# Photocatalytic and photoelectrocatalytic H$_2$-evolution combined with valuable furfural-production onTiO$_2$ supports

Claudio Maria Pecoraro, Marianna Bellardita*, Vittorio Loddo, Danilo Virtù, Francesco Di Franco, Monica Santamaria

Engineering Department, University of Palermo, Viale delle Scienze Building 6, 90128, Palermo, Italy.

Corresponding author: Marianna Bellardita (e-mail: marianna.bellardita@unipa.it)

ABSTRACT

In this work the photocatalytic (PC) and photoelectrocatalytic (PEC) reforming of furfuryl alcohol (FA) under environmental friendly conditions was investigated. Both H$_2$ evolution and partial oxidation to furfuraldehyde were followed. For the first time TiO$_2$ based photocatalysts were studied and the photocatalytic activity of home prepared photocatalysts was compared with that of commercial ones under both UVA and simulated solar irradiation. PEC tests were performed by using home prepared TiO$_2$ nanotubes (TiO$_2$ NTs) as photoanode and Pt free Ni foam as cathode to improve the Hydrogen Evolution Reaction (HER). Both the partial FA oxidation reaction rate and H$_2$ evolution rate were normalized for the lamp specific power to account for the different photon flux and the rates were higher for PEC process. PEC is a promising strategy for the valorization of biomasses with simultaneous H$_2$ production in spite of the cost of the bias.

1. Introduction

In the last decades, there has been a growing interest in renewable energy sources, due both to the almost exhaustion of the fossil fuels currently used, and to the growth of environmental pollution [1,2]. The use of renewable sources can efficiently contribute to the

1

resolution of these issues, since they can be used to produce hydrogen, a clean energy carrier, whose combustion with oxygen only produces water [3–5].

The reforming of renewable biomass into fuels and high value chemicals is an ideal and sustainable alternative to the use of fossil resources [6–11], for instance furfuryl alcohol (FA) can be upgraded to furaldehyde, one of the top value added chemicals from biomass according to the U.S. Department of Energy [12], and/or 2-furoic acid in order to produce pharmaceutical intermediates [13–16].

A survey of the published literature on partial oxidation of FA and simultaneous hydrogen production reveals that it can be achieved by both photocatalytic and electrochemical processes. Li et al. [17] fabricated a heterostructure of $LaVO_4/CN$ for efficient photocatalytic $H_2$ evolution, 0.287 mmol $g^{-1}$ $h^{-1}$, coupled with a furfural production of 0.95 mmol $g^{-1}$ $h^{-1}$, while Wang et al. [18] prepared $H_{1.4}Ti_{1.65}O_4 \cdot H_2O$ nanosheet as a photocatalyst for the oxidation of FA, obtaining FA conversion of 54 % and furfural selectivity of 99% after 6 h of irradiation. In both cases the authors did not mention if catalyst can be recovered after the process and re-used for subsequent runs.

Conversely, Fang et al. [15] investigated the possibility to carry out partial oxidation of FA by an electrochemical process. Their investigation revealed that the reaction can be successfully performed using an anode constituted by CuO nanorods in the applied potential range of 1.35 – 1.39 V versus the RHE. Under these experimental conditions a Cu(III) intermediate is released into the electrolyte that selectively oxidizes FA to furfural. However, in spite the very high selectivity and faradic efficiency, the drawback of this process is that a copper oxide sacrificial anode is necessary and that copper ions can be competitive at the cathode since they have a more positive standard potential with respect to water reduction, thus decreasing the faradic efficiency for $H_2$ production.

The aim of this work is to optimize an integrated PEC process for partial oxidation of furfuryl alcohol to furfuraldehyde in aqueous solution with the contemporary $H_2$ evolution under environmental friendly conditions exploiting advantages and limits of photocatalysis, and evaluating the potential of photoelectrochemical method.

As regards heterogeneous photocatalysis, we tried to boost the photocatalytic properties of semiconductors containing different $TiO_2$ polyforms. Although titanium dioxide is the most widely used photocatalyst in the various applications in the photocatalytic field, in the literature there are no reports on its use in this reaction. There are only a few papers on the use of some complex catalysts alternative to $TiO_2$ [14,16,19] often used in the presence of organic solvents. Many studies, instead, investigated the reverse reaction, i.e. the

hydrogenation of furfural to furfuryl alcohol, with $H_2$ consumption [20–24]. In particular, in this work the photocatalytic activity of $TiO_2$-based photocatalysts prepared in the laboratory was compared with that of commercial samples.

Photocatalytic runs were carried out under both UVA and simulated solar light irradiation. The influence of the presence of some metal species (Pt, Cu, W, Nb) and pH on the photocatalytic activity and product selectivity were investigated with the aim to improve the performance of bare $TiO_2$. Heterogeneous photocatalysis, under ambient conditions and in the presence of sunlight irradiation, represents one of the cleanest ways to obtain $H_2$. Moreover, the use of biomass derived products as sacrificial agents allows to increase the hydrogen production (reducing the $e^-/h^+$ recombination and decreasing the energy of the process) and to contemporaneously obtain value added products [25–27].

Photoelectrocatalytic tests were carried out using home prepared $TiO_2$ nanotubes as photoanode and Ni foam as cathode.

Surface, morphological and bulk characterizations of catalysts were carried out by means of the acquisition of X-ray diffraction (XRD) patterns, Raman spectra, UV−vis reflectance spectra, specific surface area (S.S.A.) determinations, scanning electron microscopy (SEM) and EDX analyses.

