# Catalysis Science & Technology

# PAPER



Cite this: Catal. Sci. Technol., 2021, 11, 4549

Received 31st March 2021, Accepted 12th May 2021

DOI: 10.1039/d1cy00569c

rsc.li/catalysis

## 1 Introduction

 $TiO_2$  is a low cost and non-toxic wide bandgap semiconductor with high photoactivity and photocorrosion resistance.<sup>1–3</sup> It is used in many different research areas such as photocatalysis, photovoltaics, photoelectrocatalysis and self-cleaning

E-mail: syurdakal@aku.edu.tr, sidikacetinkayaa@gmail.com

# Selective photocatalytic oxidation of 3-pyridinemethanol on platinized acid/base modified TiO<sub>2</sub><sup>†</sup>

Sedat Yurdakal, 跑 \*\* Sıdıka Çetinkaya, \* Vincenzo Augugliaro, ® \*<sup>b</sup> Giovanni Palmisano, <sup>cd</sup> Jacinto Sá, ® <sup>e</sup> Erik Lewin ® <sup>f</sup> and Corrado Garlisi‡<sup>cd</sup>

TiO<sub>2</sub> catalysts, modified with acidic or alkaline solutions and then platinized, were used for the partial photocatalytic oxidation of 3-pyridinemethanol to 3-pyridinemethanal and vitamin  $B_3$  under environmentally friendly conditions. The reaction took place in water under UVA light and air oxygen. Catalysts were characterized by TEM, photoluminescence, DRIFT-IR, Raman, DRS, XPS, and photocurrent measurements. The photocatalytic activity results show that Pt loading of untreated samples leads to a significant activity improvement (hence product yield) as much as acid and alkaline treatments do. Moreover, the alkaline treated TiO<sub>2</sub> samples exhibit a further increase in activity after loading with Pt. Pt acts as an electron scavenger promoting electron transfer from the TiO<sub>2</sub> conduction band, consequently boosting the photogenerated pair numbers available for the reactive process. Photocurrent measurements show that the TiO<sub>2</sub> photocatalysts' active sites increase significantly after platinization and alkaline/acid treatment. The treated and/or Pt loaded catalysts showed good thermal stability (at least up to 400 °C).

materials.<sup>1–5</sup> Despite its unique properties, there is continuous effort to improve  $TiO_2$  performance in photocatalysis, including its photo-response to visible light, process selectivity and activity.

The photocatalytic<sup>6-10</sup> or photoelectrocatalytic<sup>11-16</sup> activity of TiO<sub>2</sub> was improved by treatment with different acids such as HCl, HF, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>. After such treatments, negligible differences were observed in the diffraction patterns. Physical adsorption of SO<sub>4</sub><sup>2-</sup> and F<sup>-</sup>, however, was ascertained after H<sub>2</sub>SO<sub>4</sub> and HF treatments.<sup>10,11</sup>

Only a few studies focused on TiO<sub>2</sub> modification through alkaline treatment. Eskandarloo and co-workers investigated both NaOH treatment and Cu loading effects on TiO<sub>2</sub> photocatalytic activity for phenazopyridine degradation.<sup>17</sup> The combined effects of TiO<sub>2</sub> treatment with NaOH and H<sub>2</sub>O<sub>2</sub> were studied in the photocatalytic degradation of anionic sulforhodamine B molecules at low pH (2.27) under visible irradiation.18 TiO2 was treated in 8 M NaOH and 100 mM H<sub>2</sub>O<sub>2</sub> aqueous solutions at 50 °C for 24 h. Nevertheless, these studies<sup>17,18</sup> focused on the synergic effect of both treatments, thus not shedding light on the potential benefits brought about by only the alkaline treatment. NaOH treated and Pt loaded TiO<sub>2</sub> samples were analysed for catalytic (and not photocatalytic) oxidation of formaldehyde at room temperature by Nie and co-workers,<sup>19</sup> yet the NaOH treated samples did not show any catalytic activity. All of these studies,<sup>17–19</sup> however, did not target the application of (photo) catalysts in selective synthetic reactions.

View Article Online

<sup>&</sup>lt;sup>a</sup> Kimya Bölümü, Fen-Edebiyat Fakültesi, Afyon Kocatepe Üniversitesi, Ahmet Necdet Sezer Kampüsü, 03200 Afyonkarahisar, Turkey.

<sup>&</sup>lt;sup>b</sup> "Schiavello-Grillone" Photocatalysis Group, Dipartimento di Energia, Ingegneria dell'Informazione e Modelli Matematici (DEIM), Università degli Studi di Palermo, Viale delle Scienze (ed. 6), 90128 Palermo, Italy.

E-mail: vincenzo.augugliaro@unipa.it

<sup>&</sup>lt;sup>c</sup> Department of Chemical Engineering, Khalifa University of Science and Technology, P.O. Box 127788, Abu Dhabi, United Arab Emirates.

E-mail: giovanni.palmisano@ku.ac.ae

 <sup>&</sup>lt;sup>d</sup> Research and Innovation on CO<sub>2</sub> and H<sub>2</sub> (RICH) Center, Khalifa University of Science and Technology, P.O. Box 127788, Abu Dhabi, United Arab Emirates
 <sup>e</sup> Department of Chemistry - Ångström Laboratory, Physical Chemistry, Ångströmlaboratoriet, Lägerhyddsvägen 1, 751 20 UPPSALA, Sweden.

E-mail: jacinto.sa@kemi.uu.se

<sup>&</sup>lt;sup>f</sup>Department of Chemistry - Ångström Laboratory, Inorganic Chemistry, Ångströmlaboratoriet, Lägerhyddsvägen 1, 751 20 UPPSALA, Sweden. E-mail: erik.lewin@kemi.uu.se

 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available. See DOI: 10.1039/ d1cy00569c

<sup>&</sup>lt;sup>‡</sup> Current affiliation: Material Research and Technology Department (MRT), Luxembourg Institute of Science and Technology (LIST), 41, rue du Brill, Belvaux, L-4422, Luxembourg, corradogarlisi@hotmail.it.

