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## Tuning the Synthetic Parameters to Obtain Smart C-N Co-Doped Titania Photocatalysts for NO<sub>x</sub> Abatement

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# Cooperative effect of reactor design and titania metal promotion for sustainable carbon dioxide photoreduction

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## Abstract:

An effective process based on the photocatalytic reduction of CO<sub>2</sub> to face on one hand, the crucial problem of environmental pollution and, on the other hand, to propose an efficient way to product clean and sustainable energy sources has been developed in this work. Particular attention has been payed to the sustainability of the process by using a green reductant (water) and TiO<sub>2</sub> as a photocatalyst under very mild operative conditions (room temperature and atmospheric pressure).

It was shown that the efficiency in carbon dioxide photoreduction is strictly related to the process parameters and to the catalyst features. In order to formulate a versatile and high performing catalyst, TiO<sub>2</sub> was modified by oxide or metal species. Copper (in the oxide CuO form) or gold (as nanoparticles) were employed as promoting metal. Both photocatalytic activity and selectivity displayed by CuO-TiO<sub>2</sub> and Au-TiO<sub>2</sub> were compared and it was found that the nature of the promoter (either Au or CuO) shifts the selectivity of the process towards two strategic products: CH<sub>4</sub> or H<sub>2</sub>. The catalytic results were discussed in depth and correlated with the physiochemical features of the photocatalysts.

**Keywords:** CO<sub>2</sub> photoreduction, photocatalysis, titania, reactor design, metal promotion

## 1 Introduction

Carbon dioxide is responsible for the climate changes of the last century and for this reason it is considered as the greatest threat to the environment of the twentieth-first century [1]. The dependence of developed countries on traditional fuels has driven the research looking for sustainable and readily available energy sources [2,3]. Paris agreement, signed in Paris in December 2015, pointed out the necessity to find reliable technology to avoid a 2 °C global warming [4].

Carbon dioxide can be used as a green source of carbon for fuels and chemicals [5-7]: however, its exploitation is deeply connected to technological breakthrough and market competitiveness of these processes [8]. In this frame, photocatalysis is a promising technology since it allows the use of CO<sub>2</sub> to synthesize fuels in the presence of an irradiated semiconductor [9-11]. This means that the primary source of energy of the entire process is light, opening new possibilities to use solar light in the next future [12]. Water can be used as a green and sustainable reductant instead of other more hazardous and expensive reductants like hydrogen [13-15]. Though its many advantages from an economic point of view, the use of water may lead also to the formation of hydrogen due to water splitting reaction [16-19]. Hydrogen might be a key molecule for energy market in the next future [20,21]: however, its formation would not involve the use of carbon dioxide as a green source of energy [22,23].

Among semiconductors, titanium dioxide has proven to be a perfect candidate for this application [24-26]. In particular, its valence band (VB) is sufficiently positive to oxidize water, while, differently from many semiconductors (like WO<sub>3</sub>, SnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> [27]), the conduction band (CB) is negative enough for CO<sub>2</sub> reduction [8].

Since the pioneering work by Inoue and co-workers [28] many efforts have been devoted to increase the overall efficiency of the photoreduction process, specially by focusing on both reaction media and conditions. In particular, liquid phase systems were widely tested for this reaction, though low carbon dioxide solubility and low light permeation limited the exploitation of this technology [29,30]. Therefore, gas phase systems were investigated in the last years [31], even if in such case the reaction conditions needed to be pushed to convert carbon dioxide into fuels, hence decreasing the sustainability of the whole process [32].

In a previous work [16] we reported that carbon dioxide photoreduction can be performed in gas phase at room temperature and atmospheric pressure, making the process less energy demanding and more sustainable. However, some improvements

need to be fulfilled in order to improve the efficiency. Crucial parameters, such as light harvesting and catalyst composition, have to be further investigated.

As a matter of fact, attention has been focused on photocatalyst modification [33-36]. Indeed, the most critical issue to be controlled and tuned is the fast electron-hole recombination at the photoexcited catalytic sites [37,38].