## 2. Experimental

### 2.1. Samples preparation

Various $TiO_2$-based catalysts containing different crystalline phases have been prepared under different experimental conditions, in order to obtain different polymorphic forms of $TiO_2$. Titanium tetrachloride ($TiCl_4$ Sigma-Aldrich 98%), titanium(IV) isopropoxide (TTIP, Aldrich ≥ 97%), ethanol (Sigma-Aldrich), HCl (Sigma-Aldrich 37%), Pluronic P127 (Sigma-Aldrich), $PtCl_4$ (BDH Chemicals), CuCl (Sigma-Aldrich), $NbCl_5$ (Sigma-Aldrich) and $WCl_6$ (Sigma-Aldrich) were used as received for the synthesis of different $TiO_2$ based photocatalysts. Pt and in some cases W, Nb and Cu have been sometimes added to $TiO_2$ to improve its performance. In particular, Pt was chosen because it demonstrated excellent activity for $H_2$ formation from aqueous solution [28,29], Cu was effective in replacing Pt in reduction reactions as in the $CO_2$ valorization [30,31] and photoreforming processes [32–34] whilst W, Nb improve the charges separation efficiency and enhance the selectivity in partial oxidation reactions [35–38].

Commercial Anatase BDH and Aeroxide P25 $TiO_2$ were used in order to compare them with home prepared photocatalysts and were referred in this article as Anatase and P25.

The brookite was obtained by thermal hydrolysis of $TiCl_4$ in aqueous solution of HCl, specifically 10 ml of $TiCl_4$ were slowly added to a solution containing 420 ml of water and 160 ml of concentrated HCl. Then the solution was transferred into a Pyrex glass bottle and heated to 373 K for 48h, thus obtaining a precipitate containing a mixture of brookite and rutile. The brookite was separated by peptization by adding water at different times and removing the supernatant in which the brookite was selectively dispersed. HP-B was the code used for this sample. Brookite samples containing Cu (code Cu-HP-B, B= Brookite) or Nb (code Nb-HP-B, B= Brookite) in different weight percentages were obtained by adding a certain quantity of CuCl or $NbCl_5$ to the solution of $TiCl_4$ in HCl before being transferred to the oven.

Another $TiO_2$ photocatalyst was synthesized by adding 29 ml of TTIP to a solution containing 230 ml of ethanol, 27 ml of $H_2O$, 4 ml of HCl and 5.5 g of Pluronic F127 (Poloxamer 407). A white suspension was obtained which was kept for 24 hours at 313 K to evaporate the solvent. The final solid was dried 24 hours at 383 K and subsequently calcined 24 hours at 773 K. This sample was named as HP-AR (A=Anatase, R=Rutile). For the preparation of the photocatalyst with 1 wt%  of W an adequate amount of $WCl_6$ was added to the ethanolic solution before adding TTIP. The code W- HP-AR identifies this sample.

The pure rutile was prepared by adding 10 ml of $TiCl_4$ to 50 ml of distilled water under stirring at room temperature, the solution obtained was placed in a closed Pyrex bottle and then inside an oven at 373 K for 48h, the final solid was recovered by vacuum drying at 323 K. HP-R was the code used for this sample.

$TiO_2$ samples were loaded with 0.5 wt% Pt by the photodeposition method using $PtCl_4$. In a 500 ml Pyrex photoreactor, 200 ml of $H_2O$, 50 ml of ethanol, 1 g of $TiO_2$ and the right amount of $PtCl_4$ were added. $N_2$ was bubbled for 30 minutes in the dark to de-aerate the solution and for about 8 h under irradiation to allow metallic Pt deposition. The powders were recovered by evaporating the solution at 323 K. When Pt was present the code was accordingly modified inserting the symbol of the metal.

According to previous work [39], $TiO_2$ nanotubes ($TiO_2$ Nts) used in photoelectrocatalytic tests were prepared through anodizing process. Titanium foils (Sigma Aldrich, purity > 99.7%) with 0.127 mm thickness were properly cut and etched in a mixture of hydrofluoric acid (Sigma Aldrich, purity 39.5%), nitric acid (Sigma Aldrich, purity 69.0%) and deionized water with a volume ratio of 1:1:3 respectively for 15 seconds, then ultrasonically cleaned in

acetone and ethanol for 5 minutes each and rinsed with deionized water. Samples were used after being dried in air. $TiO_2$ Nts were formed in an ethylene glycol (Aldrich, 99.8% anhydrous) solution containing 0.25 wt% $NH_4F$ (Sigma Aldrich) and 0.75 wt% deionized water. Anodizing was conducted in a two-electrode configuration using aluminum foil as cathode and potential was kept constant during anodizing at 45 V for 10 minutes. Soon after the anodizing process, a thermal treatment was performed in order to induce crystallization in the $TiO_2$ Nts. The layers were heated up to 450°C under air exposure and kept for 3 hours at high temperature and left cooling in the furnace. Such a low annealing time was chosen to try to have a thin and not very blocking thermal oxide between bare titanium and tubes. Ni foam was used as cathode in the PEC runs as received.

## 2.2. Samples characterization

X-Ray diffraction (XRD) patterns of the photocatalysts were acquired by a PANalytical Empyrean diffractometer at room temperature equipped with a PIXcel1D (tm) detector. Measures were executed at a 2θ scan rate of 3°/min, tube voltage of 40 kV, current of 40 mA and using the CuKα radiation.

Raman spectra were collected by a Raman Microscope coupled with a Leica DMLM microscope. The laser has been focused on the sample by a 5x magnification lens in order to obtain an analyzing spot diameter around 50 microns, with a maximum laser power of 133 mW on the sample. Only the 10% of maximum power has been used in these measurements and the power was reduced by holographic filters; for each sample three spectra have been recorded using a 532 nm laser coupled with a 2400 lines per millimeter grating resulting in a spectral resolution equal to 0.5 $cm^{-1}$. Each measurement consists of two accumulations.

UV–Vis spectroscopy was used in order to study the optical properties of the samples. The Diffuse Reflectance Spectra (DRS) were acquired by using a Shimadzu UV-2401 PC spectrophotometer in the 200–800 nm wavelength at room temperature and pressure. $BaSO_4$ was used as the reference sample. The plots of the modified Kubelka-Munk function, $[F(R'_\infty)h\nu]^{1/2}$, versus the energy of the exciting light were used for the calculation of band gap values.

Flow Sorb 2300 apparatus (Micromeritics) was used for the estimation of the specific surface areas (SSA) of the powders by using the single-point BET method. The samples were degassed for 30 min at 523 K before the measurement.