## Paper

In a previous study, we investigated the NaOH treatment and Merck TiO<sub>2</sub> catalysts for selective of BDH 3-pyridinemethanol and 4-methoxybenzyl alcohol oxidation.<sup>20</sup> The modified TiO<sub>2</sub> catalyst showed an amorphous titania layer localized on the surface of anatase crystals, a higher specific surface area, and lower crystallinity compared to untreated TiO<sub>2</sub>. We have also investigated HCl treatment of TiO<sub>2</sub> catalysts for 4-nitrophenol degradation.<sup>8</sup> Similarly, the acidic treatment changed the titania structural and textural properties and increased photocatalytic activity. This activity increase may be ascribed to the presence of disordered TiO<sub>2</sub> layers grown on the surface anatase crystals. HCl treatment resulted in chlorine incorporation on amorphous regions of the samples, followed by the formation of Zundel-like structures. The interaction between the H-bonding of anatase bridging hydroxyls and those structures boosts the acidic character of surface hydroxyl groups and, hence, the TiO<sub>2</sub> photocatalytic activity.8

The present work presents a systematic investigation of the effects of acidic or alkaline treatment on TiO<sub>2</sub> structural and activity properties. Moreover, the additional effect of sample platinization was assessed. Two commercial anatase (Merck and BDH TiO<sub>2</sub>) photocatalysts were treated in 1 M HCl or NaOH aqueous solutions at a temperature of 100 °C. Pt was loaded on both treated and untreated TiO<sub>2</sub> samples by photoreduction of chloroplatinic acid. The TiO<sub>2</sub> samples were characterized by TEM, photoluminescence, DRIFT-IR, Raman, DRS, XPS, and photocurrent measurements. Finally, they were tested for the selective photocatalytic oxidation of environmentally 3-pyridinemethanol under friendly conditions. Thermal stability and cyclic tests of some samples were also carried out. Pyridine-3-carboxylic acid (vitamin B<sub>3</sub>) is one of the potential 3-pyridinemethanol partial oxidation products. This compound, whose world production amounts to ca. 35000 tons per year, is generally used to prevent and treat the pellagra disease.<sup>21,22</sup> The industrial production of vitamin B3 takes place at high pressure by oxidising picolinic isomers on vanadia-titaniazirconia oxide supported catalysts in nitric acid, permanganate or chromic acid.<sup>21</sup> In this context, production of vitamin B<sub>3</sub> via a photo-process would circumvent the need for high-pressure processes and avoid the use of toxic oxidants.

## 2 Experimental

## 2.1 Photocatalyst preparation

2.0 g of BDH or Merck  $TiO_2$  catalyst were placed in a Pyrex balloon, connected to a Graham condenser and containing 500 mL of 1 M HCl or NaOH aqueous solution.<sup>20</sup> Then, the titania suspension was refluxed under magnetic stirring at 100 °C for 8 h. The suspension was thus decanted for 16 h at room temperature to let the catalyst settle down. The powders were then neutralized by dialysis using a polymeric membrane with deionized water and finally dried at 60 °C through a rotary evaporator (Heidolph model M) at 120 rpm.

Pt-loading was achieved by suspending 0.75 g of catalyst in a solution containing 112.5 mL of water and 37.5 mL of ethanol; a suitable amount of the Pt source (H<sub>2</sub>PtCl<sub>6</sub>) was added to obtain a Pt content of 0.5% with respect to the TiO<sub>2</sub> nominal amount. This Pt percentage was optimized using a procedure reported in one of our previous studies.<sup>23</sup> The TiO<sub>2</sub> suspension was ultrasonicated for 15 minutes. Pt photodeposition was achieved in a Pyrex batch photoreactor (cylindrical, 150 mL), where the suspension was magnetically stirred to guarantee homogeneous Pt loading. A 250 W medium pressure Hg lamp (Honle UVA hand model) irradiated the photoreactor from the outside. The irradiation energy reaching the suspension, measured by using a radiometer (Delta Ohm, DO 9721), was ca. 39.2 mW cm<sup>-2</sup> (in the 315-400 nm range) and 150 mW  $cm^{-2}$  (in the 400-1050 nm range). During photodeposition, the temperature in the reactor was kept constant (ca. 30 °C) by circulating water through a Pyrex thimble surrounding it. The suspension was continuously bubbled with nitrogen starting 15 minutes prior to switching the lamp on. The gas flow, the irradiation and the stirring were maintained for 2 hours. After that, the platinized catalyst was separated by decantation. It was then neutralized by dialysis using a polymeric membrane and, finally, dried with the same procedure used for the acid or base treated catalysts.

The treated photocatalysts are named with the  $TiO_2$  brand, followed by the name of the acid or base used in the treatment. For instance, Pt–Merck–HCl indicates the  $TiO_2$ (Merck brand) sample refluxed with 1 M HCl aqueous solution at 100 °C (for 8 h) and then platinized.

In order to test the thermal stability of the HCl treated BDH sample, aliquots of the catalyst were calcined at 400, 700 and 1000 °C in a furnace (Protherm, PLF-110/10 model) through a ramp of 3 °C per min and maintaining the final temperature for 3 h. They were named as BDH-HCl-x in which x indicates the calcination temperature. The Pt-BDH-HCl and Pt-BDH-NaOH catalysts were also thermally tested at 400 °C by using the same procedure.

## 2.2 Characterization

TEM (transmission electron microscopy) analyses were performed to study the photocatalysts' morphology and identify amorphous parts by using a Tecnai G2 transmission electron microscope at 200 kV. Initially, the catalyst samples were suspended in 2-propanol and ultrasonicated for 5 minutes. 2  $\mu$ L of the suspension were dropped on a formvar/ carbon 300 mesh Cu grid (Tedpella) and left to dry completely at room temperature.

