Intrinsic Au-decoration on anodic TiO₂ nanotubes grown from metastable Ti-Au sputtered alloy allows for high density co-catalyst decoration and enhanced photocatalytic H₂ evolution

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link to the published article:

<https://www.sciencedirect.com/science/article/pii/S2352940718304426>

Abstract

Recent work demonstrated that intrinsic Au nanoparticle decoration of TiO₂ nanotube arrays (NTs) can be achieved by electrochemical anodization of Ti-Au alloy substrates. However, for a Ti-Au cast produced by melt-alloying, the Au concentration cannot exceed the solubility limit of Au in Ti of 0.2 at.% - this limits the intrinsic Au nanoparticle loading on anodic TiO₂ NTs. Here we explore “metastable” Ti-Au metal substrates that are produced by Ti and Au cosputtering and we establish Au concentrations that far exceed the solubility limit in cast Ti-Au alloys. We show the use of these “metastable” Ti-Au sputtered layers for the anodic formation of TiO₂ NTs with a much higher density of Au nanoparticle loading than using classic alloys. Using optimized conditions (Au nanoparticle density) for photocatalytic H₂ production from such Au@TiO₂ platforms provides a 15 times higher photocatalytic H₂ evolution rate than the best rates achieved with conventional alloys.

Keyword: Metastable alloy, Ti-Au Alloy, Sputtering, Anodic TiO₂ nanotube, Au nanoparticle, Photocatalytic H₂ evolution

1. Introduction

Since the report of Fujishima and Honda in 1972 on photo-electrochemical water splitting using a rutile titanium dioxide single crystal [1], TiO_2 has, due to its semiconducting properties, received enormous attention and has found wide application in photocatalysis and photo-electrochemistry [2–4]. Photocatalysis to produce H_2 from aqueous media takes advantage of the fact that photo-excited electrons generated in the conduction band of TiO_2 are sufficiently energetic to reduce water to H_2 , as the CB minimum (of TiO_2) lies above the electrochemical potential of H_2 generation from water [5].

Among various TiO_2 forms explored in photocatalytic H_2 generation, one-dimensional (1D) nanostructures such as nanowires, nanorods and nanotubes have attracted significant interest in the last decades. Particularly, highly ordered and defined arrays of TiO_2 NTs, which can be fabricated by electrochemical anodization of a Ti metal substrate, not only allows for a high control over the nanotube geometry, e.g. length, diameter, wall thickness, and surface area, but also provide advantages for charge separation in photocatalytic (and photo-electrochemical) arrangements [6,7].

Nevertheless, pristine TiO_2 is not efficient in photogenerating H_2 owing to a sluggish kinetics of electron transfer to the electrolyte [8]. Reasonable photocatalytic performances can however be obtained by decorating the TiO_2 surface with a cocatalyst. Most common cocatalysts are based on noble metal nanoparticles (NPs), such as Au (or Pt, Pd). These noble metal NPs on the TiO_2 surface act as electron transfer mediator and H_2 evolution cocatalyst [8,9].

Common methods for decorating TiO_2 with noble metal NPS are chemical bath deposition [10], sputtering [11–13], and photo-deposition [14–16].

Recently, Lee et al. demonstrated that anodization of Au-Ti alloy substrates under self-organizing electrochemical conditions can lead to a highly uniform decoration of TiO_2 NTs

with Au NPs; the Au NP decoration density can be increased by increasing the Au content in the alloy [17]. However for Ti-Au alloy substrates with Au content > 0.2 at.% no defined Au-decorated TiO₂ nanotubes can be grown – this as above 0.2 at.%, the Au solubility in Ti is surpassed, and multi-phase alloys are formed. This results in a severe constraint in terms of an optimized intrinsic loading of Au NPs on TiO₂ NTs.

In this work we fabricate the substrates for anodization by Ti-Au cosputtering to form “metastable” Ti-Au alloy films that allow to homogeneously embed controllable amounts of Au much beyond the (thermodynamic) solubility limit. For comparison, we use also high Au concentration in cast alloys that, as predicted from the phase diagram, lead to the formation of multiple phases. We confirm that these cast alloy substrates do not grow ordered and defined TiO₂ NTs for Au > 0.2 at.%. On the contrary, from the metastable Ti-Au we can incorporate high doses of Au and we demonstrate that from this substrate self-ordered anodic growth of homogeneously Au-decorated TiO₂ nanotubes can be grown with a much higher Au uniform decoration density. This allows to achieve Au@TiO₂ NTs structures that shows a significant enhancement of the photocatalytic H₂ evolution rate compared with Au-TiO₂ NTs grown from Ti-Au cast alloys.