Scanning electron microscopy (SEM) images were obtained by using a FEI Quanta 200 ESEM microscope operating at 30 kV, a thin layer of gold was deposited on specimens before the shooting. An electron microprobe used in an energy dispersive mode (EDX) was employed to obtain information on samples composition.

## 2.3.    Tests

The photocatalytic activity was determined in a 250 mL Pyrex cylindrical reactor illuminated by a 125 W UV lamp axially immersed within the photoreactor. $N_2$ was bubbled into the 150 mL aqueous suspensions for ca. 0.5 h under dark to de-aerate the solution, then the reactor was sealed, and the lamp switched on. The best photocatalysts were tested also under 50 W halogen lamp simulating the solar light irradiation. The initial furfuryl alcohol (FA) concentration was 1 mM.

The amount of the used photocatalyst was different as for every powder the quantity sufficient to absorb the 90 % of the photons emitted by the lamp was determined. It varied in the range 0.3-0.8 $g \cdot L^{-1}$ depending on the sample used (0.3 g $L^{-1}$ for P25, 0.8 g $L^{-1}$ for BDH and 0.6 g $L^{-1}$ for all of the other samples) [40].

Photoelectrocatalytic tests were carried out in a 450 mL undivided glass three electrodes cell using Ni foam as cathode, $TiO_2$ Nts as anode and an Ag/AgCl as reference electrodes. The solution was illuminated externally by six UVA fluorescent lamps with a maximum wavelength of 365 nm (8 W) and $N_2$ was bubbled into 150 mL aqueous solution for ca. 0.5 h in order to de-aerate the solution. A CH Instrument 630B Series potentiostat was used to control the cell potential.

For photoelectrocatalytic tests 0.5 M $Na_2SO_4$ was used as electrolyte (pH ~ 7) and the applied potential was 0.5 V vs Ag/AgCl.

The selectivity of the oxidation reaction and the faradic efficiency of both anodic and cathodic processes were studied. Determination of FA and reaction intermediates concentration was performed by using a Thermo Scientific Dionex UltiMate 3000 HPLC equipped with a Diode Array detector and a REZEK ROA Organic acid $H^+$ column. Gaseous species accumulated in the reactor headspace were analyzed by a HP 6890 Series GC system equipped with a Supelco GC 60/80 CarboxenTM-1000 packed column and thermal conductivity detector.

FA conversion and selectivity and yield towards the formed products were calculated with the formulas in Eqns. 1 – 3, respectively:

Eqn. 1)
$$Conversion\ [\%] = \frac{Amount\ of\ FA\ reacted\ [mmol]}{Amount\ of\ initial\ FA\ [mmol]}\ x\ 100$$

Eqn. 2)
$$Selectivity_i\ [\%] = \frac{Amount\ of\ product\ i\ formed\ [mmol]}{Amount\ of\ FA\ reacted\ [mmol]}\ x\ 100$$

Eqn. 3)
$$Yield_i\ [\%] = \frac{Amount\ of\ product\ i\ formed\ [mmol]}{Amount\ of\ initial\ FA\ [mmol]}\ x\ 100$$

For each product, in the case of PEC tests, the faradic efficiency was calculated through Eqn. 4:

Eqn. 4)
$$Faradic\ efficiency_i\ [\%] = \frac{Amount\ of\ product\ i\ formed\ [mol]}{\frac{Q\ [Couloumb]}{z\ F\ \left[Couloumb/_{mol}\right]}}\ x\ 100$$

Where:

- i is the product
- Q is the circulated charge
- z are the electrons exchanged during the partial oxidation, 2 for furfural and 4 for 2-furoic acid
- F is the Faraday constant of 96485 [Couloumb/mol]

3. Results and discussion

3.1.  Samples characterization

Selected diffractograms of some of the photocatalysts used are reported in Fig. 1. The XRD patterns confirmed the presence of the different crystalline phases of $TiO_2$ in the samples [41]. The indications of the characteristic peaks of the three main polymorphs of $TiO_2$: A = Anatase, B = Brookite, R = Rutile are shown. The peaks at $2\theta$ = 25.5°, 38.0°, 48.0°, 54.5° are characteristic of anatase, those at $2\theta$ = 27.5°, 36.5°, 41°, 54.1°, 56.5° of rutile and those at $2\theta$ = 25.34°, 25.69°, 30.81° of brookite. Commercial samples BDH and P25 consist of pure anatase and a mixture of anatase and rutile respectively, while those prepared in the laboratory present the different phases of $TiO_2$: brookite (B), rutile (R) and an anatase-rutile

7

(AR) mixture. The photodeposition of platinum or the addition of small amounts of Cu or Nb did not cause changes in the diffractograms due to their low quantity.

The peaks of commercial photocatalysts are more intense than those of the prepared ones, indicating a greater crystallinity of the former due to the higher temperature at which they were prepared. Nevertheless, photocatalysts displaying a low crystallinity present, generally, a low oxidant power and this feature is beneficial in the partial oxidation reactions as previously demonstrated [42–44]. Consequently, home prepared low crystalline powders deserve to be prepared and tested.

In Fig. 2 a) and b) the Raman spectra of pure brookite are compared with those of brookite containing different percentages of Nb and Cu. Due to their small quantity and their high degree of dispersion in the $TiO_2$ matrix, the doping species did not make changes in the characteristic bands of brookite. In Fig. 2 c) the Raman spectra of some of the samples used are shown. Anatase shows characteristic bands at 144, 196, 397, 513 and 639 cm$^{-1}$, rutile at 447 and 612 cm$^{-1}$ and brookite at approx. 153, 323, 366, 413, 459, 500, 545, 584 and 633 cm$^{-1}$. Also in this case, the addition of Pt did not change the spectra of the different types of $TiO_2$.

Figures 3 a) – c) show the reflectance spectra of the catalysts. For the bare BDH sample (Fig. 3 a) we note the typical shape of the anatase $TiO_2$ with an absorption edge at around 360 nm due to the transition of the photoexcited electrons from the valence band to the conduction band edge. Samples consisting of an anatase-rutile mixture (P25 and HP-AR) show a slight shift towards higher wavelengths due to the smaller band-gap of rutile compared to that of anatase. In all samples, the addition of Pt increases the absorption of light in the visible region without affecting the band-gap. The addition of tungsten (Pt-W-HP-AR) moves the absorption even more towards greater wavelengths.

