Intrinsic AuPt-alloy particles decorated on TiO₂ nanotubes provide enhanced photocatalytic degradation

Beatriz Eugenia Sanabria-Arenas,^[a,b] Anca Mazare,^[b] Jeongeun Yoo,^[b] Nhat Truong Nguyen,^[b] Seyed sina Hejazi,^[b] Haidong Bian,^[c] Maria Vittoria Diamanti,^[a] Maria Pia Pedferri^[a] and Patrik Schmuki^{*,[b,d]}

^a Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering “Giulio Natta”, Via Mancinelli 7, 20131 Milan, Italy

^b Department of Materials Science, Institute for Surface Science and Corrosion WW4-LKO, Friedrich-Alexander University of Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany

^c Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong, Kowloon, Hong Kong, China

^d Department of Chemistry, King Abdulaziz University, Jeddah, Saudi Arabia

* Corresponding author: schmuki@ww.uni-erlangen.de

Link to the published article:

<https://www.sciencedirect.com/science/article/pii/S0013468618322163>

Abstract

In this study we investigate the performance of noble metal co-catalysts on anodic TiO₂ nanotubes for the photocatalytic degradation of a model pollutant. We create the noble metal decoration (nanoparticles of Au, Pt and mixed AuPt) intrinsically and extrinsically. Intrinsic decoration is achieved using a noble metal containing titanium alloy for anodic tube growth. Extrinsic decoration is carried out by physical vapor deposition (PVD) of the same noble elements on pure titania tubes. We find AuPt intrinsic decoration to provide a significant enhancement for the photocatalytic decomposition of the model pollutant acid orange 7 (AO7) due to a synergistic effect in the formed AuPt alloy. The AuPt alloy provides a photocatalytic activity that is higher than comparable extrinsic decoration or single element (Pt or Au) intrinsic decoration.

Keywords: TiO₂ nanotubes; AuPt alloy; photocatalysis; dye degradation; nanoparticles

1. Introduction

TiO₂ nanotubes (NTs) obtained by electrochemical anodization of a metallic Ti substrate are widely studied in photocatalytic applications due to their unique combination of geometry and functionality.[1] These nanotube arrays are directly grown vertically aligned from a metallic titanium substrate, with an easy control of the geometry during the synthesis via the electrochemical parameters. The large surface area, as well as their unique electronic and ionic properties,[1,2] make nanotubular structures suitable for many photoelectrochemical or photocatalytic applications, including pollutant degradation or water purification.[3–8]

In photocatalytic applications the TiO₂ photoexcited charge carriers react with the environment without an external applied voltage (in contrast to photoelectrochemical reactions). Under aerated conditions, conduction band electrons react with O₂ to form O₂• radicals or superoxides, commonly referred to as reactive oxygen species (ROS) while valence band holes may be captured by water to form OH• radicals or may directly oxidize organic species to CO₂ and H₂O. This effect is used for the photocatalytic degradation of unwanted pollutants in air or waste water. Overall, ROS species produced at the valence band and at the conduction band may contribute to efficient destruction of organic pollutants. In order to increase the efficiency by accelerating charge transfer reaction rates of the electron transfer to the environment, co-catalysts are frequently used.[8–12] Most commonly used co-catalysts on TiO₂ are noble metals (NM) such as Au, Pt or Pd,[13–16] which can lead to a beneficial Schottky junction and thus not only to a significantly improved charge transfer but also may provide catalytic features for the reactions of electrons with electron acceptors (mainly O₂).[10,17] Other beneficial effects of some co-catalysts may be that visible light induced surface plasmon resonance effects can occur, enhancing the

light absorption region and therefore the catalytic activity in the visible light range.[8,18–20] The overall co-catalyst activity depends not only on the size and distribution of the noble metal particles but also significantly on their relative placement on the nanotubes.[8,21]