XPS (X-ray photoelectron spectroscopy) was performed by using an Ulvac-Phi Quantera II instrument with monochromatic Al K $\alpha$  radiation. TiO<sub>2</sub> samples were attached to carbon tape and floated electrically by using microscope slides. Measurements were carried out under constant neutralization using low energy electrons and Ar<sup>+</sup> ions because of the catalysts' isolation feature.<sup>24</sup> Survey scans and

details of selected core levels were obtained from the catalysts' surface. The adventitious carbon was chosen as a charge reference with the C 1s peak position at 284.8 eV. The sample composition was estimated by using sensitivity factors provided by the instrument manufacturer.

The characteristic molecular vibrations of the photocatalysts' surface groups were investigated by DRIFT-IR using a Bruker VERTEX 80/80v with an MCT detector cooled by liquid nitrogen. 512 consecutive scans were acquired in absorbance mode for each spectrum at a  $4 \text{ cm}^{-1}$  resolution in the 4000–400 cm<sup>-1</sup> wavenumber range.

Raman spectroscopy measurements using a Witec Alpha 300R equipment allowed investigating the possible occurrence of shifts due to oxygen vacancies on the samples. The excitation wavelength and the laser power were 532 nm and 75 mW, respectively. Two hundred consecutive scans for each spectrum were obtained over an extended a range of 100–900 cm<sup>-1</sup> with a 1 s integration time.

Photoluminescence emission spectra (PL) were taken using a Perkin Elmer LS 55 fluorescence spectrometer equipped with a front surface sample holder into which powder samples were placed. The chosen operative parameters for PL spectra were: excitation wavelength, 300 nm; scanning speed, 200 nm min<sup>-1</sup>; excitation slit width, 5 nm; and emission slit, 10 nm.

UV-vis diffuse reflectance (DRS) spectra were acquired in the 200–800 nm range using a UV-vis spectrophotometer (Shimadzu UV-2600) and  $BaSO_4$  as reference.

The samples' photocurrent measurements were carried out by using a potentiostat–galvanostat (CompactStat model, Ivium) with a three-electrode system in which the TiO<sub>2</sub> catalyst, deposited on fluorine doped tin oxide (FTO), was the working electrode, Pt was the counter one and Ag/AgCl (3.0 M KCl) was the reference one. The preparation of the working electrode was achieved by suspending 4 mg of sample in 4 mL of 2-propanol and treating in an ultrasound batch for 15 minutes. The FTO glass surface (1 cm × 2.5 cm part) was covered with 10  $\mu$ L of each suspension using a micropipette and then waiting until dried. This deposition was reiterated 15 times to build up enough catalyst (150  $\mu$ g) on the FTO surface.

Transient photocurrents were recorded in a 50 mL beaker containing Na<sub>2</sub>SO<sub>4</sub> (0.1 M) as an electrolyte. The side of the glass slides covered with TiO<sub>2</sub> samples was irradiated using 3 fluorescent lamps (Philips, 8 W) with the main emission peak centred at 365 nm. The irradiation energy reaching the supported semiconductor was *ca.* 2 mW cm<sup>-2</sup> (measured in the 315–400 nm range). Photocurrent transient curves were recorded at 1.0 V *vs.* Ag/AgCl (3 M KCl) and pH 7. Linear sweep voltammograms were acquired at a scan rate of 10 mV s<sup>-1</sup>.

### 2.3 Photocatalytic activity setup and procedure

A cylindrical beaker (volume: 250 mL; diameter: 6.7 cm) was used as a photoreactor. The aqueous suspension (150 mL)

was magnetically stirred and in contact with the atmosphere. The reactor was irradiated from the top by four fluorescent lamps (Philips, 8 W), with the main emission peak centred at 365 nm. The average value of the radiation energy reaching the surface of the suspension was 2.1 mW cm<sup>-2</sup> in the 315–400 nm wavelength range. All photocatalytic runs were performed at room temperature and neutral pH.

The initial concentration of 3-pyridinemethanol was 0.50 mM and the photocatalyst amount was 0.20 g  $L^{-1}$  for all photocatalytic experiments. Before starting the runs, the suspension was kept for 30 min under stirring in the dark and at room temperature in order to reach the thermodynamic equilibrium, and then the lamps were turned on.

The suspension in contact with the atmosphere allowed oxygen to continuously diffuse into the liquid. The mixing helps with  $O_2$  absorption. The contact surface area is also high to permit easy oxygen absorption; therefore, we assumed that the oxygen concentration is constant during the run and it can be considered as included in the kinetic constant.

During the photocatalytic runs, samples were withdrawn from the suspension and analyzed after filtration through a 0.45  $\mu$ m syringe filter (HA, Millipore).

### 2.4 Analytical techniques

A high performance liquid chromatograph (HPLC, Shimadzu, Prominence LC-20A model) equipped with an SPD-M20A photodiode array detector and Phenomenex Synergi 4  $\mu$ m Hydro-RP 80A column allowed the assessment of the species produced during the photocatalytic runs. The mobile phase was a mixture of methanol (40%) in water and its flow rate was 0.2 cm<sup>3</sup> min<sup>-1</sup>. The column's working temperature was 40 °C. Total organic carbon (TOC) was measured using a Shimadzu TOC-LCPN model to quantify the extent of substrate total oxidation.