In the presence of Cu, Fig. 3 b, the typical form associated with the presence of Cu species can be seen, and the increase in absorption between 400 and 600 nm which can be attributed to the d-d transition that occurs in $Cu^{2+}$ ions [45]. No variation can be noticed, however, following the addition of Nb.

The band gap values, calculated using the modified Kubelka Munck function are shown in Table 1. The $TiO_2$-based photocatalysts are all active under UV-visible light irradiation having band gap values ranging from 3.30 at 2.92 eV.

Pure $TiO_2$ showed band gap values typical of the different $TiO_2$ polymorphs, which are little influenced by the photodeposition of Pt and by the addition of metal species.

The S.S.A. of the used samples (Table 1) ranges between 10 and 100 $m^2\,g^{-1}$ and the lowest values were found for the commercial powders. Generally, no significant variations, with respect to the corresponding naked $TiO_2$, were noticed after the Pt photodeposition whilst a little decrease was, sometimes, observed after the introduction of the other metal species. Then the different photoactivity of the various photocatalyst cannot be strictly related to the S.S.A. values.

Table 1 Phase composition, band-gap (Eg), specific surface areas (S.S.A.) of the prepared samples. A = Anatase, R = Rutile; B = Brookite.

| Sample | Phase | $E_g$ (eV) | S.S.A. $(m^2g^{-1})$ |
|---|---|---|---|
| P25 | A, R | 3.18 | 50 |
| Pt-P25 | A, R | 3.10 | 50 |
| BDH | A | 3.20 | 10 |
| Pt-BDH | A | 3.26 | 10 |
| HP-AR | A, R | 2.92 | 73 |
| W- HP-AR | A, R | 2.96 | 79 |
| Pt- HP-AR | A, R | 2.98 | 78 |
| Pt-W-HP-AR | A, R | 3.10 | 67 |
| Pt-HP-R | R | 2.98 | 85 |
| Pt-W-R | R | 3.00 | 65 |
| HP-B | B | 3.26 | 100 |
| 1Cu- HP-B | B | 3.18 | 92 |
| Pt- HP-B | B | 3.30 | 98 |
| Pt-0.5Cu-HP-B | B | 3.30 | 96 |
| Pt-1Cu-HP-B | B | 3.29 | 92 |
| Pt-2Cu-HP-B | B | 3.32 | 86 |
| Pt-0.5Nb-HP-B | B | 3.30 | 76 |
| Pt-1Nb- HP-B | B | 3.30 | 90 |
| Pt-2Nb- HP-B | B | 3.33 | 72 |

SEM images (Figure 4 a) – e)) revealed that the different photocatalysts are constituted of aggregates of irregular spherical small particles which dimensions ranging between 100 and 500 nm. The particles sizes of home-made samples are smaller than those of commercial ones, due the lower synthesis temperature.

The addition of Pt or metal species did non influence the shape and the dimensions of the particles due to their low amount with respect $TiO_2$. EDX analyses (not reported for the sake of brevity) confirmed the presence of foreign species in quantities corresponding to the nominal ones.

## 3.2. Photocatalytic process

Table 2 shows the results of the photocatalytic tests performed with the UV lamp and the open reactor in terms of alcohol conversion and selectivity towards furfural, which was the main identified reaction product. In fact, only traces of 2-furoic acid and some peaks related to unknown intermediates were found in the reaction mixture. The activity of commercial samples P25 (anatase-rutile mixture) and BDH (anatase) was investigated at different pHs in order to identify the best operating conditions and compared with that of laboratory-prepared catalysts.

Tests were carried out at the "natural" pH of the solution (6.7) and at both acidic (pH = 2 for HCl) and alkaline (pH = 10 for NaOH) conditions. The alcohol conversion in the presence of P25 showed the following trend: pH = 2 > pH = 10 > pH = 6.7 and the selectivity decreased as the conversion increased. A higher conversion derives from a greater oxidizing power of the catalyst which indistinctly oxidizes both the furfuryl alcohol and the formed furfural with a consequent low selectivity. The increased activity at pH 2 and 10 can be attributed to the formation of Cl· and OH· radicals, respectively [46]. It is not easy to correlate the photoactivity to the variation of the pH of the solution due to the occurrence of different phenomena related both to the organic substrate and the surface of the catalyst [46]. In our system, being the pKa of FA 9.55, the different activity cannot be directly linked to a different distribution of its protonated and deprotonated forms.

By using the BDH sample at natural pH and pH = 10, almost the same conversion was obtained (approx. 70%) while the selectivity was greater at pH = 10 (ca. 4 instead of 1.7).

In order to tentatively explain these different selectivity values, also the degradation of furfural in the presence of BDH was carried out at pH= 5 and 10 (Figure S4) and not significant differences of the concentration versus time were found.  Instead, by comparing

the values of the concentration after 2 h of adsorption in the dark (FigureS5), a slightly higher absorption value was noticed at pH 5 that could justify the lower selectivity, even if the behavior in the dark is not always strictly correlated to that under irradiation.

With the HP-AR sample at pH = 10 a conversion of 79% was obtained with a selectivity of ca. 4%. The prepared sample turned out to be more active than the commercial ones with an aldehyde yield of 4.4%. In order to improve the efficiency of the process, the HP-AR sample was modified by doping with W or photodeposition of Pt. After the introduction of W, a significant decrease in conversion up to 44% and an increase in selectivity at 12% (corresponding to a yield of about 5%) were observed while in the presence of Pt a conversion of 71% and a selectivity of 8.5% (yield 6%) were obtained. In all cases, the selectivity to acid was negligible (<1%). Since in the open reactor the best results were obtained with the Pt-HP-AR sample, home-prepared $TiO_2$-based samples on which Pt was photodeposited were used under anaerobic conditions in order to produce $H_2$ simultaneously with the furfuryl aldehyde.

