# Electrochemical Properties of Transparent Conducting Films of Tantalum-Doped Titanium Dioxide

Hana Krysova[a], Piero Mazzolini[b,c], Carlo S. Casari[b,c], Valeria Russo[b], Andrea Li Bassi[b,c], Ladislav Kavan[a,*]

[a] J. Heyrovsky Institute of Physical Chemistry ASCR, v.v.i., Dolejskova 2155/3, 182 23 Prague 8, Czech Republic
[b] Department of Energy, Politecnico di Milano, via Ponzio 34/3, Milano, Italy
[c] Center for Nano Science and Technology, IIT@PoliMI, Via Pascoli 70/3, I-20133 Milano, Italy

A R T I C L E   I N F O

A B S T R A C T

Highly conducting, optically transparent Ta-doped $TiO_2$ (anatase) thin films are grown on ordinary soda-lime glass substrates by pulsed-laser deposition. They exhibit quasi-reversible cyclic voltammograms of $Fe(CN)_6^{3-/4-}$ and dimethylviologen redox couples, mimicking the electrochemical activity of F-doped $SnO_2$ (FTO). Hence, our Ta-doped titania films can prospectively replace FTO, e.g. in homo-junction dye-sensitized and perovskite solar cells. However, these films are idle for the $Ru(bpy)_3^{2+}$ oxidation, which is attributed to the space-charge barrier. The flatband potential of our Ta-doped $TiO_2$ is comparable to that of an undoped reference film and/or of the pristine anatase single-crystal electrode. Our films show photoelectrochemical activity upon irradiation with UV light at potentials positive to flatband. The UV-photocurrents decrease proportionally to the increase of Ta-content. The Li-insertion ability analogously decreases with increasing Ta-content. This is attributed to the positive charge of $Ta^{5+}$ cations which occupy the $Ti^{4+}$ sites in anatase lattice and thus impede the $Li^+$-transport. Consistent with the quasi-metallic nature of our films, the Li-extraction peak in cyclic voltammograms shows no cut at larger potentials.

## 1. INTRODUCTION

Transparent conducting oxides, such as indium-tin oxide (ITO) and F-doped $SnO_2$ (FTO) are widely used in electrochemistry, and in related applications like in dye-sensitized solar cell (DSC) [1,2] and photoelectrochemical water splitting for solar fuel generation [3]. However, there is a strong demand for their replacement by cheaper materials [4]. Other issues specific for DSC applications are the thermal instability of ITO [5] and the formation of a Schottky barrier at the heterojunction photoanode interface of $TiO_2$ with both ITO [5] and FTO [6,7]. It stems from the fact that the Fermi level of $TiO_2$ is higher than that of ITO/FTO prior to contact of the materials. This is particularly important when a dense titania layer [6,7] is deposited on top of FTO to prevent recombination [8,9]. These layers are prepared by various techniques [6–10], including electrochemical methods [8,10]. The control of energy level alignment throughout the interfaces is important for photovoltaic devices such as solid state DSCs and perovskite solar cells [11]. For instance, a homo-junction $FTO/SnO_2$ electrode [12] enables barrier-free alignment with certain perovskites [13]. However, a barrier-free titania homo-junction electrode, employing solely doped $TiO_2$ as an electron collecting terminal, was not yet reported, to the best of our knowledge.

Nb-doped [7] and Ta-doped [14] dense $TiO_2$ deposited on top of FTO improve the performance of DSC due to enhanced charge collection efficiency. Similar improvement was reported for Ta-doped $TiO_2$ which was deposited as the last over-layer on top of mesoporous $TiO_2$ [15]. Ta-doped $TiO_2$ nanotubes [16] or other Ta-doped nanostructures [17–19] were used as the photoanode material, too. Interestingly, even pure $Ta_2O_5$ (band gap of ca. 4 eV) is applicable as a DSC photoanode, but with very low efficiency. Pure $Ta_2O_5$ has a lower conduction band (CB) edge than $TiO_2$ (ca. −4.6 eV/vacuum) which obviously decreases the attainable voltage of DSC [20]. On the other hand, a composite $Ta_2O_5/TiO_2$ behaved considerably better in DSCs [19]. Ta-doped $TiO_2$ nanotubes also showed improved water splitting ability as compared to pure $TiO_2$ [21].

