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# Increase in hydrogen production from light and ethanol using a dual scale porosity photocatalyst

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Stable photo-catalytic production of hydrogen is demonstrated under simulated solar irradiation from aqueous solutions of ethanol over a dual porosity 3D TiO<sub>2</sub> nanotube array (TNTA). The photocatalytic material consists of a uniform layer of TNTAs grown on each titanium fiber of a commercial sintered titanium web (TNTA-web). Under simulated solar irradiation, a stable H<sub>2</sub> production rate of 40 mmol  $h^{-1} m^{-2}$  is observed. In comparison, TNTAs grown on a flat titanium foil (TNTA-foil) do not produce H<sub>2</sub> under the same conditions. The addition of small (4-5 nm) and well distributed Pd nanoparticles to the TNTA-web increases the production of hydrogen to 130 mmol  $h^{-1} m^{-2}$  with a Solar-to-Fuel efficiency of 0.45%. The same Pd loading on the TNTA-foil support produced a H<sub>2</sub> production rate of 10 mmol  $h^{-1} m^{-2}$ . Each catalytic materials are characterized by a combination of SEM, HR-TEM, XRD, XPS and Raman spectroscopy. The enhancement in H<sub>2</sub> production is to be due to the increased light absorption properties of the TNTA-web material enabled by its unique dual porosity. Analysis of the reaction by-products show that ethanol is transformed into acetaldehyde as single oxidation product. Additionally, it is shown that an optimal Pd loading maximizes H<sub>2</sub> production rate, since agglomeration of the metal nanoparticles takes place at high loading, decreasing the Pd-TiO<sub>2</sub> interface where the photoreforming reactions take place.

#### Introduction

Each square meter of the earth's surface receives 263 kWh of the Sun's radiant energy per year.<sup>1</sup> Nature harvests a part of this energy using photosynthesis, the process that transforms  $CO_2$  and water into biomass. We know how to turn this biomass into biofuels, the major candidates as energy vectors for the sustainable transportation in the future.<sup>2</sup> However, the production of biofuels from biomass has limited energy efficiency,<sup>3</sup> and hence large areas of land are needed, posing a serious issue for the potential competition with food production and damage to biodiversity.<sup>4</sup> A more realistic "clean" strategy relies on the utilization of second-generation biomass-derived compounds as sacrificial electron donors in photocatalytic  $H_2$  production processes.<sup>5-10</sup> Apart from being a very important and heavily utilized molecule in multiple industrial applications (e.g. for the synthesis of NH<sub>3</sub> and related fertilizers), H<sub>2</sub> has been long been proposed as one of the most promising candidate energy vectors of the future.<sup>11</sup> Any sustainable energy economy based upon hydrogen will require large-scale production of hydrogen based upon

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sustainable and environmentally friendly resources such as second generation biomass and light.<sup>12,13</sup> water. Solutions of Small Organic Compounds (e.g. alcohols) in water can increase the energy conversion efficiency of photocatalytic H<sub>2</sub> production<sup>14</sup> with an approach known as photoreforming<sup>15</sup>. This strategy relies on the utilization of biomassderived species as sacrificial electron donors in the photocatalytic H<sub>2</sub> production process.<sup>6</sup> In photo-reforming the oxidation of SOMs takes place instead of oxygen evolution. This helps to avoid the back-reaction with hydrogen that is generally responsible for reduced energy efficiency.<sup>16,17</sup> Among these compounds, ethanol is an attractive candidate as it can be a renewable resource. For example ethanol can be obtained from the fermentation of biomass or steam reforming of cellulosic materials with reasonably low energy cost.<sup>18</sup>

In terms of photocatalytic materials,  $TiO_2$  has been the most successfully employed substrate due to its well demonstrated high activity, low cost, large availability, low toxicity and stability to corrosion.<sup>19</sup> However, its utilization still suffers from inherent limitations, above all poor light absorbance in the visible spectrum and therefore poor visible light photo-activity, as well as fast recombination of the photogenerated charge carriers (electrons e<sup>-</sup> and holes h<sup>+</sup>).

The most popular method used to improve photo-catalytic hydrogen production has been the deposition onto the  $TiO_2$  surface of either noble metal (Au, Pt, Pd, Ag) or base metal (Ni, Cu) nanoparticles, that are able to capture photo excited electrons and retard the electron/hole recombination.<sup>20–22</sup> In

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the scientific literature there have been numerous reports on successful photoreforming of oxygenated compounds by TiO<sub>2</sub> loaded with metal nanoparticles.<sup>11,23,24</sup> Furthermore, the use of various nanostructures of TiO<sub>2</sub> in particular ordered nanotube arrays (TNTAs), have been shown to lead to improvements in photocatalytic activity because of this unique structure.<sup>19-21</sup>