## 3 Results and discussion

### 3.1 Characterization part

The XRD patterns of all the samples exhibit the peaks expected for anatase reflections (JCPDS n. 78-2486); the patterns are not reported here.<sup>20</sup>

In the Pt-loaded catalysts, metal nanoparticles are clearly identifiable as dark spots in TEM images (Fig. 1 and S1<sup>†</sup>). The spots are not uniformly distributed over crystalline titania nanoparticles and they are arranged into clusters with different shapes and sizes up to 10 nm. As shown in the red circles in Fig. 1, Pt particles present a lattice spacing of *ca.* 0.224 nm, which was assigned to the (111) plane of metallic Pt.<sup>25,26</sup> Treated BDH and Merck showed an amorphous layer covering the anatase surface.<sup>8</sup> Notably, the Pt clusters are dispersed exclusively over anatase crystals, while the amorphous layer's surface appears to be free from Pt particles. This feature may be attributed to the permeation of H<sub>2</sub>PtCl<sub>6</sub> through the amorphous layer, which is facilitated by

Paper



## Pt-BDH-NaOH



Fig. 1 TEM micrographs of selected platinized samples.

the latter's highly porous structure. Therefore, the liquid solution can easily reach the crystalline core of the particles where the reduction of Pt ions to metallic platinum is more likely to take place. Moreover, the lack of Pt on the amorphous layers of  $TiO_2$  provides evidence that photogenerated electron-hole pairs cannot reach these surface layers, confirming that the amorphous portion of the nanoparticles is not able to produce metallic Pt *via* photoreduction of the corresponding cation.

Table 1 shows the results of the XPS analysis. The C1s signal failed to correct the charging effect; therefore, the O1s signal for bulk was used for this purpose. No peak attributable to  $\text{Ti}^{3^+}$  was observed; consequently, all signals were very well fitted with a single component related to  $\text{Ti}^{4^+}$ . The loaded Pt on the TiO<sub>2</sub> surface was in metallic form.<sup>22</sup> The signal was shifted with respect to bulk platinum by *ca.* 0.3 eV, plus it has a large asymmetry related to the presence

Table 1	XPS analysis results of the $\mathrm{TiO}_{\mathrm{2}}$ samples	

Sample	$\begin{bmatrix} \text{Bulk } \text{O}_2^- \end{bmatrix}$ (eV)	Amount (%)	[OH] (eV)	Amount (%)	[Ti <sup>4+</sup> ] (eV)	[Pt <sup>0</sup> ] (eV)
BDH	530.6	60	532.0	40	459.5	_
BDH-HCl	530.6	71	531.6	29	459.4	_
BDH-NaOH	530.6	70	532.2	30	459.4	_
Pt-BDH	530.6	61	532.0	39	459.5	71.4
Pt-BDH-HCl	530.6	78	531.8	22	459.4	71.4
Pt-BDH-NaOH	530.6	75	531.9	25	459.4	71.4

of small particles and/or electron donation from Pt to  $TiO_2$ . Since TEM shows that the average Pt particle size is about 5 nm, the shift is most likely related to interfacial electron donation that is consistent with the changes observed from UV-vis and Raman.

UV-vis absorbance spectra of the pure and platinized BDH and Merck samples are reported in Fig. 2a and b, respectively. For all the samples, the marked increase in the absorption at wavelengths below 400 nm can be attributed to the indirect band-to-band transition of anatase (~3.2 eV). The Pt-loaded catalysts show a significant absorbance enhancement in the visible range (400-800 nm). The stronger broad background absorption can be ascribed to the darker colour of the catalyst following Pt loading, rather than to a localized surface plasmon resonance (LSPR) effect, which is usually manifested through the emergence of absorption bands in the visible region.  $^{\rm 27}$  Moreover, the platinized  ${\rm TiO_2}$ samples treated with an acid or base exhibit a slightly lower absorbance in the visible region compared to the untreated ones. This drop is more significant after alkaline treatment, especially for the BDH catalysts. This may be due to the different crystallinities, which decreased in the BDH (81 to 61%) samples following NaOH treatment, much more than the Merck samples (85 to 79%) as reported in our previous work.<sup>20</sup> These results show that Pt loading is more effective for the surface of the untreated TiO<sub>2</sub> samples with respect to that of the base/acid treated ones. On the other hand, both acid and base treatment for un-platinized TiO<sub>2</sub> did not result

Paper







Fig. 3 Raman spectra of the BDH and Pt-BDH samples. The inset of the figure shows the enlarged view of the Eg peak.

in any significant change in the absorption properties, as reported elsewhere. $^{20}$ 

The Raman spectra of the BDH and Pt–BDH catalysts (see Fig. 3) highlight the typical bands characteristic of the anatase crystal phase of TiO<sub>2</sub>.  $E_g$  modes arise from the symmetric stretching vibration of O–Ti–O, the B1g peak is due to the symmetric bending vibration of O–Ti–O and the A1g peak is due to asymmetric bending vibration of O–Ti–O.<sup>28</sup> It is worth mentioning that both acid and alkaline treatments did not bring about any noticeable shift of the Raman peaks (spectra not shown).<sup>20</sup> The main

 $E_g$  signal of anatase is of particular interest since its shifts can be correlated to the presence of oxygen vacancies in the TiO<sub>2</sub> lattice. For both BDH and Merck samples, Pt-loading, in addition to determining a broadening of the anatase peaks and a marked decrease in their intensity, leads to a significant shift of the  $E_g$ peak to higher wavenumbers, as shown in Fig. 3. This feature presumably arises from the perturbation of the Ti-O-Ti symmetry with the generation of oxygen vacancies causing lattice contractions and thus the shift and broadening of Raman modes.



