.1 M) with 0 V vs. Ag/AgCl applied potential. Bottom Cathodic photocurrent measurements recorded on a planar ITO electrode functionalized with I (electrode surface: 1 cm²) in 20 mM [Co(NH₃)₅Cl]Cl₂ / 0.1 M phosphate buffer solution at 20°C with 0V vs. Ag/AgCl applied potential.
### Table 1

Electrochemical features of variously prepared 10–layer ITO films and of planar ITO, determined from cyclic voltammetry measurements recorded at 100 mV.s⁻¹.

<table>
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<tr>
<th>ITO film preparation</th>
<th>Film thickness (nm)</th>
<th>Current density (^a)</th>
<th>Capacitive current density (^b)</th>
<th>Grafting density (^c)</th>
<th>(\Delta E_{\text{peak-to-peak}}) (^d)</th>
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<tr>
<td>H₂–treated templated nano–ITO</td>
<td>~ 420</td>
<td>287</td>
<td>58</td>
<td>4.4 (10^{-9})</td>
<td>172</td>
</tr>
<tr>
<td>Templated nano–ITO</td>
<td>~ 470</td>
<td>192</td>
<td>39</td>
<td>3.5 (10^{-9})</td>
<td>189</td>
</tr>
<tr>
<td>Dense nano–ITO</td>
<td>~ 280</td>
<td>88</td>
<td>12</td>
<td>1.3 (10^{-9})</td>
<td>116</td>
</tr>
<tr>
<td>Planar ITO</td>
<td>~ 100</td>
<td>1.9</td>
<td>—</td>
<td>3 (10^{-11})</td>
<td>(\approx) 0</td>
</tr>
</tbody>
</table>

\(^a\) in \(\mu\)A.cm\(^−2\), measured for the Ru\(^{III}/Ru^{II}\) oxidative process;

\(^b\) in \(\mu\)A.cm\(^−2\), measured on the corresponding non–functionalized electrodes;

\(^c\) in mol.cm\(^−2\), determined by integration of the Ru\(^{III}/Ru^{II}\) oxidation wave and conversion of the resulting charge to a number of moles per square centimetres;

\(^d\) in mV, between the oxidation and the reduction peak of complex 1.