Among the above aspects, a most important point for photocatalysis is that in these TNTA structures an orthogonal carrier separation is facilitated, i.e. electrons and holes are spatially separated within the tube wall (that is, e are collected in the wall center and transported to the back contact while h+ are driven to the wall/electrolyte interface).<sup>22</sup> This is particularly beneficial to overcome limitations due to the short diffusion length of holes in  $TiO_2$  (~10 nm) while exploiting the comparably long electron diffusion length (~20  $\mu m$  in TiO<sub>2</sub> nanotubes).<sup>23</sup> Ordered arrays of TiO<sub>2</sub> nanotubes grown onto a titanium substrate by anodization meet such requirements.<sup>24,25</sup> These nanotubes have a wall thickness less than 20 nm and exhibit a large surface area, which allows the fine dispersion of deposited metal co-catalyst nanoparticles. One of the major drawbacks of these nanostructures is the limited thickness of the nanotube layer. The attenuation length of the solar radiation in  $TiO_2$  is indeed 16 microns, therefore to exploit at best the energy content of the incoming radiation, the optical path in the nanotubes must be longer than this. Ordered arrays of TiO2 nanotubes with such a thickness exist, but they show severe mass transport limitations.

To overcome this limitation we have prepared a new 3D architecture of TiO<sub>2</sub> nanotubes with dual scale porosity. Dual scale porosity means a material with surface features on the nanoscale (e.g. less than the recombination length 100 nm) combined with micron sized pores and an open 3D structure that allows the flow of solutions through the material. A commercial titanium non-woven sintered web support (thickness 0.5 mm, average fibre diameter 20 µm, 73% porosity) is used as substrate. Anodization results in the formation of a finely distributed array of titania (TiO<sub>2</sub>) nanotubes that cover the surface of the titanium fibers. The individual nanotubes have an inner diameter of 100 nm with a wall thickness of ca. 10 nm and an average tube length of around 2.0 µm. The material has been demonstrated in a membrane reactor for photochemical water splitting.<sup>26</sup> In this study, the photoreforming catalytic performance under simulated solar radiation is determined with ethanol as substrate. The photo-activity is shown to be further enhanced by the addition of finely dispersed Pd nanoparticles. The activity of TiO<sub>2</sub> nanotubes with the same dimensions grown on a flat titanium foil and the same Pd loading is also determined. More than an order of magnitude improvement in hydrogen production is obtained through the utilization of this unique TNTA structure. The synthesized materials were studied by SEM, HR-TEM, Raman, XPS and XRD. Intermediates and final products from the H<sub>2</sub> generation operations were identified with the purpose of predicting the mechanism by which ethanol is consumed in a photocatalytic system. The photon source used irradiates predominantly visible light (83%) in order to approximate solar light.

#### Experimental

#### Photocatalyst synthesis procedure

All metal salts and reagents were purchased from Aldrich and used as received. All the solutions were freshly prepared with doubly distilled and deionized water.

The Titania NanoTube Array (TNTA) were prepared on two support materials (non-woven titanium web and a Titanium foil) using a procedure described previously.<sup>24</sup> The titanium web support material is a commercially available sintered non-woven titanium web supplied by NV Bekaert SA (Belgium) (thickness 0.5 mm, average fibre diameter 20  $\mu$ m, 73% porosity).

Firstly, for the titanium disk, TNTAs were synthesized by anodization at 60 V for one hour at room temperature in a solution of ethylene glycol containing 0.5 wt% of NH₄F. The TNTA-disk was then annealed by heating at 400 °C (10 °C/min) in air for 30 min. Palladium nanoparticles were deposited onto the TNTA-disk by sequential chemical bath deposition (S-CBD).<sup>24</sup> The TNTA-disk was immerged in a beaker containing a solution of PdCl<sub>2</sub> (0.3 g) in 0.7 mL of HCl (37%) and 1 mL of ethylene glycol in 50 mL of water for 30s. The sample was then washed with water. The reduction of the palladium salt adsorbed on the TNTA-disk was obtained in NaBH<sub>4</sub> (1 g) dissolved in 50 mL of deionized water. The sample was then washed with water. The whole sequence (above) was repeated ten times in order to obtain an approximate Pd loading of 0.1 mg  $\text{cm}^{-2}$ . The colour of the sample after the deposition turned from light blue of the TNTA-disk prior to the deposition to light black. Finally, the as-prepared sample (Pd/TNTA-disk) was dried in a N<sub>2</sub> stream.

The TNTA-web support and Pd/TNTA-web catalyst were prepared by the procedure previously reported as follows.<sup>25,27</sup> The TNTA-web was synthesized by anodization of a titanium non-woven web (BekaertToko Metal Fibre Co, Belgium) at 60V for 1 hour at room temperature in an electrolyte consisting of 0.5 wt.% NH<sub>4</sub>F and 99.5 wt.% Ethylene Glycol. The resulting TiO2 nanotube array (TNTA-web) was then annealed at 400°C (10 °C/min) in air for 30 min in order to obtain Anatase as the main titanium dioxide phase.