FT-IR spectra of the photocatalysts are shown in Fig. 4. Two broad bands can be observed in the 3800–2800 and 1800–800 cm<sup>-1</sup> ranges. The former absorption, including also the narrow line at 3710 cm<sup>-1</sup>, is produced by the overlap of the bands due to stretching vibration modes of hydrogen bonded <sup>-</sup>OH groups and of water molecules coordinated to surface Ti<sup>4+</sup>, whereas the latter absorption band embraces the bending vibration mode of these (1625 cm<sup>-1</sup>) and the Ti-O-Ti bridging stretching mode in the crystal below 1200 cm<sup>-1.8,29</sup> The spectra confirm that the HCl and NaOH treatments introduce a large amount of OH groups on the photocatalyst surface. In this case, hydroxyl groups are directly introduced from the sodium hydroxide solution on the catalyst surface. On the other hand, the growth of the water complex bands in the acid-treated catalysts can be ascribed to the incorporation of Cl<sup>-</sup> ions into the amorphous titania chains, which replace lightly bound oxygen ions and act as new adsorption sites for water complexes.<sup>8</sup> The photodeposition of Pt on TiO<sub>2</sub> particles results in a small decrease of the water and hydroxyl bands compared to the



Fig. 5 Photoluminescence emission spectra of the pure, platinized and platinized HCl/NaOH modified BDH (a) and Merck (b) samples.

bare catalysts. Two small peaks appeared in the 2990–2900 and 2935–2840 cm<sup>-1</sup> ranges owing to symmetric and asymmetric  $CH_2$  stretching, respectively (Fig. 4). These peaks were attributed to residual organics on the catalyst surface, mainly derived from ethanol used in the Pt photodeposition process or to hydrocarbon traces in the air.

Fig. 5 shows the PL spectra of the neat TiO<sub>2</sub>, platinized TiO2 and platinized HCl/NaOH modified TiO2 (BDH and Merck) samples. No significant difference was observed between the untreated and acid- or base-treated catalysts (their spectra are not shown).<sup>20</sup> The same consideration applies to the Pt-TiO<sub>2</sub> and Pt-TiO<sub>2</sub>-HCl/NaOH spectra (see Fig. 5). The main emission signal was localized at ca. 420-425 nm for all the catalysts, and it is produced by the bandto-band transition energy generated by the migration of electrons from states in conduction bands back to states in the TiO<sub>2</sub> valence band. Less energetic signals, observable at higher wavelengths (in the 450-550 nm range) were attributed to excitonic PL derived from recombination events that take place at defective sites of the crystals and are recurrent in nanostructured materials. The lower PL intensity in the platinized samples, as shown in Fig. 5, may be attributed to the role of Pt in suppressing photocarrier recombination. Indeed, platinum works as an electron scavenger on the TiO<sub>2</sub> surface, where electrons are transferred from the TiO2 conduction band to Pt clusters, thus enhancing the number of electron-hole pairs available for the photocatalytic process.

Fig. 6 reports the photocurrent measurements obtained at 1.0 V vs. Ag/AgCl with the Pt loaded  $TiO_2$  catalysts. The photocurrents measured in the Pt-loaded HCl or NaOH treated samples were about twice higher than that of the platinized BDH (Pt-BDH) catalyst. Photoactivity tests (see section 3.2) support these results; both platinized and acid/alkaline treated catalysts showed a much higher photocatalytic activity than those subjected to only the platinization treatment.

Photocurrent measurements of Pt-BDH-NaOH were also performed in the presence of 3-pyridinemethanol upon



Fig. 7 Photocurrent measurements of Pt-BDH-NaOH in the presence (a) and in the absence (b) of 0.5 mM 3-pyridinemethanol. [Na<sub>2</sub>SO<sub>4</sub>] =100 mM. Applied potential: 1.0 V vs. Ag/AgCl (3 M KCl). pH 7.

applying a constant voltage of 1.0 V  $\nu s$ . Ag/AgCl (Fig. 7). In this case, higher current values were obtained.

Fig. 8 shows the linear sweep voltammograms of the Pt-BDH-NaOH catalyst in the presence (Fig. 8a and c)/absence (Fig. 8b and d) of 3-pyridinemethanol in the voltage range -0.20 V to 1.50 V. By increasing the voltage, the current values also increased linearly. However, the relationship between bias and current is a logarithmic function above *ca.* 1.2 V; the current increases to *ca.* 40  $\mu$ A at 1.5 V from *ca.* 5  $\mu$ A at 1.2 V. Higher current intensities were obtained in the presence of 3-pyridinemethanol than in the absence of the substrate both under UVA or dark conditions. In the dark, a negligible current was present till a potential of 1.2 V and, after that voltage, it also increased logarithmically, similar to what was obtained under UVA.

## 3.2 Photocatalytic activity

Table 2 summarizes the selective photocatalytic oxidation results of 3-pyridinemethanol to 3-pyridinemethanal and vitamin B<sub>3</sub> using the pristine, Pt loaded, HCl/NaOH treated and Pt-HCl/NaOH treated BDH and Merck photocatalysts.



Fig. 6 Photocurrent measurements of the Pt-BDH-HCl (a), Pt-BDH-NaOH (b), and Pt-BDH (c) catalysts.  $[Na_2SO_4]$  =100 mM. Applied potential: 1.0 V vs. Ag/AgCl (3 M KCl). pH 7.



Fig. 8 Current-potential profiles of Pt-BDH-NaOH in the presence (a and c) and in the absence (b and d) of 0.5 mM 3-pyridinemethanol. The curves c and d were obtained in the dark. [Na<sub>2</sub>SO<sub>4</sub>] =100 mM. Reference electrode: Ag/AgCl (3 M KCl). pH 7. Scan rate: 10 mV/s.