2. Material and methods

Metastable Ti-Au layers were fabricated by DC magnetron sputtering using a SP-P-US-6M-32 Createch (Germany) set-up by cosputtering of Au and Ti on SiO₂/Si substrates, and the samples were denoted as “*Mx*”, where “*M*” stands for “*metastable*” alloy, and “*x*” stands for the Au content in at.% measured by EDX. The Au concentration in the Ti-Au layers was varied from 0 at.% up to 2.1 at.%, by adjusting the deposition rate of Au (while the deposition rate of Ti was kept constant). Alternatively, reference Ti-Au cast alloys were fabricated by arc-melting and subsequent thermal annealing; the formed Ti-Au metal substrates are in a state of thermodynamic equilibrium. The nominal Au content was varied

from 0.2 to 0.9 at.%. These substrates were denoted as “Ex”, where “E” stands for “*equilibrium alloy*”, and “x” stands for the Au content in at.% measured by EDX. Please note that Au contents > 0.2 at.% exceed the Au solubility limit for single phase Ti-Au solid solutions. E0.9 and E0.2 alloys were prepared by vacuum arc melting and were heat treated for 12 hours at 50 °C above the β transition temperature to reach thermodynamically stable condition (α +Ti₃Au).

TiO₂ nanotube layers were prepared by anodization of sputtered Titanium, as well as of Ti-Au sputtered layers and Ti-Au arc melted alloys, at 60 V in an electrolyte composed of 0.1 M ammonium fluoride (NH₄F) and 5 wt.% deionized H₂O dissolved in ethylene glycol (99 vol %) as described earlier [18,19]. The anodization of Ti and Ti-Au sputtered layers was conducted to completion, that is, until, full conversion of the metal films into TiO₂ NT layers was reached.

Crystallization of the as formed TiO₂ nanotubes was carried out by annealing the samples in a rapid Thermal Annealer (Jipelec JetFirst 100) at 450°C for 1 hour in air, with a heating/cooling rate of 5°C min⁻¹.

Chemical etching for microstructure characterization was carried out as follows: the arc-melted alloys were mechanically ground and polished using in a final step MASTERMET 2 colloidal silica on a MICROCLOTH pad for 30 minutes. Kroll’s etchant (3 mL HF, 6 mL HNO₃, and 100 mL water) was prepared and used fresh. The samples were immersed in the solution for 20 seconds, and were afterwards washed in deionized water and dried with hot air. Samples’ microstructure and morphology were investigated using a microscope Nikon Eclipse LV 150 as well as scanning electron microscopy (SEM) Hitachi FE-SEM 4800. Energy-dispersive Xray spectroscopy (EDAX Genesis, fitted to the SEM chamber) was used for the chemical analysis of the anodic layers.

To evaluate the open circuit photocatalytic H₂ evolution, TiO₂ layers were irradiated under open circuit potential conditions, in an aqueous ethanol (20 vol.%) solution, under

illumination of a 365nm LED light source (120 mW cm^{-2}). A gas chromatograph (GCMS-QO2010SE, SHIMADZU) with TCD detector was used to determine the amount of generated H_2 for different TiO_2 NT samples.

3. Result and discussion

Fig. 1a-h compares SEM images of nanotubes grown from conventional cast alloys, E0.2 and E0.9, with different sputter deposited samples, M0.2 and M0.9. For the cast alloys anodization of the Ti-Au substrates with a Au content of 0.2 at.% (E0.2) leads to TiO_2 nanotube structures that are, as expected [17], decorated with clearly visible Au nanoparticles (Fig. 1a,b). The gold particles have an average size of 3.5 nm and a particle density of $1.8 \cdot 10^{-4} \text{ nm}^{-2}$ – see Fig. 1i,k (sample E0.2). This is well in line with previous work on intrinsic Au decoration of TiO_2 NTs grown from Ti-Au alloys [17].

However if tube growth is attempted from arc melted Ti-Au metal substrates with a higher Au concentration, here of 0.9 at.% (E0.9), no defined NTs can be observed (Fig. 1c). For this Au concentration, the top view and cross sectional images in Fig. 1c show a ~ 500 nm-thick undefined porous oxide layer. The bottom of such anodic layer has partially the characteristic dimples of self-ordered TiO_2 NTs. However, the rest of the layer remains unordered, short, and the anodic oxide exhibits an inhomogeneous Au decoration. In this disordered structure, gold particles appear with an irregular distribution (roughly with an average size of 4.4 nm and a density of $3 \cdot 10^{-4} \text{ nm}^{-2}$, see Fig. 1i,k).

The irregular structure shows open patches (Fig. 1c), that can be as large as several μm . These results reflect the large scale inhomogeneity present in the substrate is. As we will show below, this inhomogeneity is due to secondary phases in the substrate that prevents the growth of laterally defined and ordered NT arrays. On these alloys during anodizing, strong bubble formation (O_2) can be observed (presumably originating from Au rich locations).