The Pd/TNTA-web material was obtained by the addition of Pd nanoparticles to the TNTA-web support using the following procedure: (1) 0.2 mL of a solution containing 0.3 g PdCl<sub>2</sub>, 0.7 mL HCl (37%) and 1 mL Ethylene Glycol in 50 mL of water, was added drop-wise to the surface of the TNTA-web substrate (1 cm<sup>2</sup> disk). (2) The impregnated web was then dried in an oven at 80 °C. (3) Steps (1) and (2) were then repeated until the desired loading of Pd precursor loading was obtained (0.025 – 1 mg cm<sup>-2</sup>). The sample was then reduced in an ice cold aqueous NaBH<sub>4</sub> (0.1 wt%) solution for 12 hours. After reduction, the sample was washed thoroughly in deionized water and dried at 60 °C until constant weight. A schematic of the whole material synthesis has been reported in the

supporting info section (see supplementary information Fig. S5).

#### **Material Characterization**

The Pd/TNTA-disk and Pd/TNTA-web samples were characterized by Field emission-scanning electron microscopy (FE-SEM), Transmission electron microscopy (TEM), High-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman Spectroscopy. The Pd content of the material was determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis.

FE-SEM analysis were performed at a primary beam acceleration voltage of 15.0 kV by a HITACHI S4800 microscope instrument.

TEM images were performed on a Philips CM12 microscope operating at 100 kV. The microscope was equipped with an EDS energy dispersive microanalysis system.

HRTEM analysis were recorded with a Zeiss Libra 200 FE transmission electron microscope equipped with a double tilt goniometer at 200 kV and FEI Tecnai-F30 microscope which was operated at 300kV for the present paper image acquisition.

XRD patterns were acquired at room temperature with a PANalytical X'PERT PRO diffractometer, employing CuK $\alpha$  radiation ( $\lambda$  = 1.54187 Å) and a parabolic MPD mirror. The spectra were acquired in the 2 $\theta$  range from 20° to 80°.

XPS measurements were performed with a PHI Quantum 2000 XPS system (Physical Electronics Inc., USA) using Al Ka (1486.6 eV) radiation to determine the surface composition of the as deposited Pd/TNTA-web and Pd/TNTA-foil . The base pressure in the analysis chamber was of the order of  $5 \times 10$ -8 Torr during data collection. The invariance of the peak shapes and widths at the beginning and at the end of the analyses ensured absence of differential charging. Analyses of the peaks were performed with the software provided by PHI Quantum, the binding energy values are quoted with a precision of  $\pm 0.15$  eV and the atomic percentage with a precision of  $\pm 10\%$ .

Raman measurements were carried out with a confocal Raman microscope (InVia Renishaw) in the spectral range of 110 to  $1000 \text{ cm}^{-1}$  using a 633 nm laser excitation source.

#### **Photocatalytic Testing**

The TNTA samples were tested as photoreforming catalysts for hydrogen production immersed in an aqueous solution of ethanol (50% v/v) in a Teflon-lined photoreactor illuminated with a Lot-Oriel Solar Simulator equipped with a 150 W Xe lamp and an Atmospheric Edge Filter with a cut-off at 300 nm (Fig 1). In a typical catalytic test, a 1 cm<sup>2</sup> disk of the photocatalyst was immersed in 60 mL of the aqueous ethanol solution, which is subsequently purged from air with an Ar flow of 15 mL min<sup>-1</sup> for 40 minutes. During the purge and the catalytic tests, the solution was magnetically stirred.



**Fig. 1** Schematic representation of the reactor used for photoreforming experiments.

The on-line detection of gaseous and volatile products was carried out using a gas chromatograph equipped with two analytical lines using a 10 way-two loop injection valve for injection. An Agilent 7890A Gas Chromatograph equipped with a Carboxen 1010 PLOT (Supelco, 30 m × 0.53 mm ID, 30  $\mu$ m film) column followed by a Thermal Conductivity Detector (TCD) was used for gaseous products quantification using Ar as carrier and a DB-225 ms column (J&W, 60 m × 0.32 mm ID, 20  $\mu$ m film) using He as carrier followed by a mass spectrometer (MS) HP 5975C was employed for the detection of the volatile organic compounds. After the photocatalytic tests, the liquid solutions were recovered and analysed by GC/MS to detect the accumulated soluble by-products.

The Solar-to-Fuel efficiency (SFE) was calculated using the following equation:  $^{\rm 28}$ 

#### SFE = $\Delta E/S \times 100$

where  $\Delta E$  is the energy content of the H<sub>2</sub> produced by photoreforming and S is the total incident solar radiation, as measured by adequate radiometers in the UV and Visible range (expressed in W cm<sup>-2</sup>).  $\Delta E$  is calculated as the amount of H<sub>2</sub> produced by each sample (expressed in mols<sup>-1</sup> cm<sup>-2</sup>) multiplied by hydrogen combustion enthalpy.