Table 2: Results of photocatalytic tests in aqueous solution obtained after 5 hours of UV irradiation with open reactor.

| Sample | pH | Conversion [%] | Sel. furfural [%] | Yield. furfural [%] |
|--------|-----|-----|-----|-----|
| P25 | 2 | 92.4 | 0.91 | 0.84 |
| P25 | 6.7 | 49.6 | 3.91 | 1.94 |
| P25 | 10 | 68.8 | 1.77 | 1.22 |
| BDH | 5.5 | 68.0 | 1.75 | 1.19 |
| BDH | 10 | 70.5 | 4.14 | 2.92 |
| HP-AR | 10 | 79.5 | 4.27 | 3.39 |
| W-HP-AR | 10 | 44.5 | 12.10 | 5.36 |
| Pt-HP-AR | 10 | 70.7 | 8.51 | 6.01 |

Photocatalytic tests were carried out in the closed reactor also at varying pH (Table 3). With the commercial catalyst Pt-BDH at the highest pH value a fairly high conversion (approx. 55%) was obtained with the greatest selectivity to furfural between the commercial samples and an intermediate amount of hydrogen. With the Pt-HP-AR photocatalyst instead at pH 4 the conversion reached only 25% with a selectivity to furfural of ca. 16 % (yield 3.9 %) and a concentration of $H_2$ equal to 0.026 mM, while at pH 10 a conversion of 67%, a selectivity

of 6% (yield in aldehyde 4%) and a hydrogen amount equal to 0.49 mM were measured. By taking this into account, the other tests were carried out at pH = 10. Under the same conditions (pH 10, presence of Pt) the sample prepared in the laboratory (Pt-HP-AR) was more active than the commercial P25 (Pt-P25) in terms of both conversion, selectivity and production of hydrogen. In this case the different photoactivity cannot be attributed to different crystalline phases of $TiO_2$ since both samples consist of an anatase-rutile mixture, but rather to intrinsic properties of the two catalysts (degree of hydroxylation, surface acid-base properties, crystallinity, etc.) [40,47–49] deriving from the different preparation conditions. To try to improve efficiency, different catalysts based on the various polymorphic forms of $TiO_2$ were used, bare and variously modified, to shift the absorption in the visible region and to increase its photoactivity. With the pure HP-AR sample no hydrogen is obtained, confirming the essential role of Pt [40]. Doping with W, although it is reported in the literature as one of the elements that introduced into $TiO_2$ increases its photoactivity, in this case had no beneficial effect either alone or when contemporary present with Pt [25]. Since rutile and brookite prepared in laboratory showed good photocatalytic activity towards the production of $H_2$ in solutions containing glucose [40,50], these polymorphs were tested for our reaction. In this case the rutile with Pt gave good results in terms of conversion and selectivity but no hydrogen was obtained; the addition of W also made it possible to obtain a fair amount of $H_2$ and $CO_2$, indicating the latter a higher degree of mineralization than that obtained with the other samples. From the point of view of furfural production with this photocatalyst the highest yield value (approx. 5.8%) was obtained with a conversion of 37%. Pure brookite showed moderate activity (conversion 28% and selectivity to aldehyde approx. 9%), the addition of Pt not only allowed the production of $H_2$ but also increased conversion and selectivity, reaching a yield greater than 5%.

By doping brookite with small amount of Cu, the oxidizing properties were enhanced (higher conversion and lower selectivity compared to the Pt-HP-B sample) and hydrogen was also produced without the presence of a noble metal such as Pt. The simultaneous presence of Pt and Cu or Nb allowed to obtain more hydrogen and to increase conversion and yield due both to the enhanced transfer charge process and surface properties of the modified powders [51,52]. In our system, the modified HP-B proved to be effective both for the partial oxidation of furfuryl alcohol and to produce hydrogen. As far as 2-furoic acid is concerned, low selectivity and yield values were obtained with all the catalysts. The best results were observed with the HP-AR, HP-B and Pt-2Nb-HP-B samples.

1 In anaerobic conditions the most active catalyst for the production of hydrogen was Pt-HP-
2 AR while for the production of aldehyde the best results were obtained with the Pt-2Cu-B
3 sample, highlighting that different catalysts feature are involved in the oxidation and
4 reduction processes.

5

6 Table 3: Results of photocatalytic tests in aqueous solution obtained after 5 hours of UV
7 irradiation with closed reactor.

| Sample | pH | Conversion [%] | Sel. furfural [%] | $H_2$ [mM] | $CO_2$ [mM] | Yield. furfural [%] |
|---|---|---|---|---|---|---|
| Pt-BDH | 2 | 68.4 | 1.34 | 0.203 | 0.068 | 0.91 |
| Pt-BDH | 6.1 | 84.3 | 1.57 | 0.00 | 0.000 | 1.32 |
| Pt-BDH | 10 | 55.9 | 4.78 | 0.069 | 0.009 | 2.67 |
| Pt-P25 | 10 | 62.5 | 4.48 | 0.153 | 0 000 | 2.79 |
| HP-AR | 10 | 35.0 | 7.33 | 0.000 | 0.000 | 2.56 |
| W-HP-AR | 10 | 25.0 | 7.38 | 0.000 | 0.000 | 1.84 |
| Pt-HP-AR | 10 | 67.3 | 6.15 | **0.490** | 0.016 | 4.14 |
| Pt-HP-AR | 4.1 | 25.0 | 15.5 | 0.026 | 0.022 | 3.87 |
| Pt-W-HP-AR | 10 | 52.0 | 4.98 | 0.055 | 0.014 | 2.59 |
| Pt-HP-R | 10 | 35.1 | 11.9 | 0.000 | 0.019 | 4.19 |
| Pt-W-HP-R | 10 | 37.0 | 15.6 | 0.036 | **0.033** | 5.77 |
| HP-B | 10 | 28.0 | 9.35 | 0.000 | 0.015 | 2.61 |
| Pt-HP-B | 10 | 44.0 | 12.3 | 0.119 | 0.028 | 5.41 |
| Cu-HP-B | 10 | 54.0 | 7.4 | 0.057 | 0.013 | 3.99 |
| Pt-0.5Cu-HP-B | 10 | 60.5 | 12.0 | 0.166 | 0.016 | 7.30 |
| Pt-1Cu-HP-B | 10 | 73.0 | 10.2 | 0.078 | 0.015 | 7.50 |
| Pt-2Cu-HP-B | 10 | 70.5 | 10.8 | 0.143 | 0.075 | 7.60 |
| Pt-0.5Nb-HP-B | 10 | 78.7 | 9.58 | 0.123 | 0.025 | 7.50 |
| Pt-1Nb-HP-B | 10 | 68.0 | 9.83 | 0.252 | 0.027 | 6.70 |
| Pt-2Nb-HP-B | 10 | 85.9 | 8.13 | 0.183 | 0.035 | 7.00 |