Table 2 Selective photocatalytic oxidation results of 0.5 mM 3-pyridinemethanol by using the Pt loaded HCl or NaOH treated BDH and Merck TiO<sub>2</sub> photocatalysts in water under UVA at pH 7. Un-loaded Merck and BDH were used for comparison



3-Pyridinemethanal Vitamin $B_3$ selectivity $-r_6 \times 10^6$ [%] [%]	Xab	$t_{1/2}$ [min]	<sup>a</sup> S <sub>222</sub> /6	
Catalyst $(\text{mM m h}^{-1})$ $\overline{X = 15\%}$ $X = 50\%$ $X = 15\%$ $X = 50\%$ [%]	] [%]		$[\%] X_{3h}$	Ref.
BDH 36.2 54 8 15	34		Low	(20)
Pt-BDH 136 65 58 8 15 55	91	52	3	
BDH-HCl 129 38 36 8 14 50	90	64	32	
Pt-BDH-HCl 203 46 41 8 15 66	93	33	21	
BDH-NaOH 90.0 41 39 10 15 38	81	90	22	(20)
Pt-BDH-NaOH 145 48 41 9 16 54	82	53	8	
Merck 41.1 52 8 17	37		Low	(20)
Pt-Merck 117 49 49 7 15 41	74	88	4	
Merck-HCl 117 38 36 9 14 44	87	70	17	
Pt-Merck-HCl 192 46 39 9 14 61	89	37	19	
Merck-NaOH 115 43 40 7 14 46	88	66	26	(20)
Pt-Merck-NaOH 141 49 42 10 17 50	83	60	8	

X = conversion;  $X_{1h}$  and  $X_{3h} = \text{conversion}$  after 1 or 3 h of irradiation.<sup>*a*</sup> CO<sub>2</sub> selectivity values, divided by 6 for stoichiometric normalization, were calculated for 3 h of irradiation ( $X_{3h}$ ).

Table 2 reports the initial reaction rate  $(-r_0)$ , the product selectivity for 15 and 50% conversion, the conversions for 1 h  $(X_{1h})$  and 3 h  $(X_{3h})$  of reaction time, the half-life times  $(t_{1/2})$  and CO<sub>2</sub> selectivity after a 3 h reaction time. The initial reaction rates have been calculated by the following equation:

$$(-r_0) = \left(-\frac{1}{S}\frac{\mathrm{d}n}{\mathrm{d}t}\right)_0 = \left(-\frac{V}{S}\frac{\mathrm{d}C}{\mathrm{d}t}\right)_0 \tag{1}$$

where *n* denotes the number of 3-pyridinemethanol moles, *t* is the irradiation time, *S* is the specific surface area of the used catalyst, *V* is the suspension volume and *C* is the 3-pyridinemethanol concentration. The  $(-r_0)$  value is independent of the surface area of the photocatalyst, and hence it is used as a relevant parameter to assess its intrinsic activity.<sup>5</sup>

The photoreactivity results indicate that the acid/base treatments lead to a significant activity increase with respect to the untreated samples.<sup>8,20</sup> For instance, the initial reaction rate of Merck–HCl is almost 3 times higher than that of untreated Merck ( $11.7 \times 10^{-5}$  vs.  $4.11 \times 10^{-5}$  mM m h<sup>-1</sup>). Owing to the fact that the second oxidation step of 3-pyridinemethanol is vitamin B<sub>3</sub> production, an increase in the substrate conversion implies a boost in the vitamin B<sub>3</sub> concentration. Moreover, CO<sub>2</sub> selectivity values are also correlated to the conversion ones. Indeed, the extent of the total oxidized substrate increased with irradiation time. As in the case of acid or base treatments, platinizing of untreated TiO<sub>2</sub> significantly promoted the catalyst photoactivity; the

substrate conversion for 1 h irradiation increases from 15% to 55% and from 17% to 41% for the BDH and Merck catalysts, respectively. Platinizing of the acid/base treated TiO<sub>2</sub> samples also positively affects the reactivity; for instance, the conversion values for 1 h irradiation are 66% and 61% for the Pt–BDH–HCl and Pt–Merck–HCl samples, respectively. The reactivity of the Pt–BDH–NaOH and Pt–Merck–NaOH samples, however, was lower than that of the corresponding HCl-treated catalysts; the ( $-r_0$ ) values of the former ones are  $1.45 \times 10^{-4}$  and  $1.41 \times 10^{-4}$  mM m h<sup>-1</sup>, while those of the latter ones are  $2.03 \times 10^{-4}$  and  $1.92 \times 10^{-4}$  mM m h<sup>-1</sup>.

Fig. 9 shows the photocatalytic oxidation results of 3-pyridinemethanol obtained using the BDH and Pt-BDH-HCl samples. It is clear that the reactivity and product yield improved significantly in the  $TiO_2$  catalyst modified by both acid treatment and Pt loading. The aldehyde amount reached the maximum at 90 min, transforming into vitamin  $B_3$  whose concentration increased steadily during all the reaction (Fig. 9b).

Fig. 10 reports the  $(-r_0)$  values of the acid or base treated and Pt loaded BDH and Merck TiO<sub>2</sub> photocatalysts. The results obtained from the untreated and un-platinized samples are also provided for the sake of comparison. Interestingly, the platinized (Pt-BDH and Pt-Merck) samples showed a comparable reactivity to that of the acid/base modified TiO<sub>2</sub> (BDH-HCl and Merck-HCl) catalysts. Sample modification, using both methods, platinization and acid/ base treatment simultaneously, improves the catalyst activity



**Fig. 9** Photocatalytic results of oxidation of 3-pyridinemethanol ( $\blacklozenge$ ) to 3-pyridinemethanal ( $\blacksquare$ ) and vitamin B<sub>3</sub> ( $\blacktriangle$ ) vs. irradiation time by using the BDH (a) and Pt-BDH-HCl (b) catalysts in water under UVA irradiation at pH 7. The 3-pyridinemethanal and vitamin B<sub>3</sub> values are indicated by right facing arrows.

markedly, suggesting a possible synergistic effect of these two methods.