#### **Results and discussion**

#### Photocatalyst synthetic procedure and characterization

An anodization synthesis technique was used to obtain  $TiO_2$  nanotube arrays on two different support materials (a titanium foil and a titanium non-woven web). In this way, we compare an essentially 2D material with a 3D material. For the TNTA-web material we used a non-woven titanium web with a thickness of 0.2 mm and square section of the fibres of 20 microns (Fig. 2A and B). The resulting structure has large pores that allow fast transport of reactants and products in the liquid phase and provides additional external surface area for the formation of a high density of  $TiO_2$  nanotube arrays. Prior to

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the anodization, we polished the web electrochemically, to reduce the surface roughness of the fibres (Fig. 2A and B). After anodization and annealing we observe the formation of nanotube arrays that completely cover the surface of the fibres with the nanotubes homogeneously distributed over the whole web structure (Fig. 2 C,D,E). The dimensions are homogeneous in terms of both length and diameter (2340 nm and 102 nm). The nanotubes have a diameter of 100 nm, with walls of ca. 10 nm (Fig. 2E) and an average length of 2.3  $\mu$ m. The selected area Fourier Transform (FT) of the High Resolution Transmission Electron Microscopy (HRTEM) image shows a six fold symmetry, demonstrating that the HRTEM image was taken along the <101> direction, with an interplanar spacing of 0.36 nm typical of anatase (Fig. 2I). When decorated with Pd nanoparticles (0.1 mg cm-2), a fine distribution of the NPs can be seen with an average particle size of approximately 4 nm (Fig. 2G, H and 3C). The Pd metal NPs are also confirmed by the interfacial planar spacing (0.19 nm) (Fig. 2I).



**Fig. 2** Electron microscopy analysis of the Pd/TNTA-web photocatalyst morphology and structure. Scanning Electron Microscopy (SEM) of the pristine titanium-web substrate (A,B) and of the TiO<sub>2</sub> nanotubes arrays on the web (C,D,E); HR-TEM of a nanotube (F) SEM image (G), TEM (H) and HRTEM (I) of the TNTA-web with 0.1mg cm<sup>-2</sup> Pd (0.26 wt.%).



**Fig. 3** (A, B) SEM images of the  $TiO_2$  nanotube arrays on the titanium web substrate (TNTA-web) and after the addition of 0.1mg cm<sup>-2</sup> Pd nanoparticles (C and D). SEM images of the  $TiO_2$  nanotube arrays on the titanium foil substrate (TNTA-foil) with the same Pd loading (E-H).

In Fig. 3, further SEM images of the Pd/TNTA-web are shown together with images of the Pd/TNTA-foil (both 0.1 mg cm<sup>-2</sup>). It is clear that the lengths of the TNTA layer is around 2300 nm on both the foil and web supports. The Pd NPs are also distributed evenly over the nanotubes in the foil support with an average size distribution (7 nm) larger with respect to the TNTA-web supported Pd nanoparticles.



**Fig. 4** XRD patterns of the Titanium web (black line), the Titanium web with nanotubes on top (TNTA-web red line), and the TNTA-web with different Pd nanoparticles loading.

The XRD traces of the titanium web, TNTA-web and various Pd/TNTA-web samples are shown in Fig. 4. The XRD pattern of the TNTA-web after annealing at 400 °C shows a complete conversion of the phases of titania nanotubes to anatase (previously prevalently amorphous), also increasing the crystallinity (Fig. 4). Conversion to anatase is essential to improve light conversion properties.<sup>21</sup> The presence of nanostructured Pd is confirmed by the signals at 40 and 45° that increase in intensity with increasing loading. The broad and low intensity nature of these peaks confirms the small size distribution of the NPs as seen in the SEM/TEM investigations.



**Fig. 5** Raman spectrum of the Pd/TNTA-web (A in red); the TNTA-web (A in black); the Pd/TNTA foil (B in orange) and the TNTA-foil (B in green). Excitation with 633 nm radiation.

To investigate further the catalyst structure and difference between the two supports, Raman studies were performed on Pd/TNTA-foil (0.1 mgPd cm<sup>-2</sup>), TNTA-foil, Pd/TNTA-web (0.1 mgPd cm<sup>-2</sup>) and TNTA-web (Fig. 5). The main peaks centered at approximately; 146, 397, 516, and 638 cm<sup>-1</sup> for all the spectra are typical characteristics of the anatase phase of TiO, thus corroborating the XRD data.<sup>29,30</sup> The absence of other phase-related peaks (e.g. for rutile, or brookite) indicates complete anatase TiO<sub>2</sub> formation. Generally, anatase titania has six possible Raman active modes, namely A1g+2B1g+3Eg. In the corresponding modes are assigned as 146 cm<sup>-1</sup> (Eg), 397 cm<sup>-1</sup> (B1g), 516 cm<sup>-1</sup> (a combination of A1g and B1g and 639 cm<sup>-1</sup> (Eg). The other Eg mode at 196 cm<sup>-1</sup> is very weak.