Usually, for NM@TiO₂ systems that are based on nanotubular structures, the deposition of metal particles is carried out by chemical or photoassisted chemical deposition[15,22,23] or by conventional sputtering.[23,24] Another common NM deposition approach is by sputtering-dewetting. Here first noble metal films are PVD-deposited on the top of highly organized TiO₂ nanotubes, and then these films are dewetted thermally, *i.e.* the film splits up into particles.[25–27] When sputtering noble metals on the tubular structures, the loading can be controlled, and the cluster size and distribution of the NM particles can be influenced by the dewetting conditions of the noble metal film – this allows to maximize the efficiency as co-catalyst for photocatalytic reactions.[25–28]

Another most straightforward and unique approach to dope or decorate anodic TiO₂ nanotubular structures, is the growth of the nanotube layers from Ti-alloy substrates. For Ti-alloys with non-noble metals, such as Nb, Ru or Ta, during the anodic reaction these alloyed metals are oxidized and can lead to mixed-oxide or doped nanotubes – *i.e.*, these metal ions can be incorporated in the oxide lattice.[2] In contrast, for noble metals at low amounts *e.g.* < 1% for Au or Pt in the Ti alloy,[29–31] the NM is not oxidized but instead a self-decoration of the TiO₂ nanotubes with metallic nanoparticles (NP) takes place.[29,30]

In the present work, we use both techniques: i) thin noble metal dewetted films, and ii) intrinsic noble decoration, and compare their effectiveness as photocatalyst. For intrinsic decoration we use anodic oxidation of titanium alloys that contain either

the individual noble metals such Au (Ti0.2at%Au), Pt (Ti0.2at%Pt), or both (i.e. Ti0.1at%Au0.1at%Pt), to produce uniformly and intrinsically NP decorated NTs, that can then act as co-catalyst for the degradation of a model pollutant acid orange 7 (AO7). For these tubes we find that the activity is significantly enhanced for the intrinsic decoration with bimetallic AuPt compared with the single element tubes or any extrinsically decorated NTs.

2. Materials and Methods

For the nanotube preparation, Ti sheets (99.6 purity) of 0.2 mm thickness and alloys containing 0.2 at.% Au, 0.2 at.% Pt, 0.1 at.% Au + 0.1 at.% Pt were used (purchased from HMW Hauner GmbH & Co). Prior to anodization, samples were mechanically ground with #320, 800, 1200 and 2000 grit size SiC paper. Subsequently, samples were degreased by sonication in acetone and ethanol, followed by rinsing with deionized water and drying with nitrogen gas. Anodization was performed in ethylene glycol containing 0.2 M NH_4F and 2 M H_2O at 45 V for 30 min in a two-electrode system. After anodization, samples were immersed in ethanol for 20 min, rinsed with deionized water, and dried with nitrogen. For the extrinsically decorated samples, loading of the noble metal was done using plasma sputter deposition (Leica, EM SCD500). All nanotubular samples (intrinsically and extrinsically decorated) were annealed/dewetted at 450°C for 1 hour using a Rapid Thermal Annealer with a heating and cooling rate of 30°C/min.

Current-voltage curves for the characterization of the oxygen reduction reaction were measured for AuPt alloy and bimetallic Au-Pt layer on fluorine doped tin oxide (FTO) substrates. AuPt alloy was fabricated by DC magnetron sputtering using a SP-P-US-6M-32 Createch (Germany) set-up by co-sputtering of Au and Pt on FTO substrates, Au and Pt concentration was measured by EDX. The Au concentration in

the AuPt alloy was set to 50 % by adjusting deposition power. The deposition was done for 2 min to achieve a thickness of 40 nm. Bimetallic AuPt layer was fabricated by shuttered sputtering of Pt and Au target. The electrochemical experiments were carried out in a three electrode setup (a Pt counter electrode and a Ag/AgCl in 3 M KCl reference electrode) with a scan rate of 10 mV s⁻¹ in an aqueous solution of 0.5 M KOH under continuous O₂ bubbling.

Morphological characterization was performed in a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800) and in a transmission electron microscope (30 TEM/STEM Philips) coupled with EDS. The composition and chemical state were characterized by X-ray photoelectron spectroscopy (XPS, PHI 5600, US), and peaks were shifted to C1s at 284.8 eV. For the crystallographic properties of the materials, X-ray diffraction (XRD, X'pert Philips MPD) equipped with a Panalytical X'celerator detector, with graphite monochromized Cu K_α radiation ($\lambda = 1.54056 \text{ \AA}$) was used.

