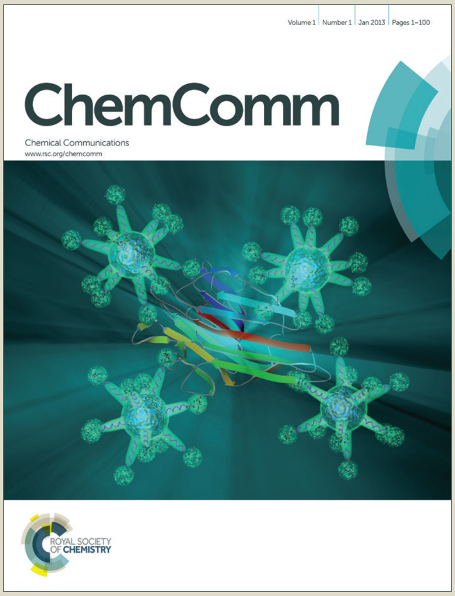

Journal Name

RSCPublishing

Chemical Communications

Cite this: DOI: 10.1039/x0xx00000x

Self-decoration of Pt metal particles on TiO_2 nanotubes used for highly efficient photocatalytic H_2 production

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Pt decorated TiO_2, has over the past decades, been a key material for photocatalytic hydrogen production. The present work shows that growing anodic self-organized TiO_2 nanotubes from Ti-Pt alloy with a low Pt content of 0.2 at% leads to oxide nanotube layers that are self-decorated with Pt nanoparticles of 4 ~ 5 nm in diameter. The average particle spacing is in the range of ~ 50 nm and is partially adjustable by the anodization conditions. This intrinsic decoration of TiO_2 nanotubes with Pt leads to a highly active photocatalyst for the production of H_2 under UV or visible light conditions.

Since Fujishima and Honda in 1972 showed the feasibility to produce hydrogen, the fuel of the future, by photoelectrochemical water splitting using a TiO_2 electrode, vast efforts have been dedicated to optimize systems to enhance the hydrogen yield [1]. The principle of this pathway to hydrogen is based on using a semiconductor for light absorption and formation of excited electron-hole pairs, that then on the semiconductor surface react with an environmental H-source. A key requirement to the semiconductor is that it has suitable band-edge positions to allow generation of H_2 (namely a conduction band edge with a negative potential to the H_2/H^+ redox potential). If the goal is to achieve a photocatalytic hydrogen production system that operates without external bias (i.e., under open circuit conditions), then also the transfer of holes from the valence band to the environment should be not only thermodynamically possible but also kinetically fast [2-3]. In the case of TiO_2, most measures to enhance the kinetics are the use of sacrificial agents such as methanol, ethanol and decorating the surface with suitable charge transfer co-catalysts.

Other key parameters for an effective hydrogen evolution from TiO_2 are a large surface area and an optimized geometry of the photocatalyst. For the latter reason, one-dimensional nanostructures have attracted wide interest in this field, as they provide a high aspect ratio with optimized light absorption path and an orthogonal carrier separation. A most straightforward approach towards directional structures are self-organized TiO_2 nanotube arrays. To produce these nanotube structures a Ti metal substrate can be anodized under self-organizing electrochemical conditions [4]. The advantage of an anodic formation is not only simplicity of the process but also the easiness of geometry control (length, diameter, wall thickness) via the selection of suitable anodization parameters [4]. In the context of H_2 production from TiO_2, as co-catalysts most active are noble metal nanoparticles (mainly Pt) that act very efficiently as co-catalyst on TiO_2 nanostructures - in fact in order to obtain measurable contents of H_2 from TiO_2 under non-biased conditions (without the use of a counter electrode and applying a potential difference) co-catalyst decoration is mandatory [5-7].