**Fig. 6** (A) XPS spectrum of the Pd/ TNTA-web; (B) Ti 2p region; (C) Pd 3d region and (D) O 1s region. According to the spectra, titanium is oxidized to its 4+ state, while palladium is mostly present in its metallic state.

The Eg peak is mainly caused by the symmetric stretching vibration of O–Ti–O linkages in  $TiO_2$ , the B1g peak is assigned

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to symmetric bending vibration of O–Ti–O, and the A1g peak is associated with antisymmetric bending vibration of the O–Ti– O linkage.<sup>31</sup> The well-resolved lowest Eg mode at 147 cm<sup>-1</sup> shown also as insert arises from the external vibration of the anatase structure and indicates the formation of long-range order. It is notable that for the TNTA-foil and Pd/ TNTA-foil samples the peak positions do not change after Pd metal deposition. By comparison, the TNTA-web signals shift slightly and broaden after the addition of Pd nanoparticles. This suggest a disruption in the long-range order brought about by the presence of small metal nanoparticles well dispersed over the TNTAs with strong electronic interactions between the metal and support.<sup>32</sup>

The photochemical properties of anatase highly depend on the purity of the material and particularly on the oxidation state of the titanium and the presence of oxygen vacancies. To investigate this aspect, we have acquired X-ray photoelectron spectra (XPS) on the TNTA-web nanotube arrays with 0.1 mg cm<sup>-2</sup> Pd metal loading. Fig. 6(B) shows the Ti 2p region. Binding energies are 458.8 for Ti  $2p_{3/2}$  and 464.4 eV Ti  $2p_{1/2}$  respectively. These values are those expected for Ti<sup>4+</sup> in TiO<sub>2</sub>. We have not detected any other titanium species (Ti<sup>3+</sup> and Ti<sup>2+</sup>  $2p_{3/2}$  are expected at 457.6 and 456.4 eV respectively). The Pd signals shown in Fig. 6C confirm that the Pd NPs exist mainly in the metallic state.

The optical properties of the materials based on TNTA-web were analysed by Diffuse Reflectance UV-vis spectroscopy (Fig. 7). The samples show a strong light absorption in the UV range, with a significant absorption in the visible range depending on sample composition. TNTA-web revealed only a shoulder in visible light absorption above 400nm, probably related to residual fluoride ions adsorbed from the liquid bath used during growth of TiO<sub>2</sub> nanotube array. After loading with Pd, light absorption in the visible range above 400 nm strongly increases, proportionally to the Pd loading. The band-gap of the materials is 3.0 - 3.1 eV, in agreement with the formation of anatase phase in TiO<sub>2</sub> nanotubes.



**Fig. 7** Diffuse Reflectance UV-vis spectra of TNTA-web and relevant Pd-loaded samples.

Catalytic experiments with simulated solar radiation



**Fig. 8** Hydrogen production by photoreforming in a 1:1 water/ethanol solution. Comparison between nanotutbes on the web and on the foil, with and without the addition of Pd (A); comparison between the activity of the nanotubes on the web with different Pd loadings (B); Solar-to-Fuel Efficiency dependence on Pd loading (C).

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The photoreforming activity of each of the catalyst materials was studied in a 1:1 volume solution of water and ethanol, under simulated solar irradiation using a 150 W Xe lamp equipped with a cut-off filter at 300 nm. The resulting radiating power flux at the sample surface was 25 mW cm<sup>-2</sup> in the UV range and 180 mW cm<sup>-2</sup> in the visible range. Firstly, we have tested and compared the TNTA-web and TNTA-foil materials without Pd and with a 0.10 mg cm<sup>-2</sup> loading of Pd nanoparticles (Fig. Fig. 8A). The TNTA-web produced a stable hydrogen production around 40 mmol h<sup>-1</sup> m<sup>-2</sup>. Interestingly, the H<sub>2</sub> production from the TNTA-foil is below the detection limits of the analytical system employed. With the addition of Pd onto the TNTA-foil, solar driven production of hydrogen does occur (~ 10 mmol  $h^{-1} m^{-2}$ ). This level of hydrogen production is still much lower than that observed with the TNTA-web free of any added metal. Indeed, with the addition of 0.10 mg cm<sup>-2</sup> of Pd to the TNTA-web material the hydrogen production rate increased to 130 mmol h<sup>-1</sup> m<sup>-2</sup>.