Anatase phase is the most suitable titania crystalline phase because of its slightly lower recombination rate, a feature highly required in this process [39-42]. Crystal phase aside, the addition of another semiconductor as a co-catalyst has been applied to limit electron-hole recombination [43-45]. The differences in valence and conduction levels in the two semiconductors allow an electron flow at the heterojunction of the two species, modifying the circulation of photoexcited electrons on the final material [46]. In order to be effective in injecting electron into titania CB, the coupled semiconductor must be characterized by a higher Fermi level and a more negative CB [47]. Copper(II) oxide appears to be a good candidate as a co-catalyst due to its electronic properties, great availability and low cost [48]. According to Qin *et al.*, the addition of surface copper species improves titania photoactivity by enhancing the separation of strong oxidative holes and reductive electrons [49]. Interestingly, Isahak *et al.* reported that CuO is an efficient CO<sub>2</sub> adsorbent, favouring the interaction between substrates and the photocatalytic surface [50].

Another strategy to suppress electron-hole recombination is the introduction of noble metal nanoparticles (such as silver and gold) on the titania surface [51-54]. In these materials, the excited electrons flow from the semiconductor to the metal under light irradiation [55]. Then the Schottky barrier at the interphase between the titanium oxide and the metal nanoparticle, hinders electron flow to titanium dioxide, preventing electron-hole recombination and thus acting as an electron trap [52,56-60]. Beside these electron-trapping properties, gold and silver nanoparticles are also characterized by the surface plasmonic resonance (SPR) effect [61]. Moreover, the collective oscillation of the valence electrons in semiconductors can occur under irradiation, increasing electronic propagation on the semiconductor surface [62-64]. Although all these phenomena modify the overall electronic circulation, they have different effect on the activity and selectivity displayed by titania in the CO<sub>2</sub> photoreduction, with consequences on the efficiency of the overall process. Actually, in order to make this process an efficient and sustainable technology, it is important to develop an active and selective photocatalytic process. Therefore, sustainability will be a feature not only for

the catalyst, but also for the process itself. In fact, gas phase medium was chosen maintaining mild conditions (i.e. room temperature and atmospheric pressure). Catalyst efficiency was also considered and a new thin film reactor was developed to increase the titania effectiveness in light harvesting and reduce the amount of catalyst.

Therefore the goal of the work is to investigate the possibility of an efficient system for CO<sub>2</sub> photoreduction using CuO-TiO<sub>2</sub> and Au-TiO<sub>2</sub> photocatalytic materials for a sustainable process focusing on activity and selectivity, though maintaining very mild conditions (i.e. room temperature and atmospheric pressure).

## **2 Experimental**

### *2.1 Materials*

The following reagents were used as received: TiOSO<sub>4</sub>·xH<sub>2</sub>O·yH<sub>2</sub>SO<sub>4</sub> (Ti assay > 29 % Sigma Aldrich), sodium hydroxide (assay > 97% Carlo Erba) and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (assay >99%, Sigma–Aldrich) and 2-propanol (assay 99.8 % Fluka). A standard TiO<sub>2</sub> reference material (MIRKAT 211) has been purchased by Euro Support s.r.o. This commercial titania has been chosen as a reference material since it possesses a large surface area (217 m<sup>2</sup>/g) and it is in the anatase form, i.e. the most suitable titania crystalline phase for photocatalytic applications.

### *2.2 Synthesis of the catalysts*

#### *2.2.1 Titania synthesis*

The precipitation method has been chosen to synthesise the titania samples. In a typical synthesis, a 1.2 M titanyl sulphate solution and a 9.0 M NaOH solution have been added drop wise and simultaneously to 200 mL of distilled water under vigorous stirring, in order to keep a neutral pH. Then the Ti(OH)<sub>4</sub> suspension has been aged at 60 °C for 20 h. Afterwards, the precipitated has been filtered and washed with distilled water to remove the sulphate ions. The absence of sulphates has been verified by means of the barium chloride test [65]. The obtained wet Ti(OH)<sub>4</sub> has been dried overnight at 110 °C and calcined at 400 °C for 4 h in air flow to obtain TiO<sub>2</sub>. This sample has been labelled as TiO<sub>2</sub>.