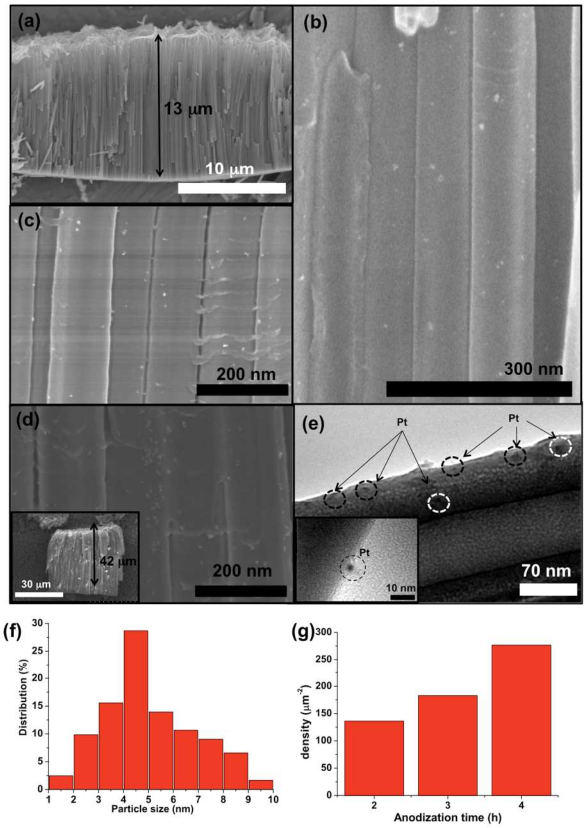

Figure 1. Cross-sectional SEM images of Pt decorated TiO_2 nanotubes that are formed by anodization of on 0.2 at % Pt containing TiPt alloy for (a)-(c) 2 h, and (d) 4 h. (e) TEM image of decorated Pt on TiO_2 nanotubes. (f) Distribution of the Pt particle size, (g) density of Pt particles with different anodization times.

There are mainly two beneficial effects ascribed to Pt decoration: i) changes in surface band bending in TiO_2 induced by the metal contact (Fermi level pinning) which leads to a faster transport of electrons, and ii) its role as a hydrogen recombination catalyst that promotes H_2 formation from reduced atomic hydrogen [8-13]. In order to modify TiO_2 surfaces with noble metal nanoparticles, several methods are commonly used such as photoassisted deposition, impregnation, and physical mixing [14-17].

In the present work, we demonstrate that a very facile and straightforward Pt self-decoration of TiO_2 nanotube walls can be achieved in-situ, that is during tube growth by using Ti-Pt alloys with a small amount of Pt (in our case 0.2 at %) for the anodization process. We find that such self-decorated noble metal on TiO_2 nanotubes provides a drastic improvement of the photocatalytic hydrogen evolution under UV as well as under visible light conditions.

Figure 1 shows typical SEM and TEM images of cross-sections of Pt self-decorated TiO_2 nanotubes formed on 0.2 at% Pt containing TiPt alloy by anodization in the 0.2M HF/ethylene glycol electrolyte for 2 h. Under these conditions nanotube layers of an average thickness of 13 μm are formed that consist of individual tube units with ~ 120 nm outer diameter (figure 1 (a)). A close inspection (SEM in figure 1 (b)-(c) and TEM in figure 1 (e) show that the oxide tube walls are decorated with Pt nanoparticles of ≈ 2 – 5 nm in diameter and with an average spacing of approximately 50 nm (i.e., corresponding to a particle density of ~130 μm^{-2}). If anodization is carried out for longer times, remarkably not only the tube length is extended but also the particle density on the walls is increased to approximately 250 μm^{-2} (figure 1(d)). In fact the particle density can be almost doubled if anodization is extended from 2 h to 4 h. The individual particle size over this time is not significantly increased. This suggests that noble particle formation and embedment in the anodic structures may be based on a mechanism similar to a process reported by Habazaki et al. for noble metal/Al alloys. I.e, by anodization of TiPt alloy, a sequence of selective oxidation, noble metal accumulation underneath the oxide and incorporation of critical particle size takes place as described in reference [18].

In order to create a sufficiently active photocatalyst the nanotube layers were crystallized to anatase. For this, we annealed the as-formed layers at 450 °C for 1 h in air. A comparison of the XRD of “as-formed” and annealed sample is shown in figure 2 (a). Clearly, annealing leads to a conversion to anatase with small amounts of rutile. Pt peaks cannot be detected because the concentration is lower than the detection limit of XRD. Nevertheless, using XPS one can clearly detect the Pt4f peaks with a concentration of 1.02 at% of the oxide (figure 2 (b)). The peak position and slope is in line with metallic Pt being present in both, the as-formed and the annealed samples.

In order to evaluate the photocatalytic hydrogen-production-potential of the Pt self-decorated TiO_2 nanotubes, we investigated the open circuit hydrogen production rates from 20 vol% methanol solution using different light sources. For this we used tube layers grown for 2 h as shown in figure 1 (a).