These results indicate that the dual scale porosity of the TNTAweb structure greatly increases the hydrogen production compared to the TNTAs grown on a flat foil. This result is derived from the unique properties related to the dual scale porosity of the TNTA-web materials. The formation of TiO<sub>2</sub> nanotubes with a diameter around 100 nm around the Ti fibres of the web guarantees a high surface area for the dispersion of the metal nanoparticles and to interact with the sacrificial agent (ethanol). Moreover, the intricate network of the Ti web allows a good exposure to incoming light. As a confirmation of this, a reference material prepared growing the same TiO<sub>2</sub> nanotubes grown on a flat Ti foil (therefore having only the porosity due to the nanotubes) showed lower activity in H<sub>2</sub> production from ethanol photoreforming.

For the TNTA-web material, we have also investigated the effect of the amount of Pd loading on the hydrogen production rate. Using the TNTA-web material, we have prepared samples with 0.025, 0.10, 0.50 and 1.00 mg  $\text{cm}^{-2}$  of Pd. Considering the mass of the web support, this corresponds to weight percentages of 0.065, 0.26, 1.3 and 2.6 % respectively. The data (Fig. 8B) shows a maximum of hydrogen productivity is achieved with the 0.10 mg  $\text{cm}^{-2}$  loading of Pd. At higher Pd loadings the production rate drops. The activity with the highest Pd loading of 1.0 mg cm<sup>-2</sup> is lower than the sample containing 4 times less palladium. This behaviour indicates that an optimum metal content exists to achieve the highest H<sub>2</sub> production activity. In agreement with H<sub>2</sub> production rates, Solar-to-Fuel Efficiency (SFE) shows a maximum (0.45%) for the Pd content of 0.10 mg (Fig. 8C). Notably, selected experiments have been performed introducing a cut-off filter at 420 nm on the light beam, therefore irradiating the photocatalysts only with visible light.

Investigation of the reaction by-products of ethanol photoreforming by GC/MS analysis of the solution recovered after photocatalytic tests revealed the presence of acetaldehyde and 1,1-diethoxyethane. This last species is formed by acetalization of acetaldehyde with the excess of ethanol, confirming that acetaldehyde is the major by-product of  $H_2$  production from ethanol. No other by-products have

been detected in both the gas phase (e.g.  $CH_4$ ,  $CH_2CH_2$ ,  $CH_3CH_3$ , CO,  $CO_2$ ) or liquid phases (e.g. acetic acid, 2,3dihydroxybutane), confirming that these compounds are formed only when more intense UV radiation is used.<sup>5</sup> Therefore, the photodegradation of ethanol to acetaldehyde is the major process involved in hydrogen evolution.

Increasing the Pd loading leads to an increase in the particle size where more and more of the Pd atoms reside in the bulk rather than on the surface where the electrochemical reactions occur. Indeed the coverage and average Pd nanoparticle size increases significantly with 1.0 mg cm<sup>-2</sup> loading (Fig. 9). In this image, it is clear that there is a high coverage of Pd agglomerates on the TNTA surface. The increase of size of metal nanoparticles with the metal loading has been already observed in other photocatalysts.<sup>8</sup>



**Fig. 9** SEM images of the Pd/TNTA-web with 1 mg cm<sup>-2</sup> of Pd nanoparticles. The insert shows a statistical particle size count distribution.

To understand the enhancement bought about by the presence of Pd NPs, we must consider how the photoreforming reaction proceeds on both metal free  $TiO_2$  and Pd- $TiO_2$  surfaces. Ethanol (and, in general, alcohols) is adsorbed on the surface of  $TiO_2$  in a dissociative way, forming ethoxide ions bound to uncoordinated Ti centres and surface OH groups:<sup>33</sup>

$$CH_3CH_2OH \xrightarrow{TiO_2} CH_3CH_2O_{(ads)}^- + OH_{(ads)}$$

After absorption of a photon with adequate energy, charge carriers (electrons and holes) are generated.  $H_2$  is evolved by reduction of protons from surface OH groups consuming the photogenerated electrons:

$$2 \text{ OH}_{(ads)} + 2 \text{ e}^{-} \xrightarrow{\text{TiO}_2} \text{H}_{2 (g)}$$

At the same time, holes in the valence band react with adsorbed ethoxide ions removing one proton from  $C\alpha$  and forming new OH groups on the surface of  $\text{TiO}_2$  and acetaldehyde:

$$CH_3CH_2O_{(ads)}^- + h^+ \xrightarrow{TiO_2} CH_3CHO + OH_{(ads)}$$

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This product is very weakly adsorbed on the surface of an oxide and is released into the solution, where it undergoes acetalization with the excess ethanol present.

