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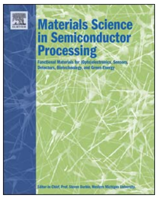

Anions and cations distribution in M^{5+}/N^{3-} co-alloyed TiO_2 nanotubular structures for photo-electrochemical water splitting

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ABSTRACT

Co-alloyed (M,N) titanium dioxide nanotubes were synthesized by a simple anodization process with M-Ti alloys (M = Ta or Nb), followed by a thermal treatment in ammonia to introduce nitrogen in those nanostructure. The photo-electrochemical performances of these co-alloyed samples was compared with the ones of N doped and undoped TiO_2 NTs. Different conditions of thermal treatment under ammonia were studied in order to control the amount of nitrogen introduced in the TiO_2 structure and tend to achieve a balance of charges between Ta^{5+}/Nb^{5+} cations and N^{3-} anions. The structure and composition of these materials were characterized by X-Ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM) EDX mapping. This combination of methods confirm the successful introduction of doping atoms, and allowed us to estimate the amount of M^{5+} cations and N^{3-} anions in the TiO_2 NTs. TEM EDX mapping indicates a heterogeneous distribution of Nb^{5+} and Ta^{5+} cations in the nanotubes that can originate from the use of highly concentrated alloys. External quantum efficiency measurements were used to determine the photo-electrochemical activity of our samples in different spectral domains. A significant improvement of activity in the visible region of the solar spectra was observed for co-alloyed TiO_2 samples when compared to undoped nanotubes but also when compared to N doped TiO_2. The obtained results indicate that the parameters of the NH_3 thermal treatments should be finely controlled to improve the conversion efficiency in the visible domain for the co-alloyed samples by introducing a precise amount of N^{3-} in substitution of oxygen in the TiO_2 lattice and to avoid the damaging of the nanotubular structure.

1. Introduction

Development of new materials for solar energy conversion is an expending research area. Solar energy is an inexhaustible, decentralized natural resource and solar power reaching the earth surface is far greater than actual energy consumption [1]. Beside photovoltaic (PV) technologies, which converts solar energy to electricity, it is important to develop devices that use solar radiation to induce chemical reaction that produce energetic molecules that are storable and can be used on demand (solar fuel) [2,3]. Hydrogen is a promising storable chemical fuel, which can be implied in different processes such as electricity production in fuel cells or for chemical synthesis. Hydrogen possesses a specific energy density three times higher than methane and the product of its combustion is only water. Therefore, developing an eco-friendly and viable process to produce hydrogen is a challenge to achieve for the scientific community. One of the solar to hydrogen energy conversion process is the water splitting, which relies on the use of a semi-conductor (SC) as photo-electrode to convert photon into electron-hole pairs in charge of the reduction and oxidation of water into hydrogen and oxygen [4]. This process requires a specific semi-conductor material, which should exhibits specific properties in order to achieve efficient solar to chemical energy conversion. The SC conduction band (CB) energy must be above the hydrogen evolution reaction energy (HER) and its valence band (VB) energy must be below the oxygen evolution reaction energy (OER) in order to thermodynamically achieve the two reactions [5]. Moreover, the semi-conductor must absorb a significant part of the solar spectra and must possess good charge carriers transport properties in order to efficiently separate the photo-generated charges that must rapidly reach the sites where oxidation and reduction reactions take place.

Titanium dioxide (TiO_2) is one of the most investigated materials for photo-electrochemical water splitting. TiO_2 has a suitable energy band positions and other excellent properties such as stability against photo-corrosion, low synthesis cost, non toxicity *etc*… [6,7] To enhance its

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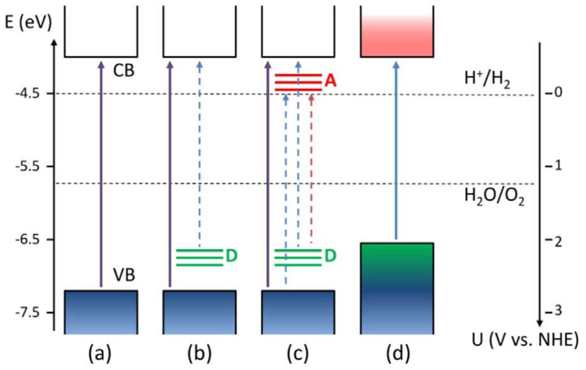

Fig. 1. Representation of electronic band structure of (a) TiO_2; (b) anion doped TiO_2; (c) co-doped TiO_2 with low concentration of dopants and (d) co-alloyed TiO_2 (high concentration of dopants) with cation states at the same energy as TiO_2 CB. The dashed lines correspond to electronic transition that will result in low mobility carriers. (Adapted from reference [18]).

reactivity and its charge transport properties, it is important to control the synthesis of TiO_2 at the nano-metric scale. For instance, 1D aligned TiO_2 nano-structures, such as nanotubes and nanorods, result in higher photo-current since this architecture allows an unidirectional path of electrons and it has few grain boundaries that act as recombination centers [8,9]. However, due to its large band gap (*i.e.* 3.0–3.2 eV), TiO_2 only harvests the UV part of the solar spectrum ($\lambda < 400$ nm; Fig. 1.a). In order to improve the light absorption properties of TiO_2, a common approach is to introduce doping heteroatom (*e.g.* C, N, Sn, Fe *etc*…) into the TiO_2 structure [10–13]. These doping methods allow a shift of the light absorption in the visible part of the solar spectrum, provided that the insertion of the heteroatoms in the TiO_2 lattice results in the introduction of energy levels into the band gap (Fig. 1.b). For instance, Yi Zhang *et al.* have studied nitrogen doping of a TiO_2 nanotubes array, which exhibit better photocurrent density under visible light when compared to undoped TiO_2 nanotubes array [12]. However, nitrogen doping also lead to a significant activity loss in the UV part, due to the presence of defects induced by the introduction of N^{3-} in the structure. These defects (e.g. oxygen vacancies) increase recombination's rate of the electron hole pairs and therefore result in a reduced overall efficiency [14,15]. Consequently, the dopant concentration in mono-doping approach should stay low to avoid excessive charge carrier recombination but this result in weak absorption and conversion of visible light.