Elemental depth profile analysis was performed using a Horiba Jobin-Yvon 5000 RF glow discharge optical emission spectroscopy (GDOES) instrument in an argon atmosphere of 650 Pa by applying an RF of 3000 MHz and a power of 27 W. Light emissions of characteristic wavelengths were monitored throughout the analysis with a sampling time of 0.1 s to obtain depth profiles. The signals were detected from a circular area of approximately 4 mm diameter.

The reflectance spectra of all the samples were measured by using a Lambda 950 UV-VIS spectrometer with a 150 nm integrated sphere (Perkin Elmer) in the wavelength range of 800-200 nm (as background, a white-flat surface of BaSO₄ was employed).

For the photodegradation tests, the samples were immersed in a solution 2.5×10^{-5} M of acid orange 7 (AO7) and were irradiated with a UV LED 365 nm (50 mW/cm^2) for 2 h. Every 20 min the absorbance of the solution was measured in a UV/VIS Perkin Elmer Lambda XLS spectrophotometer.

3. Results and discussion

Figure 1a shows a schematic representation of the NTs used in this work: a) using intrinsic decoration by direct electrochemical anodization of the NM-alloy (NM: Au, Pt or both Au and Pt), and b) by using an extrinsic decoration of the tubes by sputtering, where particles are mainly present at the tube top. All nanotube layers were grown in a fluoride containing ethylene glycol electrolyte at 45 V for 30 min (more details are given in the experimental part) using the alloys or pure titanium as substrates. Subsequently, the layers were converted to anatase by annealing in air at 450°C for 1 h. For the intrinsically decorated layers, metallic particles are observed not only at the top of the morphology (Figure 1b), but are also uniformly distributed along the NTs length, independently of the alloy used, as shown for NTs on TiAuPt in Figure 1d and for NTs on TiAu and TiPt alloys in Figures S1 and S2, respectively.

All NT array layers exhibit similar thickness (i.e., a tube length of $\approx 4 \mu\text{m}$). Due to the low NM content in the alloys, the tube growth and morphology is not affected by the noble metal. For all intrinsic noble metals the uniform distribution of nanoparticles can be ascribed to a mechanism that has been reported for Au-Al alloys,[32] that is, the matrix metal is selectively oxidized out of the alloy leaving behind noble metal that accumulates to particles underneath at the metal/oxide interface. NM clusters then are decorated onto the growing oxide while the oxide tube grows.[33–35] In analogy, the intrinsic decoration in the present work occurs as the Ti

metal substrate is oxidized to form NTs during anodization while Au and Pt atoms agglomerate to form an alloy particle at the oxide/substrate interface. These AuPt alloy particles are then transferred to the outer wall and wander with the growing TiO₂ NTs – this finally leads to decorated tube walls.

For extrinsically decorated TiO₂ nanotubes, Figure 1c shows an example of Au decorated TiO₂ NTs after sputtering, coating and dewetting; clearly, the Au layer is visible after dewetting as Au particles at the top of the nanotubes (see experimental part for details). Using this approach the Au nanoparticles have a maximum penetration depth of around 300 nm into the nanotubes (as observed in the cross-section SEM images, see also Figure S3). This is in line with TEM results that show Au and Pt are extrinsically deposited not only at the top of the tubes but also inside the nanotubes (Figure S4). On the other hand, for the intrinsic decoration, AuPt alloy nanoparticles are homogeneously deposited on the outer wall and through the entire length of TiO₂ nanotubes (Figure S5). The size distribution of noble particles are comparable for all samples (Figure S6).

Figure 2a shows the XRD patterns of TiO₂ NTs before (*i*) and after annealing in air at 450°C for 1 hour (*ii*), after annealing only an anatase pattern is observed (besides the titanium peaks from the substrate). Before annealing, all as-formed nanotubes grown on either Ti or the noble metal alloys are amorphous. From the XRD patterns of TiO₂ nanotubes grown on alloys and annealed under similar conditions (i.e. (*iii*) - TiAu, and (*iv*) - TiPt alloy), not only anatase but also some traces of rutile can be identified. However, no Au or Pt peaks are detected, due to the low concentration of the noble metals in both alloys (i.e. lower than the detection limit of XRD).