8

9 The results obtained at the same FA conversion degree (25%) with the most efficient
10 samples are reported in Fig. 5. At this conversion the sample Pt-1Cu-HP-B was the most
11 active photocatalyst being the selectivity towards furfural after 1.5 h of irradiation ca. 30%.

Nevertheless, for longer reaction times, due to the high oxidant power of this sample, both FA and furfural were converted with a consequently decrease of the selectivity at 5 h (Table 1). The contemporary presence of Pt and W showed a beneficial effect both on the FA conversion and furfural selectivity. The highest selectivity towards 2-furoic acid was ca. 10% with the sample Pt-HP-R.

Chronoamperometry analysis, i.e.: current transient under monochromatic light by manually stopping irradiation on the sample, has been performed for the catalysts providing the highest FA conversion (Pt-2Nb- HP-B), the highest $H_2$ production rate (Pt- HP-AR) and, for comparison, for HP-B and HP-AR (see Fig. S6). HP-AR without and with Pt, do not show evidence of recombination phenomena. Indeed, photocurrent raises reaching an almost stationary value soon after irradiation. Conversely in the case of HP-B the photocurrent raises slowly probably due to a low mobility of photogenerated carriers. This leads to charge trapping phenomena and consequent inversion of band bending explaining why at high wavelength a cathodic photocurrent is measured. The Nb doping enhances the concentration of charge carriers and thus photoconductivity of the catalyst reducing or even canceling the recombination phenomena.

In Fig. 6 the results of the photocatalytic test under simulated solar light irradiation are showed. Also, in this case the best results were obtained in the presence of modified $TiO_2$ brookite samples confirming the high activity of this polymorph both in the partial oxidation of alcohol and in the $H_2$ formation [40,53].

The low selectivity values towards furfural and 2-furoic acid and the formation of small $CO_2$ amount (indicating a low mineralization degree) indicate the formation of different not identified intermediates, in accordance with HPLC analyses.


3.3.    Photoelectrocatalytic process


Photoelectrocatalytic processes were carried out using cheap and high durable $TiO_2$ nanotubes as photoanode and Ni foam as cathode. Large array of $TiO_2$ NTs were grown by anodizing commercially pure titanium in ammonium fluoride ethylene glycol solution as described in detail in the experimental section (see Fig. S1). After annealing at 350°C the nanotubes show the Raman bands of anatase (see Fig. S2).

Photoelectrochemical experiments were carried out in a three electrode cell (see Fig. S3) containing 0.5 M $Na_2SO_4$ aqueous solution. Light irradiation allows the formation of electron - hole pairs, that are efficiently separated inside the space charge region of the

semiconductor due to the potential difference at the metal/electrode/electrolyte interface, in turn generated by applying a cell bias. Holes produced in the valence band of $TiO_2$ are strongly oxidants and thus can oxidize both water and FA in the electrolytic solution. Electrons can easily reach the cathode through the external circuit since they are collected by the Ti beneath the $TiO_2$ layer. Table 4 summarizes all the experimental details related to the operating conditions and obtained results.

Table 4: Results of photoelettrocatalytic (PEC) tests in aqueous solution obtained after 5 hours, FA initial concentration 100 mM, photoanode $TiO_2$ NTs, $I_{ph}$: photocurrent, applied potential 0.5 [V vs Ag/AgCl], X: FA conversion, $S_{ald}$: selectivity towards furfural, $S_{acid}$: selectivity towards 2-furoic acid, FE Faradic efficiency.

| Cathode | Ni foam |
|---|---|
| $I_{ph}$ [mA] | 2.3 |
| Cell Voltage [V] | 1.28 |
| X [%] | 6.4 |
| $S_{ald}$ [%] | 0.42 |
| $FE_{ald}$ [%] | 1.92 |
| $S_{acid}$ [%] | 0 |
| $FE_{acid}$ [%] | 0 |
| $CO_2$ [mM] | 0.041 |
| $H_2$ [mM] | 0.484 |
| $FE_{H2}$ [%] | 61 |

The FA oxidation has a very poor selectivity toward the aldehyde as suggested by the data of table 4. Indeed, HPLC analysis of the solution as a function of reaction time reveals the presence of not identified peaks thus suggesting the formation of products arising from FA oxidation other than furaldehyde and 2-furoic acid (see section 3.1). Moreover, we have also to take into account that FA oxidation competes with oxygen evolution. Fig. 7 shows the cyclic voltammetry recorded in 0.5 M $Na_2SO_4$ solution without and with the addition of 0.1 M FA using a Pt mesh as working electrode. As expected, by scanning the potential toward the anodic direction a current starts to circulate at 1.1 V vs Ag/AgCl due to the onset of oxygen evolution reaction, as it can be better appreciated in the inset of Fig. 7, whose standard equilibrium potential at pH 7 is 0.6 V vs (Ag/AgCl). However, when FA is present in the electrolyte a current plateau appears in the cyclic voltammetry at ~ 1.5 V, that can be

due to FA adsorption on Pt mesh then stripped as furfural and/or 2-furoic acid at potential more positive than ~ 1.7 V (see inset).

Comparison of the current – potential transient without and with the addiction of FA clearly proves that oxygen evolution is competitive with respect to FA oxidation, thus explaining the low values of selectivity assessed for the photocatalytic process (max ~ 16% after 5 hours of irradiation) as well as for the photoelectrocatalytic process. Notably, oxidation of water produces oxygen that can diffuse toward the cathode, where its reduction will in turn compete with $H_2$ evolution thus reducing the hydrogen production rate during the photocatalytic process and the faradic efficiency during the photoelectrocatalytic process.