Under UV light (laser, 325 nm, 60 mW/cm^2) illumination, the Pt self-decorated TiO_2 nanotubes show a drastically higher hydrogen production rate in comparison with pure TiO_2 nanotubes (18.5 $\mu L \bullet cm^{-2} \bullet h^{-1}$) with values of 100.4 $\mu L \bullet cm^{-2} \bullet h^{-1}$**.** This value is about a 5 times higher than for a reference samples that was decorated optimally by Pt-sputtering (figure 3(b)) [19]. For further comparison, we produced samples with longer and shorter anodization times. Both samples, shorter (30 min) and longer (4 h) anodized tubes, show less hydrogen production (figure 3 (b)). These results reflect that the optimum particle interspacing is a critical factor for an effective photocatalyst performance. Optimally self-decorated Pt on TiO_2 nanotubes also shows a significantly higher hydrogen production rate under simulated sun light (AM 1.5 solar simulator, 300 Xenon lamp) and visible light with 400 nm cut-off filter. In fact, under solar simulated light irradiation the amount of hydrogen production with Pt decorated TiO_2 nanotubes is over 60 times higher than the value obtained for bare TiO_2 nanotubes. Under visible light, hydrogen can only be detected for the Pt decorated TiO_2 nanotubes (in this context it should be noted that anodic TiO_2 nanotubes produced in organic electrolyte can show a mild visible absorption due to carbon remnants [C-doping] [4]).

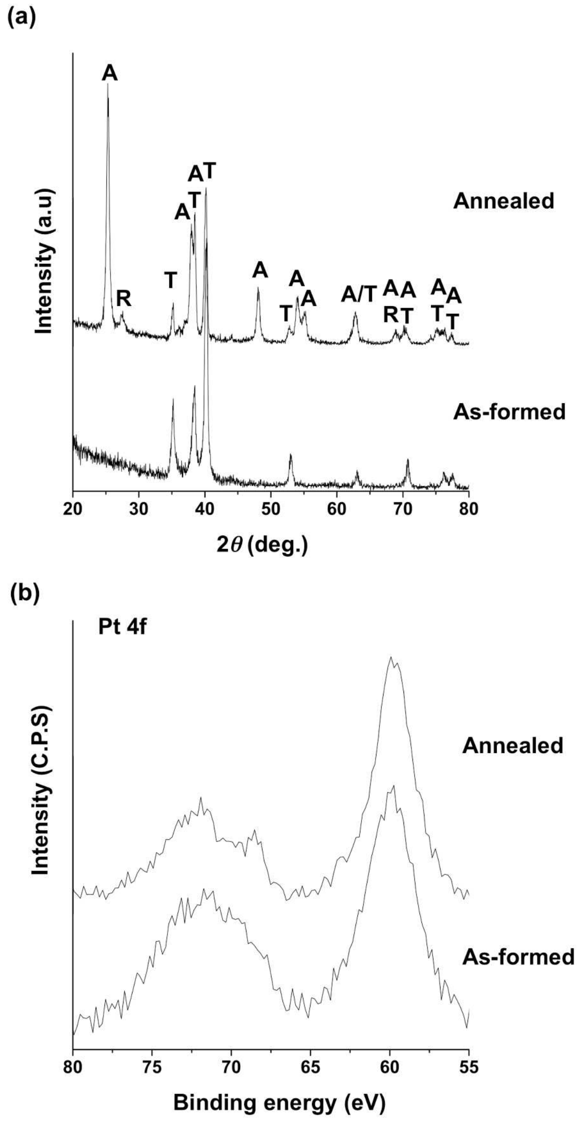

Figure 2. (a) XRD patterns of annealed Pt decorated TiO_2 nanotubes. The peaks are annotated as anatase (A), rutile (R), and Ti metal (Ti). Annealing was carried out at 450 °C in air for 1h. The thickness of the nanotube layer is ca. 13 μm. (b) XPS spectra of Pt 4f doublet in the Ti-Pt alloy.

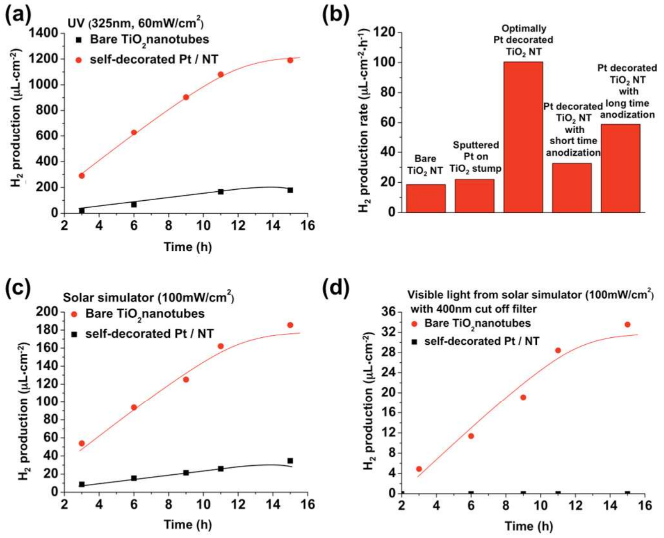

Figure 3. (a) Photocatalytic H_2 production with Pt self-decorated TiO_2 nanotubes over time and (b) comparison of H_2 production rate with different types of Pt decorated TiO_2 nanotubes in 6 h under UV light. (c)-(d) Photocatalytic H_2 production with Pt self-decorated TiO_2 nanotubes over time under (c) simulated sun light and (d) visible light. The hydrogen productions were performed in 20 vol% methanol solution.