It is well known that TiO2 catalysts are highly stable and resistant to photocorrosion.<sup>1-3</sup> In order to check if the HCl treatments affect the catalyst stability, the treated samples underwent thermal treatments at different temperatures (until 1000 °C) for 3 h in air. These samples were used for 3-pyridinemethanol partial oxidation. The reactivity results, reported in Table 3, highlight that the BDH-HCl samples did not show a significant activity loss up to 700 °C, thus indicating that these samples are very stable even at high temperatures. As expected, extreme calcination temperature (1000 °C) detrimentally affected the catalyst activity; indeed BDH-HCl-1000 showed an even lower activity than untreated BDH. Likely explanations of this drastic decrease are that at 1000 °C, TiO<sub>2</sub> particles sinter with a great decrease of active surface area and that the amount of surface hydroxyl groups, responsible for O2 absorption, decreases. The thermal stability of the NaOH treated samples up to 700 °C was already investigated in our previous work and the sample was stable until 400 °C.<sup>20</sup>



Fig. 10 Initial reaction rate  $(-r_0)$  values of the acid or base treated and/or Pt loaded BDH and Merck TiO<sub>2</sub> samples. Data of the un-treated and un-platinized samples are provided for the sake of comparison.

The platinized BDH samples were also heated at 400 °C for 3 h (Pt-BDH-HCl-400 and Pt-BDH-NaOH-400) to check their thermal stability. This thermal treatment did not affect the samples' photoreactivity in a significant way (see Table 3), however the 3-pyridinemethanal selectivity values increased by about 15–20%. In agreement with the XPS results obtained with untreated Degussa P25 and home-prepared TiO<sub>2</sub> catalysts,<sup>22</sup> in the uncalcined Pt-TiO<sub>2</sub> samples, metallic Pt<sup>0</sup> is present on the TiO<sub>2</sub> surface and, in the calcined ones, platinum is present in both metallic  $(Pt^{0})$  and cationic  $(Pt^{2+})$  forms. In conclusion, these stability results show that the investigated TiO2 samples could also be used in photo(thermo)catalytic processes.

Besides thermal stability, cyclic tests were also performed. Our samples are powdered, and in a slurry system, it is difficult to reuse them without losing a small amount. However, TiO<sub>2</sub> samples in powder form could be re-used by using a filtration system, centrifuge, or decantation. It is well known and valid for all powdered nanoparticles that a small quantity of TiO<sub>2</sub> may be lost during the separation. However, in practical application, TiO<sub>2</sub> is used in a supported form on a suitable material to solve the separation process without losing any TiO<sub>2</sub> particles.<sup>30</sup> On these grounds, in order to do cyclic tests, the Pt-BDH-NaOH sample was deposited on an FTO surface (Pt-BDH-NaOH/FTO) as described in section 2.2. After that, the Pt-BDH-NaOH/FTO sample was used for 3-pyridinemethanol oxidation under UVA irradiation (see Fig. S2<sup>†</sup>). The TiO<sub>2</sub> amount deposited on FTO is very low (150  $\mu$ g) and then the irradiation time was increased to 20 h. In the slurry system, the irradiation time was 3 h so that the selected 20 h is equal to 6-7 cycles of a slurry run. Two consecutive experiments showed almost the same substrate conversion value (ca. 20%) thus suggesting that the prepared catalyst is highly stable. Electrochemical characterization (photocurrent measurements) of the Pt-BDH-NaOH/FTO sample before and after a photocatalytic run lasting 20 h has also been performed. As it may be noted in Fig. S3,† almost

Table 3 Photocatalytic oxidation results of 3-pyridinemethanol (0.5 mM) under UV irradiation at pH 7: thermal treatment effect on the treated and/or Pt loaded BDH  $TiO_2$  samples

Catalyst	$-r_0  imes 10^6$ [mM m h <sup>-1</sup> ]	3-Pyridinemethanal selectivity [%]		Vitamin B <sub>3</sub> selectivity [%]		<i>X</i> 1	$X_2$	t1/2
		X = 15%	<i>X</i> = 50%	X = 15%	<i>X</i> = 50%	[%]	[%]	[min]
BDH-HCl	129	38	36	8	14	50	90	64
BDH-HCl-400	129	46	38	11	15	47	86	65
BDH-HCl-700	121	43	38	9	14	43	78	78
BDH-HCl-1000		73		9		6	15	
Pt-BDH-HCl	203	46	41	8	15	66	93	33
Pt-BDH-HCl-400	203	58	51	9	16	64	92	34
Pt–BDH–NaOH	145	48	41	10	16	54	82	53
Pt-BDH-NaOH-400	144	62	47	11	20	55	81	52

X = conversion;  $X_{1h}$  and  $X_{3h} =$  conversion after 1 or 3 h of irradiation.

the same photocurrent values were observed, with the last four switch on-switch off measurements overlapping. All previous results suggest that the prepared catalysts are stable.

# 4 Conclusions

The effect of Pt loading and acid/base treatment on TiO<sub>2</sub> catalysts was investigated by characterization methods and performing photocatalytic 3-pyridinemethanol oxidation under environmentally friendly conditions. The activity was significantly increased by these treatments. Even though selectivities were not particularly affected by these treatments, product yields increased considerably due to enhanced activity. The characterization of treated TiO2 catalysts revealed that the occurrence of disordered regions on anatase crystal surfaces was more significant upon acid and basic treatments. Pt was deposited on catalysts which previously underwent an acid/basic treatment or not: Pt clusters work as electron scavengers, collecting electrons transferred from the TiO<sub>2</sub> conduction band with a consequent increase in the number of photogenerated charges triggering the reactive processes. The samples loaded with platinum, a noble metal, exhibited a reactivity increase similar to that obtained with HCl or NaOH treatments. Photocurrent measurements show that TiO<sub>2</sub> active sites were increased significantly by platinization and alkaline/acid treatment.

The main finding of this investigation is that, in order to improve the  $TiO_2$  (the most used photocatalyst in powder or deposit form for many applications) photocatalytic activity, a simple and cheap treatment under acidic or basic conditions is as effective as Pt loading; finally, as expected, both treatments increased the activity in a likely synergic way.

The treated and/or Pt loaded catalysts showed good thermal stability (at least up to 400 °C). In addition they were stable after cyclic tests. These stability results show that the investigated  $TiO_2$  samples could also be used in photo(thermo)catalytic processes.

# Conflicts of interest

There are no conflicts to declare.