#### *2.2.2 Copper oxide loading to titania*

According to a previous work [16], the introduction of copper oxide into titania provides the highest effect on the photoactivity when the Cu amount is 0.2 wt.%. In

particular, incipient wetness impregnation with a copper precursor, namely  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , has been performed on dried  $\text{Ti}(\text{OH})_4$ . Then the copper-impregnated sample has been calcined at 400 °C in air flow in order to obtain the  $\text{CuO-TiO}_2$  photocatalyst.

### 2.2.3 Gold introduction into titania

In this case, the incipient wetness method would not allow to deposit small gold nanoparticles on the titania surface [66]. Therefore, in order to obtain small gold nanoparticles, gold has been added to titania by using the deposition–precipitation (DP) method maintaining the pH equal to 8.6 [67]. Titanium dioxide has been suspended in an aqueous solution of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  for 3 h, while controlling the pH value by the addition of NaOH (0,5 M). The Au amount was 0.2 wt. %, the same as in the case of the  $\text{CuO-TiO}_2$  photocatalyst, for comparison purposes. After filtration, the samples have been washed with distilled water to remove chlorides. The absence of chlorides was verified by the silver nitrate test. The samples have been dried at 35 °C overnight and finally calcined in air for 1 h at 400 °C. The final sample has been labelled  $\text{Au-TiO}_2$ .

### 2.3 Characterization of the photocatalysts

The thermal analyses (TG/DTA) have been performed on a NETZSCH STA 409 PC/PG instrument in air flux (20 mL/min) using a 10 °C/min temperature rate between 25–800 °C.

X-Ray Diffraction (XRD) patterns have been collected on a Bruker D8 Advance powder diffractometer with a sealed X-ray tube (copper anode; operating conditions, 40 kV and 40 mA) and a Si(Li) solid state detector (Sol-X) set to discriminate the Cu  $K\alpha$  radiation. Apertures of divergence, receiving and detector slits were 2.0 mm, 2.0 mm, and 0.2 mm, respectively. Data scans have been performed in the  $2\theta$  range 5°–75° with 0.02° step size and counting times of 3 s/step. Quantitative phase analysis and crystallite size determination have been performed using the Rietveld method as implemented in the TOPAS v.4 program (Bruker AXS) using the fundamental parameters approach for line-profile fitting. The determination of the crystallite size was accomplished by the Double-Voigt approach and calculated as volume-weighted mean column heights based on integral breadths of peaks.

$\text{N}_2$  adsorption–desorption isotherms at 196 °C were performed using a MICROMERITICS ASAP 2000 analyser to obtain information on the surface

properties. All samples were previously outgassed at 200 °C for 2 h. The mesopore volume was measured as the adsorbed amount of N<sub>2</sub> after capillary condensation. The surface area was evaluated using the standard BET [68] equation and the pore size distribution was obtained using the BJH method applied to the isotherm desorption branch [69].

The real amount of copper and gold in the promoted catalysts was determined by flame atomic absorption spectroscopy (FAAS) using a PerkinElmer Analyst 100.

Temperature programmed reduction (TPR) experiments were carried out in a lab-made equipment: each sample (50 mg) was heated at 10 °C/min from 25 °C to 800 °C in a 5% H<sub>2</sub>/Ar reducing mixture (40 mL·min<sup>-1</sup> STP). The effluent gases were analysed by a Gow-Mac TCD detector using a magnesium perchlorate trap to stop H<sub>2</sub>O.

Diffuse reflectance UV–Vis-NIR spectra were collected at r.t. on a Varian Cary 5000 spectrophotometer with an integrating sphere attachment using BaSO<sub>4</sub> powder as an internal reference, working in the 50000-4000 cm<sup>-1</sup> range. UV–Vis-NIR spectra of the as prepared samples are reported in the Kubelka-Munk function [ $f(R_{\infty})=(1-R_{\infty})^2/2R_{\infty}$ ;  $R_{\infty}$ =reflectance of an “infinitely thick” layer of the sample [70]. The layer of powder sample was made sufficiently thick such that all incident light was absorbed or scattered before reaching the back surface of the sample holder. Typically a thickness of 1–3 mm was required.