In recent years, an innovative co-alloying approach has been proposed from first principles calculation studies to overcome the limitation of mono doping [16,17]. This strategy combines the substitution of Ti^{4+} by a transition metal cation $M^{(4+n)+}$, with the substitution of O^{2-} by an anion $A^{(2+p)-}$. Achieving co-alloyed TiO_2 material with a stoichiometric charge balance between anions $A^{(2+p)-}$ and cations $M^{(4+n)+}$, according to Eq. (1), should lead to more stable structure with fewer defects.

$$Ti^{4+}_{(1-x)}M_x^{(4+n)+}O^{2-}_{\left(2-\frac{n}{p}x\right)}A^{(2+p)-}_{\frac{n}{p}x} \tag{1}$$

Consequently a large quantity of heteroatoms can be introduced in the TiO_2 crystal structure to strongly modify the electronic band structure in order to enhance the photo-conversion properties. The hybridization between *p* and *d* orbitals of the introduced co-alloying species and the TiO_2 orbitals should form a continuum of energy that lowers the band gap and allows the generation of charge carrier with high mobility (Fig. 1.d) [18]. The band structure expected from different doping and co-alloying approaches are illustrated in Fig. 1. So far, only a few studies reported the synthesis of co-alloyed TiO_2 materials as proposed in these theoretical studies [19–22]. Furthermore, none of them achieve the stoichiometric balance of the charge defined in Eq. (1), which should lead to the ideal co-alloyed TiO_2 structure as described in a recent and clear review by Brancho & Bartlett [18]. This can be explained by the difficulty to control precisely the incorporation of anionic and cationic species in the forming TiO_2.

Our group reported for the first time, the synthesis of (Nb,N) co-doped aligned TiO_2 nanotubes (NTs) [21]. These materials, obtained by electrochemical anodization [23], exhibit a promising photo-electrochemical (PEC) activity in the visible light domain. The incorporation of niobium was done *in situ* during the anodization process and nitrogen was introduced by thermal treatment under ammonia. In the present work, we report the synthesis of co-alloyed TiO_2 M^{5+}-N^{3-} (M = Ta or Nb) NTs starting from metallic foils of titanium alloyed with tantalum or niobium. Two aspects are specifically studied: firstly, the influence of the thermal treatment procedure on the photo-electrochemical performances of the electrode. Secondly, the distribution of the incorporated Ta or Nb cations in the TiO_2 nanotubular structure is investigated by material characterization methods (XPS, DRX, MET). Finally, the performances of the co-alloyed TiO_2 photo-electrodes are compared to the one of undoped and N-doped TiO_2 and measured in a photo-electrochemical water splitting experiment.

2. Experimental

2.1. Material synthesis

Undoped (TiO_2), anionic doped (TiO_2-N) and co-alloyed (TiO_2Nb-N and TiO_2Ta-N) nanotubes were synthesized using a simple anodization process in a typical 2 electrode cell. Raw titanium foils (50 µm thick; 99.6%; MaTecK) and $5\%_{at.}$ M-Ti alloys (with M = Nb or Ta; 250 µm HMW GmbH) were used as anode (2 cm × 1.5 cm), with a platinum electrode as a cathode. Prior to experiments, Ti and alloy foils were washed by ultrasonication during 5 min in successive bath of acetone, ethanol, and water in order to remove the organic pollutants, and dried under nitrogen flow. Nanotubes growth was performed by anodization of the foils in an ethylene glycol (EG; 99.8%; Sigma-Aldrich) based electrolyte, with $0.3\%_{w/w}$ NH_4F (98%; Sigma-Aldrich) and $1\%_{v/v}$ ultrapure water. To enhance the adhesion between the nanotube film and the titanium foil, a pre-anodization step was performed during 1.5 h under 45 V voltage applied with a Bio-Logic SP300 potentiostat, at room temperature [24]. The TiO_2 nanotubes were removed from the surface, and the pre-anodized titanium foil was kept for the anodization step. Growth of the nanotubes was performed on the pre-anodized foil at 20 °C, under a 45 V applied voltage until a charge of 5 C cm^{-2} was reached. After the anodization step, samples were washed with ultrapure water and dried under a nitrogen flow.

Finally, samples were annealed in order to crystallize their structure and introduce nitrogen anion in controllable atmosphere oven (Annealsys AS1). The thermal treatment procedure is illustrated in Fig. 2. In order to remove the carbon contaminations from the organic electrolyte and ensure initial crystallization of the samples, the temperature is raised to a first plateau at 450 °C (cleaning step) and maintained for t_1 = 4 h under a 100 cm^3 min^{-1} air or nitrogen flow.

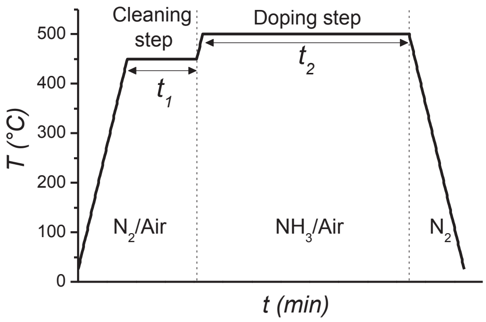

Fig. 2. Schematic of the thermal treatment applied for the TiO_2 NTs samples.