In Table 5 the best results obtained by photocatalytic and photoelectrocatalytic processes are compared. Both the partial FA oxidation reaction rate and $H_2$ evolution rate, normalized for the lamp specific power to account for the different photon flux, are higher for PEC process. Notably, the employed materials both at the anode (TiO$_2$ NTs) and at the cathode (Ni foam) are Pt free and, since they are chemically and physically stable during the runs, they can be used for many tests without loosing their activity. Therefore, PEC is a promising strategy for the valorization of biomasses with simultaneous $H_2$ production in spite the cost of the bias.

Table 5: Comparison of the highest HER and furfural rate formation, photon flux, their ratio for photocatalytic tests (PC) and photoelectrocatalytic (PEC) tests and power supplied for PEC.

| Test | PC | PC | PEC |
|---|---|---|---|
| Sample | Pt-HP-AR | Pt-2Cu-HP-B | TiO$_2$ NTs/Ni foam |
| HER rate [$\mu$mol h$^{-1}$] | 9.8 | | 13.7 |
| Furfuraldehyde production rate [$\mu$mol h$^{-1}$] | | 2.39 | 3.78 |
| Photon flux [W m$^{-2}$] | 110 | 110 | 8 |
| HER rate / Photon flux [($\mu$mol h$^{-1}$)/(W m$^{-2}$)] | 0.089 | | 1.71 |
| Furfural rate formation / Photon flux [($\mu$mol h$^{-1}$)/(W m$^{-2}$)] | | 0.0218 | 0.473 |
| Power supplied [mW] | - | - | 0.051 |

## 4. Conclusions

At the best of our knowledge, for the first time the reforming of furfuryl alcohol in aqueous solution was carried out by means of heterogeneous photocatalysis under green experimental conditions by using $TiO_2$ based photocatalysts. Although the conversion values and the $H_2$ production were not high, we proved the effectiveness of our system even under visible light irradiation and the results are interesting in the view of the utilization of reactors working in continuous and in the presence of a selective membrane with the aim of recovering the formed valuable intermediates by preventing its further oxidation, by considering also the high degradation rate of furfural.

The presence of Pt and metal species resulted essential to produce both furfural and $H_2$.

The structural features of the photocatalysts, the modification of the surface due to different pH conditions (responsible for different adsorption) and the types of sites present on the different samples influenced the conversion of the substrate and the selectivity towards the partial oxidation products and allowed to enhance the performance of the process. The best results were obtained at pH=10 and by using home prepared $TiO_2$ brookite containing both Pt and Cu or Nb.

Interesting results were obtained by the photoelectrocatalytic reforming of aqueous solutions containing FA carried out using $TiO_2$ NTs as photoanode and Ni foam as cathode. In this case, although the applied bias represents an additional cost for the process, higher $H_2$ and furfural production rates were obtained with respect to PC although the absence of Pt. Moreover, the electrodes are chemically and physically stable in the employed experimental conditions, thus they can be reused for other runs.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] R. Michal, S. Sfaelou, P. Lianos, Molecules 2014, Vol. 19, Pages 19732-19750 19 (2014) 19732–19750.

[2] P.A. Owusu, S. Asumadu-Sarkodie, Http://Www.Editorialmanager.Com/Cogenteng 3 (2016).

[3] J.D. Holladay, J. Hu, D.L. King, Y. Wang, Catal Today 139 (2009) 244–260.

[4] K. Brlec, S.R. Kavanagh, C.N. Savory, D.O. Scanlon, ACS Appl Energy Mater 5 (2022) 1992–2001.

[5] Y. Li, D. Bahamon, M. Sinnokrot, K. Al-Ali, G. Palmisano, L.F. Vega, Journal of Photochemistry and Photobiology C: Photochemistry Reviews 49 (2021) 100456.

[6] K.E. Sanwald, T.F. Berto, A. Jentys, D.M. Camaioni, O.Y. Gutiérrez, J.A. Lercher, ACS Catal 8 (2018) 2902–2913.

[7] M. Bowker, H. Bahruji, J. Kennedy, W. Jones, G. Hartley, C. Morton, Catal Letters 145 (2015) 214–219.

[8] H. Ahmad, S.K. Kamarudin, L.J. Minggu, M. Kassim, Renewable and Sustainable Energy Reviews 43 (2015) 599–610.

[9] V. Maslova, A. Fasolini, M. Offidani, S. Albonetti, F. Basile, Catal Today 380 (2021) 147–155.

[10] J.C. Serrano-Ruiz, R. Luque, A. Sepúlveda-Escribano, Chem Soc Rev 40 (2011) 5266–5281.

[11] C.H. Christensen, J. Rass-Hansen, C.C. Marsden, E. Taarning, K. Egeblad, ChemSusChem 1 (2008) 283–289.

[12] T.A. Werpy, J.E. Holladay, J.F. White, Top Value Added Chemicals From Biomass: I. Results of Screening for Potential Candidates from Sugars and Synthesis Gas, Richland, WA, 2004.

[13] M. Bellardita, V. Loddo, L. Palmisano, Mini Rev Org Chem 17 (2020) 884–901.

[14] G. Han, Y.H. Jin, R.A. Burgess, N.E. Dickenson, X.M. Cao, Y. Sun, J Am Chem Soc 139 (2017) 15584–15587.

[15] Z. Fang, P. Zhang, M. Wang, F. Li, X. Wu, K. Fan, L. Sun, ACS Sustain Chem Eng 9 (2021) 11855–11861.

[16] Y.H. Li, F. Zhang, Y. Chen, J.Y. Li, Y.J. Xu, Green Chemistry 22 (2020) 163–169.

[17] X. Li, J. Hu, T. Yang, X. Yang, J. Qu, C.M. Li, Nano Energy 92 (2022) 106714.

[18] H. Wang, Y. Song, J. Xiong, J. Bi, L. Li, Y. Yu, S. Liang, L. Wu, Appl Catal B 224 (2018) 394–403.