In this context, Pd nanoparticles play different roles in enhancing the photoreforming process. They are directly involved in the draining of photogenerated electrons from conduction band of TiO<sub>2</sub> to their Fermi level, favouring charge separation and increasing  $e^{-}/h^{+}$  pairs lifetime. Being accumulated on Pd nanoparticles, e easily react with OH groups on the TiO<sub>2</sub> support at the interface, forming H atoms adsorbed on the metal surface, from which H<sub>2</sub> evolution to the gas phase proceeds very fast. Moreover, Pd nanoparticles can be reasonably involved in the activation of the C-H bond during abstraction of H from  $C\alpha$  of adsorbed ethoxide ions, a key step in the oxidation semireaction of the photoreforming process. Despite the absorption of light in the visible range that happens with the presence of added Pd nanoparticles (Fig. 7), the data reported here suggest that this is not an effective way for activation of the photocatalyst, since no activity is observed using a cut-off filter at 420nm. Activation of photocatalysts by visible light through excitation of surface plasmon bands is a well know process for Au-based photocatalysts<sup>34, 35</sup> while it is still the object of debate when Pd nanoparticles are present in the photocatalyst <sup>36,37,38,39</sup> Considering all this evidence, we believe that activation of the present photocatalysts takes place through the excitation of TiO<sub>2</sub> component of the material.

The increase in Pd loading leads to the formation of larger nanoparticles and aggregates. This can work negatively on the photochemical activity in two ways. Firstly, the accumulated Pd particles reduce the amount of light radiation reaching the TNTA surface, decrease the amount of  $e^-/h^+$  couples formed in the photoactive material. Secondly, larger/aggregated Pd nanoparticles reduce the extension of the Pd-TiO<sub>2</sub> interface, where the activation of ethoxide species take place with the help of Pd metal surface. From the data reported in fig 4B we have calculated the Solar-to-Fuel efficiency for each of the TNTA-web samples with various Pd loadings.<sup>28</sup> We have found (Fig. 8C) a maximum value of 0.45% was obtained for the sample with 0.1 mg cm<sup>-2</sup> Pd while bare TNTA-web delivered a conversion of 0.13% efficiency.

#### Conclusions

In this article, a dual porosity TNTA-web material has been employed for the sustainable production of hydrogen by ethanol photoreforming, achieving highly efficiency under sunlight irradiation. By comparison, TNTAs grown on a flat titanium foil show no activity under solar irradiation, demonstrating that the enhanced activity of the web material is due to increased harvesting of light. The addition of Pd nanoparticles to TiO<sub>2</sub> materials is well known to drive H<sub>2</sub> evolution from alcohols. A small amount of Pd NPs deposited on both TNTA supports enhances H2 evolution in both cases. The TNTA-web with 0.1 mg cm<sup>-2</sup> of Pd reaches a H<sub>2</sub> production rate of 130 mmol h<sup>-1</sup> m<sup>-2</sup> with a Solar-to-Fuel efficiency of 0.45%. The Pd nanoparticles are small (mean size ~ 4 nm) and well distributed, maximizing the Pd-TiO2 interfaces where the photocatalytic reactions occur. The small Pd NPs enhance the overall activity by promoting both the conversion of  $H^+$  to  $H^2$  (using photogenerated e<sup>-</sup>) and the ethanol oxidation reactions (involving the photogenerated h<sup>+</sup>). At higher metal loadings, aggregates of Pd NPs are formed, resulting in a negative effect on the photocatalytic activity as the amount of active interface is reduced and the extended Pd aggregates block incident light from penetrating into the TNTA-web structure. What this investigation has shown is that improvements in H<sub>2</sub> generation efficiency by solar light driven photoreforming with ethanol can be obtained by applying known components (e.g. Pd and TiO<sub>2</sub>) in new and innovative synergies.

#### **Conflicts of interest**

There are no conflicts to declare.

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#### Notes and references

- G. L. Stephens, J. Li, M. Wild, C. A. Clayson, N. Loeb, S. Kato, T. L'Ecuyer, P. W. Stackhouse Jr, M. Lebsock and T. Andrews, *Nat. Geosci.*, 2012, 5, 691.
- 2 K. Srirangan, L. Akawi, M. Moo-Young and C. P. Chou, Appl. Energy, 2012, 100, 172.
- 3 X. G. Zhu, S. P. Long and D. R. Ort, Curr. Opin. Biotechnol., 2008, **19**, 153.
- 4 A. Demirbas, Appl. Energy, 2009, **86**, Supplement 1, S108.
- 5 A. Beltram, M. Melchionna, T. Montini, L. Nasi, P. Fornasiero and M. Prato, Green Chem., 2017, **19**, 2379.
- A. Gallo, T. Montini, M. Marelli, A. Minguzzi, V. Gombac, R. Psaro, P. Fornasiero and V. Dal Santo, Chemsuschem, 2018, 5, 1800.
- 7 D. Barreca, G. Carraro, V. Gombac, A. Gasparotto, C. Maccato, P. Fornasiero and E. Tondello, Adv. Funct. Mater., 2011, 21, 2611.
- 8 T. Montini, V. Gombac, L. Sordelli, J. J. Delgado, X. Chen, G. Adami and P. Fornasiero, Chemcatchem, 2011, **3**, 574.
- 9 K. C. Christoforidis and P. Fornasiero, Chemcatchem, 2017, 9, 1523.
- 10 D. I. Kondarides, A. Patsoura and X. E. Verykios, J. Adv. Oxid. Technol., 2010, **13**, 116,
- 11 N. Armaroli and V. Balzani, Chemsuschem, 2011, 4, 21.
- 12 V. Balzani, A. Credi and M. Venturi, Chemsuschem, 2008, 1, 26.
- 13 N. S. Lewis and D. G. Nocera, P. Natl. Acad. Sci. USA, 2006, 103, 15729.
- V. Gombac, L. Sordelli, T. Montini, J. J. Delgado, A. Adamski, G. Adami, M. Cargnello, S. Bernal and P. Fornasiero, J. Phys. Chem. A, 2010, **114**, 3916.
- 15 A. V. Puga, Coord. Chem. Rev., 2016, 315, 1.
- 16 M. Bowker, Catal. Lett., 2012, 142, 923.
- 17 T. Kawai and T. Sakata, Nature, 1980, 286, 474.
- 18 J. Goldemberg, Science 315, 808 (Feb 9, 2007).