From XPS, the Au4f and Pt4f peaks can easily be evaluated in the intrinsically decorated NTs, namely NTs grown on the TiAu, TiPt and TiAuPt alloys (Figure 2b

and c, using as reference a TiO₂ NTs layer grown on Ti), as well as for the extrinsically doped tubes (Figure S7). The composition evaluated from the XPS data of the intrinsically decorated nanotubes, i.e. grown on Ti_{0.2}at%Au, Ti_{0.2}at%Pt alloys or on TiAuPt (0.1at%Au and 0.1at%Pt) – see Table S1, is in good correlation with their nominal noble metal amount. Considering the Au and Pt peak positions for the intrinsic and extrinsic decorations, it is worth mentioning that the Au + Pt extrinsic decoration (sputtered 1 nm Au and 1 nm Pt, followed by dewetting) on the NTs shows no shift in the Au4f and Pt4f peak positions, namely the Au4f_{7/2} is at ≈ 83.53 eV and the Pt4f_{7/2} is ≈ 70.61 eV (as shown in Figure S7). In other words, the dewetting process does not produce AuPt alloy particles but separate Au and Pt particles.

In contrast, for intrinsically decorated NTs, we observe a shift in the Au4f peak and Pt4f peak that together with TEM-EDS investigations confirm the alloy nature of the nanoparticles (Figure 2d-f and Table S2).[31,36]

In order to characterize the distribution of the NM nanoparticles we carried out XPS and GDOES measurements of such layers. The XPS sputter depth profile of the first 300 nm of the intrinsically decorated nanotubes with AuPt particles (Figure S11a), i.e. nanotubes grown on the TiAuPt alloy, confirms that similar amounts of Au and Pt of ≈ 0.1 at% are present. To obtain the distribution over the entire length, glow discharge optical emission spectroscopy (GDOES) sputter depth profiles were acquired resulting in similar amounts of Au and Pt content throughout the length of the NTs on TiAuPt alloy (using as reference NTs on pure Ti) – as shown in Figure S11b, for more details see supporting information. To compare the overall loading of the tubes with noble metals, namely to compare the PVD coated and intrinsic layers, we performed EDX analysis as given in Table S3. The data shows that in all cases a

composition close to the nominal values was obtained – but more importantly that the overall amount of noble metal after PVD is comparable to the intrinsic amount.

These tubes were then used to investigate the photocatalytic degradation of the model pollutant (AO7). Figure 3a shows the kinetics of the photodegradation of AO7 for intrinsically decorated TiO₂ NTs and Figure 3b shows the kinetics for extrinsically decorated NTs. From these data, the kinetic constants can be evaluated (compiled in Figure 3c). Overall, for Au decoration a beneficial effect on the degradation efficiency of AO7 can be observed. However, it is also evident that a decrease in photoefficiency is observed when only Pt is present, both for intrinsic and extrinsic decoration of the tubes. This can be ascribed to an inactivation of the co-catalyst by forming Pt oxides as a result of annealing in air, as indicated by the XPS data in Figure S7-S10.[24,37] Clearly, a signature of PtO is obtained for these tubes (Figure S7 and S9). If one compares nanotubes with extrinsic decoration and with intrinsic decoration, clearly much higher efficiencies are obtained for the intrinsic decoration. This may be ascribed to the combination of particle size and distribution as well as their embedding in the nanotube wall. However, most remarkable is that the synergetic effect in the photodegradation of AO7 observed for the alloyed nanoparticles intrinsically decorated on the NTs (NTs grown on TiAuPt alloy) is not present for the Au+Pt nanoparticles decorated extrinsically onto the NTs, i.e. if this enhancement would only be related to the simultaneous presence of both noble metals (Au and Pt), then it follows that the Au+Pt nanoparticles decorated onto tubes would also have a higher efficiency than the elements alone. However, as this is not the case we ascribe the enhanced photocatalytic activity for AO7 of the intrinsically decorated tubes to the formation of mixed AuPt alloy nanoparticles that takes place only for the intrinsic decoration (i.e. obtained as a result of anodizing TiAuPt alloys).