[19] S. Dhingra, M. Sharma, V. Krishnan, C.M. Nagaraja, J Colloid Interface Sci 608 (2022) 1040–1050.

[20] X. Chen, L. Zhang, B. Zhang, X. Guo, X. Mu, Sci Rep 6 (2016).

[21] W. Tolek, N. Nanthasanti, B. Pongthawornsakun, P. Praserthdam, J. Panpranot, Sci Rep 11 (2021).

[22] J. Zhang, D. Mao, D. Wu, ACS Sustain Chem Eng 9 (2021) 13902–13914.

[23] S. Huang, B. Gong, Y. Jin, P.H.-L. Sit, J.C.-H. Lam, ACS Catal 12 (2022) 11340–11354.

[24] C.L. Tan, M.Y. Qi, Z.R. Tang, Y.J. Xu, Appl Catal B 298 (2021).

[25] M. Bellardita, E.I. García-López, G. Marcì, G. Nasillo, L. Palmisano, Eur J Inorg Chem 2018 (2018) 4522–4532.

[26] D.I. Kondarides, V.M. Daskalaki, A. Patsoura, X.E. Verykios, Catal Letters 122 (2008) 26–32.

[27] M. Muscetta, R. Andreozzi, L. Clarizia, I. di Somma, R. Marotta, Int J Hydrogen Energy 45 (2020) 28531–28552.

[28] J.C. Colmenares, A. Magdziarz, M.A. Aramendia, A. Marinas, J.M. Marinas, F.J. Urbano, J.A. Navio, Catal Commun 16 (2011) 1–6.

[29] F.J. López-Tenllado, J. Hidalgo-Carrillo, V. Montes, A. Marinas, F.J. Urbano, J.M. Marinas, L. Ilieva, T. Tabakova, F. Reid, Catal Today 280 (2017) 58–64.

[30] I.H. Tseng, J.C.S. Wu, in: Catal Today, 2004, pp. 113–119.

[31] H.C. Yang, H.Y. Lin, Y.S. Chien, J.C.S. Wu, H.H. Wu, Catal Letters 131 (2009) 381–387.

[32] M. Muscetta, S. al Jitan, G. Palmisano, R. Andreozzi, R. Marotta, S. Cimino, I. di Somma, J Environ Chem Eng 10 (2022) 107735.

[33] Y.H. Zhang, M.M. Liu, J.L. Chen, K.F. Xie, S.M. Fang, Journal of Physics and Chemistry of Solids 152 (2021).

[34] K. Sekar, C. Chuaicham, B. Vellaichamy, W. Li, W. Zhuang, X. Lu, B. Ohtani, K. Sasaki, Appl Catal B 294 (2021).

[35] A. di Paola, M. Bellardita, B. Megna, F. Parrino, L. Palmisano, Catal Today 252 (2015) 195–200.

[36] M. Bellardita, M. Feilizadeh, R. Fiorenza, S. Scirè, L. Palmisano, V. Loddo, Photochemical and Photobiological Sciences (2022).

[37] H. Zhang, Q. Wu, C. Guo, Y. Wu, T. Wu, ACS Sustain Chem Eng 5 (2017) 3517–3523.

[38] J. Yan, G. Wu, N. Guan, L. Li, Appl Catal B 152–153 (2014) 280–288.

[39] M. Santamaria, G. Conigliaro, F. di Franco, F. di Quarto, Electrochim Acta 144 (2014) 315–323.

[40] M. Bellardita, E.I. García-López, G. Marcì, L. Palmisano, Int J Hydrogen Energy 41 (2016) 5934–5947.

[41] D. Reyes-Coronado, G. Rodríguez-Gattorno, M.E. Espinosa-Pesqueira, C. Cab, R. de Coss, G. Oskam, Nanotechnology 19 (2008) 145605.

[42] V. Augugliaro, T. Caronna, V. Loddo, G. Marcì, G. Palmisano, L. Palmisano, S. Yurdakal, Chemistry - A European Journal 14 (2008) 4640–4646.

[43] S. Yurdakal, G. Palmisano, V. Loddo, V. Augugliaro, L. Palmisano, J Am Chem Soc 130 (2008) 1568–1569.

[44] L. Palmisano, V. Augugliaro, M. Bellardita, A. di Paola, E. García López, V. Loddo, G. Marcì, G. Palmisano, S. Yurdakal, ChemSusChem 4 (2011) 1431–1438.

[45] M. Bellardita, A. di Paola, E. García-López, V. Loddo, G. Marcì, L. Palmisano, Curr Org Chem 17 (2013) 2440–2448.

[46] M. Bellardita, S. Yurdakal, B.S. Tek, C. Degirmenci, G. Palmisano, V. Loddo, L. Palmisano, J. Soria, J. Sanz, V. Augugliaro, J Environ Chem Eng 9 (2021).

[47] F. Parrino, M. Bellardita, E.I. García-López, G. Marcì, V. Loddo, L. Palmisano, ACS Catal 8 (2018) 11191–11225.

[48] J. Kou, C. Lu, J. Wang, Y. Chen, Z. Xu, R.S. Varma, Chem Rev 117 (2017) 1445–1514.

[49] A. di Paola, M. Bellardita, L. Palmisano, Z. Barbieriková, V. Brezová, J Photochem Photobiol A Chem 273 (2014) 59–67.

[50] R. Chong, J. Li, Y. Ma, B. Zhang, H. Han, C. Li, J Catal 314 (2014) 101–108.

[51] K. Su, H. Liu, Z. Gao, P. Fornasiero, F. Wang, Advanced Science 8 (2021) 2003156.

[52] J. Araña, C. Fernández Rodríguez, O. González Díaz, J.A. Herrera Melián, J. Pérez Peña, Catal Today 101 (2005) 261–266.

[53] E. Wierzbicka, M. Altomare, M. Wu, N. Liu, T. Yokosawa, D. Fehn, S. Qin, K. Meyer, T. Unruh, E. Spiecker, L. Palmisano, M. Bellardita, J. Will, P. Schmuki, J Mater Chem A Mater 9 (2021) 1168–1179.