A purely titania-based 'transparent metal' with resistivity as low as $(2-3)\cdot10^{-4}\,\Omega\cdot cm$ was demonstrated through Nb-doping

* Corresponding author.
   E-mail address: ladislav.kavan@jh-inst.cas.cz (L. Kavan).

[22,23] and Ta-doping [24]. These doped titania layers are degenerate n-type semiconductors thanks to an efficient electron release from the pentavalent dopant [23,25]. The $Ta^{5+}$ ions occupy $Ti^{4+}$ sites in the anatase lattice and sometimes also concomitant doping by $Ti^{3+}$ and $Ta^{5+}$ was observed [26]. Ta-doping is favored over Nb-doping by higher Ta solubility in $TiO_2$, higher electron mobility and by retardation of anatase/rutile transformation [26]. Compared to ITO, the doped $TiO_2$ provides higher refractive index, higher transmittance in the IR-region, and good stability in reducing atmosphere [23]. Highly-conductive titania can be prepared through sputtering or pulsed-laser deposition (PLD) [23,27–29]. Sporadic reports about other fabrication techniques, such as chemical vapor deposition, show that these Ta-doped $TiO_2$ films are less conducting ($\approx 10^{-3}\,\Omega \cdot cm$) [26]. Some of us have recently optimized PLD deposition of polycrystalline Ta-doped $TiO_2$ on glass substrates, and investigated the role of the deposition conditions and annealing atmosphere [27,28] on the electrical, optical [28] and vibrational [29] properties. In particular, the obtained carrier density is influenced not only by the dopant (Ta) content, but also by the presence of intrinsic defects in the crystalline structure. This is controlled in a complex way by the oxygen partial pressure during deposition and by the vacuum-annealing conditions. The explanation is still debated [27–29] and involves the formation of 'electron killer' defects such as Ti vacancies or O interstitials.

As mentioned above, the replacement of FTO by metal-like conducting $TiO_2$ for a homo-junction electron-collector in DSC (i.e. the 'all-$TiO_2$ photoanode') is a straightforward challenge. The first step in this effort is obviously the exploration of electrochemical properties of this material, which is the central motivation of our study. We are not aware of any similar work on electrochemical properties of Ta-doped $TiO_2$ electrodes. To fill the gap, we characterize here the electrochemical performance of Ta-doped $TiO_2$ films obtained by PLD, focusing on voltammetric response of model redox couples, electrochemical impedance spectroscopy, photoelectrochemistry under band-gap excitation and the Li-insertion electrochemistry.

## 2. EXPERIMENTAL SECTION

### 2.1. Preparation of electrodes

$TiO_2$ thin films with the nominal doping amount (Ta content) 1, 5, and 10 atomic % were deposited by PLD on soda-lime glass substrates at room temperature using a lamp-pumped Q-switched Nd:YAG pulsed laser (fourth harmonic, $\lambda = 266$ nm, repetition rate 10 Hz, pulse duration $\approx 6$ ns, target-to-substrate distance = 50 mm). Films with about 1% Ta content were obtained by uniform ablation of $TiO_2$ target (powder purity 99.9%) partially covered with Ta metallic wires, so that a fraction of the surface corresponding to roughly 1% Ta with respect to Ti is covered. Pure $TiO_2$ films were grown starting from the same ceramic target, while Ta-doped films with 5 and 10% Ta content were obtained by ablating sintered $Ta_2O_5$:$TiO_2$ targets (molar ratios of 0.025:0.975 and 0.05:0.95 corresponding to 5% and 10% nominal Ta content respectively, powder purity 99.99%). Different oxygen partial pressures (in the range of 1–2 Pa) have been used to tune the film properties, as discussed in [28]. The pulsed laser energy density on the target was typically 1.15 J/$cm^2$. The PLD process was always followed by ex-situ annealing performed in air or in vacuum ($p < 4 \times 10^{-5}$ Pa) at 550 °C with a dwell time of 60 min in a homemade heating system and heating/cooling ramp of 10 °C/min.