In order to explore if additional plasmonic effects contribute to the photocatalytic efficiency, we performed reflectivity measurements for the tubes that were decorated with nanoparticles (Figure S12). For the nanotubes decorated intrinsically with Pt or AuPt, no plasmon resonance was observed. However, in presence of Au nanoparticles extrinsically decorated onto the nanotubes, a plasmonic effect is apparent (i.e., a clear plasmonic band is only visible for 2 nm nominal thickness Au decoration or partially for nanotubes grown on the TiAu alloy with 0.2at% Au). From these data it can be concluded that the enhancement in the photodegradation reactions of the intrinsically decorated nanotubes with the mixed AuPt nanoparticles is not due to plasmonic features.

Previous works on electrocatalysis have reported an enhanced rate for the oxygen reduction reaction (ORR) on AuPt compared with the same loading of Pt or Au alone. A key effect was attributed to the ability of Au atoms to provide $\text{Au-OH}_{\text{ads}}$ intermediates that are formed from O_2 and water that then can easily react with neighboring Pt atoms to form a range of ROS-products.[38] This is evident from current-voltage curves for oxygen reduction reaction measured for AuPt alloy versus a bimetallic Au-Pt layer (Figure 3d). The AuPt alloy obviously exhibits an onset potential clear shifted in the anodic direction with a difference in overpotential of - 0.16 mV at $200 \mu\text{A cm}^{-2}$. In other words, on an AuPt alloy the electron transfer to the electrolyte oxygen is facilitated which also diminishes electron recombination with valence band holes – thus enabling a higher life-time of holes and therefore a higher reaction possibility of the holes with the organic compound to oxidatively destroy it. As a result, bimetallic AuPt co-catalysts on titania NTs show a much higher photocatalytic activity for AO7 degradation compared to a plain combination of Au or Pt nanoparticles. This is evident by the comparison with Au and Pt nanoparticles that

were fabricated on the NTs by sputtering and dewetting. In this case no bimetallic alloyed particles are formed and the photocatalytic dye degradation tests do not show a synergetic effect of Au and Pt features.

4. Conclusions

In conclusion, we demonstrate that bimetallic AuPt decorated TiO₂ nanotubes can efficiently be produced by anodization of Ti-Au-Pt alloys, while only individual Au + Pt nanoparticle decoration is achieved by an element sputtering/dewetting approach. We show that the intrinsically formed bimetallic AuPt co-catalytic particles show a synergetic beneficial co-catalytic effect in the photocatalytic destruction of pollutants when using TiO₂ nanotubes. This synergy is absent if Au and Pt are present as individual decorations on the tubes. We ascribe the overall effect to a facilitated ORR on the bimetallic AuPt co-catalyst; this leads to an enhanced ROS production at the conduction band and at the valence band which in turn provide an enhanced pollutant degradation rate.

Acknowledgements

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

Shiva Mohajernia is acknowledged for XPS measurements.

Supporting Information

Supporting Information is available in the attached file.

Conflicts of interest

There are no conflicts to declare.