The situation is different for sputtered Ti-Au layers with the same high Au contents (0.9 at.%). For metastable substrates, not only on M0.2 but also on M0.9, after anodization ordered and defined decorated TiO₂ nanotube layers can be grown. Complete anodization of 750 nm thick Ti-Au layers forms approximately 2 μm thick self-organized TiO₂ NT arrays that are homogenously decorated with Au NPs (Fig. 1d-h). Interestingly for both M0.2 and M0.9, the average particle size of Au is approximately 3.4 nm, i.e., it is virtually identical to that seen for the conventional low concentration cast alloy (3.5 nm). The main difference observed for the higher concentration M0.9 sample is a significantly higher particle density of $6.8 \cdot 10^{-4} \text{ nm}^{-2}$ (vs. $2 \cdot 10^{-4} \text{ nm}^{-2}$ for the sample M0.2) – see Fig. 1i,k.

Fig. 2a,b shows current density-time (*j-t*) characteristics that were recorded during the anodization of sputtered and arc-melted Ti-Au alloy layers with different Au concentrations. The *j-t* curve for all the sputtered samples (Ti, M0.2, and M0.9) as well as for the arc-melted alloy with low Au concentration (E0.2) show a typical profile observed for the anodic growth of TiO₂ nanotubes layers [20]. A minor difference for the Au containing alloys compared to tube growth from pure Ti is that the steady state current is slightly higher (Fig. 2b). This is likely due to facilitated O₂ evolution on the Au containing samples. In contrast to the metastable alloys, the cast alloy with a higher Au concentration than E0.9 shows a significantly higher, partially irregular, anodic current over the entire anodization time (Fig. 2a). This can be explained by the microstructure of these cast alloys; SEM analysis of the sample E0.9 reveals the presence of “craters” and cavities in the oxide film. In fact, the different anodic behavior of the Au-Ti sputtered layers from cast alloys can to a large extent be explained by their different microstructures. Fig. 2c,d show optical microscopy metallographic images of sputtered and arc-melted alloys, respectively, (with nominally identical Au content of ~ 0.9 at.%) after chemical etching. The image of substrate E0.9 (Fig. 2c) clearly shows the presence of domains of intermetallic phase (dark “flakes”) in the Ti metal matrix. While such an intermetallic phase could not be detected by XRD probably due

to the corresponding detection limits (Fig. 2e), SEM analysis confirmed its presence. In fact, two distinguishable phases can be identified: the darker areas in the SEM image (inset in Fig. 2c) represent the Ti-rich phase (intermetallic matrix), while the bright areas are the Au-rich phase.

The situation is clearly different for the sputtered Au-Ti layer as both optical and electronic microscopy reveal a homogeneous single phase structure (no intermetallic phase) in spite of a Au content (0.9 at.%) well above the solubility limit. In other words, for metal substrates with a relatively high Au content, a secondary phase-free microstructure can be obtained by Ti-Au cosputtering, and this is a key for the growth of self-organizing Au-TiO₂ nanotube arrays with higher Au NP loadings.

Additionally we explored a sample with an even higher Au content (M2). In this case, only a thin sponge is formed, i.e., the Au content is too high to allow self-organized nanotube formation.

XRD analysis of sputtered an equilibrium alloys were performed to acquire information on their crystallographic phase composition. The XRD patterns of the homogenous (E0.9) and sputtered (M0.9) alloys are shown in Fig. 2e, and are compared with that of sputtered pure Ti. Sputtered pure Ti metal layers show an hexagonal close packed (hcp) crystal α phase structure, and the position of the XRD reflections correspond well to data in the literature (JCPDS card no. 44-1294). XRD patterns of homogenous (E0.9) and sputtered (M0.9) metal alloys are similar to each other and also to the pattern of sputtered pure Ti metal.

The EDX data in Fig. 2f confirm that different Au concentrations in the sputtered metal alloy layers could be successfully obtained by controlling the Au and Ti relative deposition rates, which led to an adjustable Au content in the alloys in the 0-2 at.% range. EDX analysis of the nanotube layers (see Fig. 3a) show a drop in Au concentration with respect to that in the sputtered substrate (Fig. 2f). This result may originate on the one hand

from O incorporation during anodic oxide formation (oxidation effect), and on the other hand from some Au loss into the solution.