# Acknowledgements

S. Yurdakal and S. Çetinkaya thank the University of Afyon Kocatepe (BAP project no: 17.KARİYER.15) for financial support.

## References

- 1 *Photocatalysis: Fundamentals and Applications*, ed. N. Serpone and E. Pelizzetti, Wiley, New York, 1989.
- 2 Heterogeneous Photocatalysis: From Fundamentals to Green Applications, ed. J. C. Colmenares and Y.-J. Xu, Springer-Verlag, Berlin Heidelberg, 2016.
- 3 V. Augugliaro, G. Camera-Roda, V. Loddo, G. Palmisano, L. Palmisano, J. Soria and S. Yurdakal, *J. Phys. Chem. Lett.*, 2015, **6**, 1968–1981.
- 4 M. J. Torralvo-Fernández, E. Enciso, S. Martínez, I. Sobrados, J. Sanz, D. Tonti, J. Soria, S. Yurdakal, G. Palmisano and V. Augugliaro, *ACS Appl. Nano Mater.*, 2018, **1**, 2567–2578.
- 5 F. Parrino, V. Loddo, V. Augugliaro, G. Camera-Roda, G. Palmisano, L. Palmisano and S. Yurdakal, *Catal. Rev.: Sci. Eng.*, 2019, **61**, 163–213.
- 6 J. C. Yu, J. Yu and J. Zhao, Appl. Catal., B, 2002, 36, 31-43.
- 7 B. Cheng, J.-G. Yu, X.-Q. Zang and X.-J. Zhao, *J. Mater. Sci. Lett.*, 2003, **22**, 967–970.
- 8 J. Soria, J. Sanz, M. J. Torralvo, I. Sobrados, C. Garlisi, G. Palmisano, S. Çetinkaya, S. Yurdakal and V. Augugliaro, *Appl. Catal., A*, 2017, **210**, 306–319.
- 9 W. Fang, M. Xing and J. Zhang, Appl. Catal., A, 2014, 160– 161, 240–246.
- 10 S. K. Park and H. Shin, J. Nanosci. Nanotechnol., 2014, 14, 8122-8128.
- 11 K. Iyatani, Y. Horiuchi, S. Fukumoto, M. Takeuchi, M. Anpo and M. Matsuoka, *Appl. Catal.*, *A*, 2013, **458**, 162–168.
- 12 G. H. Guai, Q. L. Song, Z. S. Lu, C. M. Ng and C. M. Li, *Renewable Energy*, 2013, **51**, 29–35.

## **Catalysis Science & Technology**

- 13 L. Song, P. Du, X. Shao, H. Cao, Q. Hui and J. Xiong, *Mater. Res. Bull.*, 2013, 48, 978–982.
- 14 H.-J. Kim, J.-D. Jeon and S.-Y. Kwak, *Powder Technol.*, 2013, 243, 130-138.
- 15 T. Liu, B. Wang, J. Xie, Q. Li, J. Zhang, M. I. Asghar, P. D. Lund and H. Wang, *Appl. Surf. Sci.*, 2015, 355, 256–261.
- 16 Q. Wen, J. Yu, X. Sun, J. Zhuang, Q. He, X. You, J. Guo and L. Tao, *New J. Chem.*, 2016, 40, 3233–3237.
- 17 H. Eskandarloo, A. Badiei, M. A. Behnajady and G. M. Ziarani, *Photochem. Photobiol.*, 2015, **91**, 797–806.
- 18 C.-Y. Wu, K.-J. Tu, Y.-S. Lo, Y. L. Pang and C.-H. Wu, *Mater. Chem. Phys.*, 2016, **181**, 82–89.
- 19 L. Nie, J. Yu, X. Li, B. Cheng, G. Liu and M. Jaroniec, *Environ. Sci. Technol.*, 2013, 47, 2777–2783.
- 20 S. Yurdakal, S. Çetinkaya, V. Augugliaro, G. Palmisano, J. Soria, J. Sanz, M. J. Torralvo-Fernández, S. Livraghi, E. Giamello and C. Garlisi, *Catal. Sci. Technol.*, 2020, **10**, 5000–5012.
- 21 D. Spasiano, R. Marotta, I. Di Somma and G. Mancini, *Appl. Catal.*, B, 2015, 163, 248–257.

- 22 S. Yurdakal, Ş. Ö. Yanar, S. Çetinkaya, O. Alagöz, P. Yalçın and L. Özcan, *Appl. Catal., B*, 2017, **202**, 500–508.
- 23 S. Yurdakal, B. S. Tek, Ç. Değirmenci and G. Palmisano, *Catal. Today*, 2017, 281, 53–59.
- 24 P. E. Larson and M. A. Kelly, J. Vac. Sci. Technol., A, 1998, 16, 3483–3489.
- 25 X. Zhu, B. Cheng, J. Yu and W. Ho, *Appl. Surf. Sci.*, 2016, 364, 808–814.
- 26 N. Shang, P. Papakonstantinou, P. Wang and S. R. P. Silva, J. Phys. Chem. C, 2010, 114, 15837–15841.
- 27 S. Kunwar, M. Sui, P. Pandey, Z. Gu, S. Pandit and J. Lee, *Sci. Rep.*, 2019, 9, 1329.
- 28 C. Garlisi, G. Scandura, J. Szlachetko, S. Ahmadi, J. Sa and G. Palmisano, *Appl. Catal.*, A, 2016, 526, 191–199.
- 29 V. Augugliaro, S. Coluccia, V. Loddo, L. Marchese, G. Martra, L. Palmisano and M. Schiavello, *Appl. Catal., B*, 1999, **20**, 15–27.
- 30 V. Augugliaro, V. Loddo, M. Pagliaro, G. Palmisano and L. Palmisano, *Clean by Light Irradiation: Practical Applications of Supported TiO<sub>2</sub>*, RSC Publishing, 2010.