References

- [1] P. Roy, S. Berger, P. Schmuki, TiO₂ nanotubes: synthesis and applications, *Angew. Chem. Int. Ed.* 50 (2011) 2904–2939. doi:10.1002/anie.201001374.
- [2] K. Lee, A. Mazare, P. Schmuki, One-dimensional titanium dioxide nanomaterials: nanotubes, *Chem. Rev.* 114 (2014) 9385–9454. doi:10.1021/cr500061m.
- [3] P. Roy, D. Kim, K. Lee, E. Spiecker, P. Schmuki, TiO₂ nanotubes and their application in dye-sensitized solar cells., *Nanoscale.* 2 (2010) 45–59. doi:10.1039/b9nr00131j.
- [4] J. Gong, J. Liang, K. Sumathy, Review on dye-sensitized solar cells (DSSCs): Fundamental concepts and novel materials, *Renew. Sustain. Energy Rev.* 16 (2012) 5848–5860. doi:10.1016/J.RSER.2012.04.044.
- [5] S. Park, S. Kim, S. Park, W. Lee, C. Lee, Effects of Functionalization of TiO₂ Nanotube Array Sensors with Pd Nanoparticles on Their Selectivity, *Sensors.* 14 (2014) 15849–15860. doi:10.3390/s140915849.
- [6] K. Siuzdak, R. Bogdanowicz, M. Sawczak, M. Sobaszek, Enhanced capacitance of composite TiO₂ nanotube/boron-doped diamond electrodes studied by impedance spectroscopy, *Nanoscale.* 7 (2015) 551–558. doi:10.1039/C4NR04417G.
- [7] Q. Gui, Z. Xu, H. Zhang, C. Cheng, X. Zhu, M. Yin, Y. Song, L. Lu, X. Chen, D. Li, Enhanced Photoelectrochemical Water Splitting Performance of Anodic TiO₂ Nanotube Arrays by Surface Passivation, *ACS Appl. Mater. Interfaces.* 6 (2014) 17053–17058. doi:10.1021/am504662w.
- [8] I. Paramasivam, H. Jha, N. Liu, P. Schmuki, A review of photocatalysis using self-organized TiO₂ nanotubes and other ordered oxide nanostructures., *Small.* 8 (2012) 3073–3103. doi:10.1002/smll.201200564.
- [9] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, *J. Photochem. Photobiol. C Photochem. Rev.* 1 (2000) 1–21. doi:10.1016/S1389-5567(00)00002-2.
- [10] A. Fujishima, X. Zhang, D. Tryk, TiO₂ photocatalysis and related surface phenomena, *Surf. Sci. Rep.* 63 (2008) 515–582. doi:10.1016/j.surfrep.2008.10.001.
- [11] A.I. Kontos, V. Likodimos, T. Stergiopoulos, D.S. Tsoukleris, P. Falaras, I.

- Rabias, G. Papavassiliou, D. Kim, J. Kunze, P. Schmuki, Self-Organized Anodic TiO₂ Nanotube Arrays Functionalized by Iron Oxide Nanoparticles, *Chem. Mater.* 21 (2009) 662–672. doi:10.1021/cm802495p.
- [12] H.Y. Yang, S.F. Yu, S.P. Lau, X. Zhang, D.D. Sun, G. Jun, Direct growth of ZnO nanocrystals onto the surface of porous TiO₂ nanotube arrays for highly efficient and recyclable photocatalysts., *Small.* 5 (2009) 2260–2264. doi:10.1002/smll.200900724.
- [13] X. Chen, S.S. Mao, Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications., *Chem. Rev.* 107 (2007) 2891–2959. doi:10.1021/cr0500535.
- [14] S.K. Mohapatra, N. Kondamudi, S. Banerjee, M. Misra, Functionalization of Self-Organized TiO₂ Nanotubes with Pd Nanoparticles for Photocatalytic Decomposition of Dyes under Solar Light Illumination, *Langmuir.* 24 (2008) 11276–11281. doi:10.1021/la801253f.
- [15] I. Paramasivam, J.M. Macak, P. Schmuki, Photocatalytic activity of TiO₂ nanotube layers loaded with Ag and Au nanoparticles, *Electrochem. Commun.* 10 (2008) 71–75. doi:10.1016/J.ELECOM.2007.11.001.
- [16] H. Yu, X. Wang, H. Sun, M. Huo, Photocatalytic degradation of malathion in aqueous solution using an Au–Pd–TiO₂ nanotube film, *J. Hazard. Mater.* 184 (2010) 753–758. doi:10.1016/J.JHAZMAT.2010.08.103.
- [17] M.A. Nadeem, M. Murdoch, G.I.N. Waterhouse, J.B. Metson, M.A. Keane, J. Llorca, H. Idriss, Photoreaction of ethanol on Au/TiO₂ anatase: Comparing the micro to nanoparticle size activities of the support for hydrogen production, *J. Photochem. Photobiol. A Chem.* 216 (2010) 250–255. doi:10.1016/J.JPHOTOCHEM.2010.07.007.
- [18] S.K. Ghosh, T. Pal, Interparticle Coupling Effect on the Surface Plasmon Resonance of Gold Nanoparticles: From Theory to Applications, *Chem. Rev.* 107 (2007) 4797–4862. doi:10.1021/CR0680282.
- [19] H. Zhang, G. Chen, D.W. Bahnemann, Photoelectrocatalytic materials for environmental applications, *J. Mater. Chem.* 19 (2009) 5089–5121. doi:10.1039/b821991e.
- [20] A. Naldoni, F. Riboni, U. Guller, A. Boltasseva, V.M. Shalaev, A. V. Kildishev, Solar-Powered Plasmon-Enhanced Heterogeneous Catalysis, *Nanophotonics.* 5 (2016) 112.