In order to evaluate the photocatalytic performance of the different Au decorated TiO₂ nanotubes, the structures were crystallized by annealing at 450°C (air, 1 h) [6]. Their photocatalytic H₂ evolution rate (r_{H_2}) from water-ethanol solution was measured under UV light irradiation for 4 hours (see Fig. 3b). The data in Fig. 4b shows that pristine TiO₂ nanotubes, i.e. grown from pure sputtered Ti layers (Ti), deliver a negligible H₂ generation performance. On the contrary, the H₂ evolution rate is higher for all the Au-decorated oxide layers regardless of the substrate fabrication approach (arc-melting or cosputtering).

In general, this result is ascribed to the co-catalytic activity of Au, where the Au nanoparticles can act as electron-mediators for TiO₂ CB electrons to the electrolyte and thus lead to an enhanced H₂ evolution [21,22].

For Au-decorated NT structures grown from sputtered Ti-Au layers, M0.1, M0.2 and M0.9 (i.e. Au atomic concentration of 0.1, 0.2 and 0.9, respectively), we found that an increase of the Au content in the alloy corresponds to an increase of the Au loading on the NTs, and specifically in the density of Au nanoparticles on the tube wall. Accordingly, Au-TiO₂ NTs grown from M0.9 lead to the highest r_{H_2} of 34 $\mu\text{L h}^{-1} \text{cm}^{-2}$ [17,23]. The structures grown from M2 show a much lower r_{H_2} due to presence of only a porous structures.

The photocatalytic activity of tubes grown from arc-melted substrates E0.2 is comparable to that of NTs grown from sputtered substrates M0.1 and M0.2; this is in line with their similar Au loading on the oxide NTs (see data in Fig. 3a). The situation is, however, different when the Au content in the Ti-Au metal substrate exceeds the Au solubility limit, i.e. when Au content > 0.2 at.%. When comparing the H₂ evolution rate of tubes grown from substrates M0.9 and E0.9, we found that NTs formed from metastable sputtered Ti-Au alloy are > 15 times more active than the irregular structures grown from arc-melted alloys (r_{H_2} of 34 and 2.2 $\mu\text{L h}^{-1} \text{cm}^{-2}$, respectively).

For the M0.9 sample, a remarkable stability over the testing period is observed. Over the investigated time, H₂ is produced at a steady rate, and no indication of activity fading or poisoning can be observed (Fig. 3c).

4. Conclusions

In summary we showed that Ti-Au cosputtering allows for the fabrication of secondary phase-free “metastable” Ti-Au layers that can homogeneously accommodate Au concentrations that are well above the Au solubility limit in Ti-Au solid solution (0.2 at.%). We demonstrate that for Au concentrations of Au up to ~ 1 at.% in the “metastable” Ti-Au substrates, highly-ordered, homogeneously Au-decorated TiO₂ nanotubes can be grown. This allows to reach higher Au loadings and decoration densities on the TiO₂ nanotubes, which can consequently deliver up to 15 times higher photocatalytic H₂ evolution rates compared to nanotubes grown from classic cast Ti-Au substrates. We believe that the concept outlined in the present work can be extended to a numerous of other alloying elements that could enhance specific functionalities of anodic TiO₂ NT layers towards on advanced performance in applications such as e.g. catalysis and sensing.

Acknowledgements

We would like to acknowledge the ERC, the DFG, the Erlangen DFG cluster of excellence EAM, the project EXC 315 (Bridge), and the DFG funCOS for financial support.

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Figure captions

Figure 1 – Structural characterization (a) and (b) top view and high magnification cross sectional SEM image of TiO₂ NTs grown on E0.2, respectively; Inset in (a): cross sectional SEM image of TiO₂ NTs grown on E0.2; (c) top view SEM image of TiO₂ NTs grown on E0.9; Inset in (c): cross sectional SEM image of TiO₂ NTs grown on E0.9; (d) cross sectional SEM image of M0.2 sputtered layer; (e,g) and (f,h) top view and cross high magnification sectional SEM image of TiO₂ nanotube grown on M0.2 and M0.9, respectively; Inset in (e) and (g): cross sectional SEM images of TiO₂ nanotube grown on M0.2 and M0.9 respectively; (i) average particle size and (d) particle density of different TiO₂ NTs samples.

Figure 2 – Electrochemical anodization and material characterization (a) and (b) Current-time curves of different samples during anodization; Inset in (b): cross sectional SEM images of irregular oxide grown on M2; (c) and (d) metallographic images of E0.9 and M0.9, respectively; Inset in (c) and (d): metallographic SEM images of E0.9 and M0.9, respectively; XRD diffractograms of pure titanium, E0.9 and M0.9; (f) gold content of different Ti-Au alloys.

Figure 3 – Photocatalysis performance (a) gold content, (b) hydrogen evolution rate of different TiO₂ nanotube samples; (c) hydrogen production rate from M0.9 sample over 1 day.

Figures

Figure 1

Figure 2

Figure 3