Each electrode was prepared from a sample layer with dimensions approx. $5 \times 10$ $mm^2$. Contact was made by Ga-In alloy to Cu-wire and protected by TorrSeal epoxy. In some cases, the contact was made simply by Ag-epoxy or by ultrasonic solder (Cerasolazer CS186). The exposed area was defined by TorrSeal encapsulation between 0.16 to 0.36 $cm^2$.

### 2.2. Characterization of electrodes

Film thickness was evaluated by scanning electron microscopy (SEM, Zeiss SUPRA 40 field-emission microscope) on samples grown on silicon. Layer thickness of most samples was 150 nm, sometimes also larger thicknesses (290 nm and 500 nm) were grown (see Fig. S1 in Supporting Info). The crystalline structure and its dependence on the deposition/annealing conditions have been investigated in previous works [27–29] by a combination of X-ray diffraction and Raman spectroscopy; in this work we checked the crystalline phase by micro-Raman measurements (Renishaw In Via spectrometer with $Ar^+$ laser, $\lambda = 514.5$ nm, power on sample 1 mW). Example spectrum is shown in Fig. S2 (Supporting Info). The electrical characterization was performed in the 4-point probe configuration with a Keithley K2400 Source/Measure Unit as a current generator (from 100 nA to 10 mA), an Agilent 34970A voltage meter, and a 0.57 T Ecopia permanent magnet for Hall measurements.

Electrochemical experiments were carried out in a one-compartment cell using Autolab PGstat-30 (Metrohm) with the FRA module. The reference electrode was Ag/AgCl (sat. KCl) for experiments in aqueous electrolyte solutions, and Li-metal for aprotic media. The Li insertion experiments were carried in 1 M $LiClO_4$ in (1/1 w/w) mixture of ethylene carbonate (EC) + dimethoxy ethane (DME) electrolyte solution. In this case, the reference and counter electrodes were from Li metal, hence, potentials were quoted against the $Li/Li^+$ reference electrode in this medium. The electrolyte solutions were purged with argon, and the measurement was carried out in a glove box under Ar atmosphere. A commercial FTO glass, TEC 15 from Libbey-Owens-Ford, was used as a reference material. Its sheet resistance was 15 $\Omega$/sq (declared by the manufacturer; own measurement provided 13.4 $\Omega$/sq), visible-light transmittance 82–85%, layer thickness ca. 500 nm. Electrolytes, solvents and redox-active molecules were of the standard quality (p.a. or electrochemical grade) purchased from Aldrich or Merck and used as received.

Impedance spectra were measured in the frequency range from 100 kHz to 0.1 Hz at varying potentials, which were scanned from positive to negative values and back (typically between 1.0 V to −0.7 V vs. Ag/AgCl in 0.5 M KCl, pH 2.5). The counter electrode was a platinum mesh. Impedance spectra were evaluated using Zview (Scribner) software.

Photoelectrochemical measurements were performed in an Ar-saturated 0.1 M $Na_2SO_4$ (pH 10) solution. The counter electrode was a platinum rod and the reference electrode was Ag/AgCl (sat. KCl). The photoelectrochemical cell was placed in a dark room and controlled by a potentiostat (Autolab PGstat 101, Metrohm with NOVA software). The working electrode was illuminated through fused silica optical window by a Hg lamp (Oriel); the spectral range was 320–380 nm, defined by optical filters.

## 3. RESULTS AND DISCUSSION

### 3.1. Structural and electrical properties

Table 1 summarizes the used preparative conditions and the measured values of sheet resistance ($R_{sheet}$), resistivity ($\rho$) and layer thickness. Raman spectra of as-deposited (non-annealed) films show broad bands typical of amorphous/highly disordered titanium oxide corresponding to high resistivity values of about 10 $\Omega \cdot cm$. Five distinct peaks at about 144, 197, 399, 519, 639 $cm^{-1}$, related to the Raman modes of anatase [30], are found in all heat-treated films, regardless of the annealing atmosphere (Fig. S2,