- [21] X. Zhou, N. Liu, P. Schmuki, Photocatalysis with TiO₂ Nanotubes: “Colorful” Reactivity and Designing Site-Specific Photocatalytic Centers into TiO₂ Nanotubes, *ACS Catal.* 7 (2017) 3210–3235. doi:10.1021/acscatal.6b03709.
- [22] J. Kiwi, M. Graetzel, Optimization of conditions for photochemical water cleavage. Aqueous platinum/TiO₂ (anatase) dispersions under ultraviolet light, *J. Phys. Chem.* 88 (1984) 1302–1307. doi:10.1021/j150651a012.
- [23] Y.-Y. Song, Z.-D. Gao, P. Schmuki, Highly uniform Pt nanoparticle decoration on TiO₂ nanotube arrays: A refreshable platform for methanol electrooxidation, *Electrochem. Commun.* 13 (2011) 290–293. doi:10.1016/j.elecom.2011.01.006.
- [24] J. Yoo, M. Altomare, M. Mokhtar, A. Alshehri, S.A. Al-Thabaiti, A. Mazare, P. Schmuki, Photocatalytic H₂ Generation Using Dewetted Pt-Decorated TiO₂ Nanotubes: Optimized Dewetting and Oxide Crystallization by a Multiple Annealing Process, *J. Phys. Chem. C.* 120 (2016) 15884–15892. doi:10.1021/acs.jpcc.5b12050.
- [25] J.E. Yoo, K. Lee, M. Altomare, E. Selli, P. Schmuki, Self-organized arrays of single-metal catalyst particles in TiO₂ cavities: a highly efficient photocatalytic system., *Angew. Chem. Int. Ed.* 52 (2013) 7514–7517. doi:10.1002/anie.201302525.
- [26] J. Yoo, K. Lee, P. Schmuki, Dewetted Au films form a highly active photocatalytic system on TiO₂ nanotube-stumps, *Electrochem. Commun.* 34 (2013) 351–355. doi:10.1016/j.elecom.2013.07.008.
- [27] N.T. Nguyen, J. Yoo, M. Altomare, P. Schmuki, “Suspended” Pt nanoparticles over TiO₂ nanotubes for enhanced photocatalytic H₂ evolution., *Chem. Commun.* 50 (2014) 9653–9656. doi:10.1039/c4cc04087b.
- [28] M. Altomare, N.T. Nguyen, P. Schmuki, Templated Dewetting: Designing Entirely Self-Organized Platforms for Photocatalysis, *Chem. Sci.* 7 (2016) 6865–6886. doi:10.1039/C6SC02555B.
- [29] K. Lee, R. Hahn, M. Altomare, E. Selli, P. Schmuki, Intrinsic Au decoration of growing TiO₂ nanotubes and formation of a high-efficiency photocatalyst for H₂ production., *Adv. Mater.* 25 (2013) 6133–6137. doi:10.1002/adma.201302581.
- [30] S.N. Basahel, K. Lee, R. Hahn, P. Schmuki, S.M. Bawaked, S. a Al-Thabaiti, Self-decoration of Pt metal particles on TiO₂ nanotubes used for highly efficient photocatalytic H₂ production., *Chem. Commun.* 50 (2014) 6123–