The results in figure 3 show that under all illumination conditions the amount of produced H_2 increases linearly in 11 h, then the production rate shows a trend to mild decrease. To evaluate the stability of the layer the photocurrent values were measured at OCV for 17h (see SI) - over several cycles the activity is stable. To the best of our knowledge, the result is most efficient photocatalytic hydrogen production reported for anodic TiO_2 nanotube structures investigated under open circuit conditions with 1.52% of apparent quantum efficiency. This value is even higher than reported photo electrochemical data (with applied external potential) [20]. A key point may be that the self-decoration of Pt on TiO_2 nanotubes under the conditions used here yield a Pt particle spacing of approximately 50 nm. If it is assumed that a Pt particle mainly affects the electronic properties of TiO_2 by forming a semiconductor/metal junction one may estimate the range of the effect from a simple Shottky approach $\boldsymbol{W = [\frac{2}{q\varepsilon_o\varepsilon N_D}(U_s - \frac{kT}{q})]^{-\frac{1}{2}}}$ with U_s being the difference in work functions between metal and TiO_2 ($U_s \approx 1$ V). For TiO_2 nanotubes annealed to anatase a value of $N_d \approx 10^{19}$ cm^{-3} with ε= 30 - 90 has been reported which yields for W≈ 30 - 60 nm. In other words, the lateral range of electronic effects induced by a single Pt particle of 30 - 60 nm is in a comparable range as the spacing of the decoration shown in figure 1 (b) and this may be an explanation for the observed high efficiency [21].

Overall, the results show that anodization of a low Pt-content alloy is a highly effective means to achieve Pt self-decoration of TiO_2 nanotube layers. Such self-Pt decorated TiO_2 nanotubes show a high hydrogen production rate and may be anticipated to have a high potential for applications in any sort of TiO_2/Pt co-catalyzed reaction.

Notes and references

This research work was funded by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, under grant number (22-130/1433HiCi). The authors, therefore, acknowledge with thanks DSR technical and financial support.The authors would like to acknowledge DFG and the Erlangen DFG cluster of excellence for financial support, and Helga Hildebrand for valuable technical help.

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Electronic Supplementary Information (ESI) available: Experimental details. See DOI: 10.1039/c000000x/

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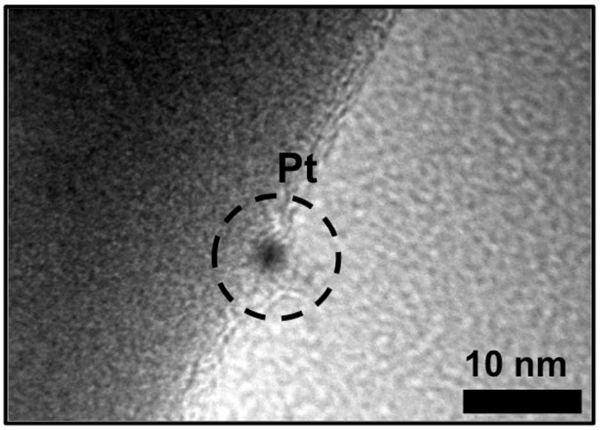
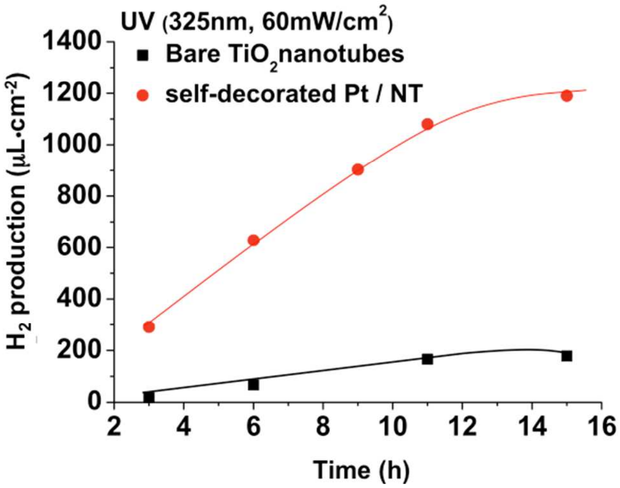

Pt
10 nm


UV (325nm, 60mW/cm^2)
■ Bare TiO$_2$nanotubes
● self-decorated Pt / NT
H$_2$ production (μL·cm^{-2})
0
200
400
600
800
1000
1200
1400
Time (h)
2
4
6
8
10
12
14
16