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Journal Name

- 19 A. B. Aritonang, H. Surahman, Y. K. Krisnandi and J. Gunlazuardi, Material Chemistry Development for Future Medicine, Industry, Environmental and Biomaterial Application, 2017, **172**.
- 20 Slamet, Ratnawati, J. Gunlazuardi and E. L. Dewi, Int. J. Hydrogen Energy, 2017, **21**, 24014.
- 21 X. M. Zhou, N. Liu and P. Schmuki, Acs Catal., 2017, 7, 3210.
- 22 I. Paramasivam, H. Jha, N. Liu and P. Schmuki, Small, 2012, **8**, 3073.
- 23 R. P. Lynch, A. Ghicov and P. Schmuki, J. Electrochem. Soc., 2010, **157**, G76.
- 24 Y. X. Chen, A. Lavacchi, S. P. Chen, F. di Benedetto, M. Bevilacqua, C. Bianchini, P. Fornasiero, M. Innocenti, M. Marelli, W. Oberhauser, S. G. Sun and F. Vizza, Angew. Chem., Int. Ed., 2012, **51**, 8500.
- 25 Y. X. Chen, A. Lavacchi, H. A. Miller, M. Bevilacqua, J. Filippi, M. Innocenti, A. Marchionni, W. Oberhauser, L. Wang and F. Vizza, Nat. Commun., 2014, 5, 4036.
- 26 T. Stoll, G. Zafeiropoulos and M. N. TsampasInt Int. J. Hydrogen Energy, 2016, **41**, 17807.
- 27 Y. Chen, M. Bellini, M. Bevilacqua, P. Fornasiero, A. Lavacchi1, H. A. Miller, L. Wang and F. Vizza, Chemsuschem, 2015, 8, 524.
- 28 G. Carraro, C. Maccato, A. Gasparotto, T. Montini, S. Turner, O. I. Lebedev, V. Gombac, G. Adami, G. Van Tendeloo, D. Barreca and P. Fornasiero, Adv. Funct. Mater., 2014, 24, 372.
- 29 Y. Ou, J. D. Lin, S. M. Fang and D. W. Liao, Chem. Phys. Lett., 2006, **429**, 199.
- 30 M. C. Yan, F. Chen, J. L. Zhang and M. Anpo, J. Phys. Chem. B, 2005, **109**, 8673.
- 31 U. Balachandran and N. G. Eror, J. Solid State Chem., 1982, **42**, 276.
- 32 A. A. Melvin, K. Illath, T. Das, T. Raja, S. Bhattacharyya and C. S. Gopinath, Nanoscale, 2015, 7, 13477.
- 33 Y. Z. Yang, C. H. Chang and H. Idriss, Appl. Catal., B, 2006, 67, 217.
- 34 J. B. Priebe, M. Karnahl, H. Junge, M. Beller, D. Hollmann, A. Brückner, Angew. Chem. Int. Ed., 2013, 52, 11420.
- 35 S. Wang, Y. Gao, S. Miao, T. Liu, L. Mu, R. Li, F. Fan, and C. Li, J. Am. Chem. Soc. 2017, **139** (34), 11771.
- 36 M. A. Nadeem, M. Al-Oufi, A. K. Wahab, D. Anjum and
- 37 H. Idriss, ChemistrySelect 2017, 2, 2754.
- 38 J. Zou, Z. Si, Y. Cao, R. Ran, X. Wu, and D. Weng, J. Phys. Chem. C 2016, **120**, 29116.
- 39 W. Yang, Y. Xiong, L. Zou, Z. Zou, D. Li, Q. Mi, Y. Wang, and Hui, Nanoscale Res. Lett. 2016, **11**, 283.
- 40 C. A. Emilio, M. I. Litter, M. Kunst, M. Bouchard and C. Colbeau-Justin, Mater. Sci. Mater. Electron. 2017, 28, 16718.



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