6125. doi:10.1039/c4cc01287a.
- [31] H. Bian, N.T. Nguyen, J. Yoo, S. Hejazi, S. Mohajernia, J. Müller, E. Spiecker, H. Tsuchiya, O. Tomanec, B.E. Sanabria-Arenas, R. Zboril, Y.Y. Li, P. Schmuki, Forming a Highly Active, Homogeneously Alloyed AuPt Co-catalyst Decoration on TiO₂ Nanotubes Directly During Anodic Growth, *ACS Appl. Mater. Interfaces*. 10 (2018) 18220–18226. doi:10.1021/acsami.8b03713.
 - [32] S.J. Garcia-Vergara, M. Curioni, F. Roeth, T. Hashimoto, P. Skeldon, G.E. Thompson, H. Habazaki, Incorporation of Gold into Porous Anodic Alumina Formed on an Al–Au Alloy, *J. Electrochem. Soc.* 155 (2008) C333–C339. doi:10.1149/1.2917214.
 - [33] O. Jessensky, F. Müller, U. Gösele, Self-Organized Formation of Hexagonal Pore Structures in Anodic Alumina, *J. Electrochem. Soc.* 145 (1998) 3735–3740. doi:10.1149/1.1838867.
 - [34] W. Lee, K. Schwirn, M. Steinhart, E. Pippel, R. Scholz, U. Gösele, Structural engineering of nanoporous anodic aluminium oxide by pulse anodization of aluminium, *Nat. Nanotechnol.* 3 (2008) 234–239. doi:10.1038/nnano.2008.54.
 - [35] J.E. Houser, K.R. Hebert, Modeling the Potential Distribution in Porous Anodic Alumina Films during Steady-State Growth, *J. Electrochem. Soc.* 153 (2006) B566–B573. doi:10.1149/1.2360763.
 - [36] D. Tongsakul, S. Nishimura, K. Ebitani, Platinum/gold alloy nanoparticles-supported hydrotalcite catalyst for selective aerobic oxidation of polyols in base-free aqueous solution at room temperature, *ACS Catal.* 3 (2013) 2199–2207. doi:10.1021/cs400458k.
 - [37] J. Lee, W. Choi, Photocatalytic Reactivity of Surface Platinized TiO₂: Substrate Specificity and the Effect of Pt Oxidation State, *J. Phys. Chem. B*. 109 (2005) 7399–7406. doi:10.1021/JP044425+.
 - [38] J. Luo, P.N. Njoki, Y. Lin, L. Wang, C.J. Zhong, Activity-composition correlation of AuPt alloy nanoparticle catalysts in electrocatalytic reduction of oxygen, *Electrochem. Commun.* 8 (2006) 581–587. doi:10.1016/j.elecom.2006.02.001.

Figure 1. a) Schematic representation of TiO₂ NTs intrinsically decorated by direct anodization of alloy (left) and extrinsically decorated by sputtering and dewetting a noble metal on the top of the NTs anodically growth on Ti foil (right); b) Top view of the NTs on TiAuPt alloy; c) Top view of the TiO₂ NTs with 1 nm of Au dewetted and d) Cross section of the NTs on TiAuPt alloy with magnifications in the top, middle and bottom part.

Figure 2. a) XRD patterns of (i) as-formed TiO₂ NTs; (ii) annealed at 450°C TiO₂ NTs; (iii) NTs on TiAu and (iv) NTs on TiPt alloys. b) and c) high resolution XPS spectra of Au4f and Pt4f for NTs on Ti (Ref) and on TiPt (Pt alloy), TiAu (Au alloy) and TiAuPt (AuPt alloy) alloys. d) TEM image of AuPt nanoparticle on the top of NTs grown on TiAuPt alloy. TEM-EDS elemental mapping of e) Au and f) Pt in the selected region of d).

Figure 3. Photodegradation curves of AO7 with: a) intrinsically and b) extrinsically decorated TiO_2 NTs; (c) kinetic constants of AO7 degradation with intrinsically and extrinsically decorated TiO_2 NTs; (d) Current vs potential curve of AuPt alloy and bimetallic Au-Pt layer measured in 0.5 M KOH with O_2 bubbling.