The samples in the form of powders were placed in a quartz cell, allowing treatments in controlled atmosphere and temperature. The band gap energy ( $E_g$ ) of the catalysts were determined by the intercept of a linear fit to the absorption edge and they can be estimated using the standard equation, which is based on the relationship between frequency ( $c/\lambda$ ) and photon energy ( $E_g = 1240/\lambda$ ).

The FTIR analyses were performed using a Perkin Elmer 2000 spectrometer (equipped with a cryogenic MCT detector). As for the analyses at increasing temperature, each sample, in the form of self-supporting pellet, was placed in an AABSPEC 2000 cell allowing to run the spectra in situ in controlled atmosphere and temperature. The samples were outgassed from room temperature up to 150°C. As for the measurements of CO<sub>2</sub> adsorption at room temperature, the samples were submitted to outgassing at r.t. for 1 hour in order to remove water, that is adsorbed at the surface due to the exposition to air. The spectrum of the sample before the inlet of CO<sub>2</sub> was subtracted from each spectrum and all spectra were normalised with respect to the density of the pellets.

## 2.4 Photoactivity tests

The catalytic apparatus was reported in a previous work [Errore. Il segnalibro non è definito.], however in this paper two new experimental setups, such as the reactor geometry and the catalyst introduction, were used. In the former case a tubular borate glass fixed bed reactor (length 40 mm, diameter 4 mm) was exploited. The catalyst (400 mg) was introduced as small particles with size 0.2-0.3 mm. In the latter case, the CO<sub>2</sub> photoreduction was performed using a borate glass thin film reactor (length 33 mm, height 18 mm, thickness 2 mm). Here the catalyst (10 mg) was inserted by depositing the catalyst suspended in 2-propanol on the light-exposed side of the reactor.

The samples were illuminated using a 125 W mercury UVA lamp (purchased from Helios Italquartz s.r.l. with emission range 315–400 nm shielded by a special tubular quartz, to select the 366 nm wavelength), with an average irradiance of 50 W·m<sup>-2</sup>. Afterwards, a gaseous mixture of carbon dioxide and water has flown through the reactor. Compressed CO<sub>2</sub> (99.99%) regulated by a mass flow controller was carried through a water bubbler kept at 40 °C to generate CO<sub>2</sub> and H<sub>2</sub>O vapour mixture (13.3 CO<sub>2</sub>/H<sub>2</sub>O molar ratio). The reactor was closed when the system reached the equilibrium state and this point was taken as the beginning of the reaction. Therefore, the reaction was not performed under a continuous gas flow, but it took place in static conditions. A total of 9.2 μmol of CO<sub>2</sub> and 0.7 μmol of H<sub>2</sub>O were present within the sealed reactor. In all catalytic tests, the reaction time was 6 h.

The reaction products were analyzed by a gas chromatograph (HP G1540A) equipped with a Porapak Q column and a TCD detector. Activity results are expressed in turn over numbers (TONs) in μmol·g<sub>cat</sub><sup>-1</sup>, as commonly used in literature [71,72]. Quantum yield (Φ) was calculated according to IUPAC recommendations [73]:

$$\Phi (\%) = \frac{CH_4(mol)}{incident\ photons\ (mol)} \cdot 100$$

## 3 Results and discussion

### 3.1 On the reactor design

All reaction configurations found in the literature for a gas phase reaction were considered. In particular, in fixed bed reactors [74], which are the simplest systems, only a small fraction of the photocatalyst is activated by light, decreasing the effectiveness of the whole process. The use of honeycomb monoliths [75] and optical fibres could solve the problem, though narrowness of cells would limit the light transfer

and the mass transport of reagents/products to/from the active sites. An appealing alternative is the impregnation of the photocatalyst on a moist quartz wool [76], as reported by Bazzo and Urawaka [77]. However, in this case, the amount of water in the gas phase is not controlled leading to differences in the CO<sub>2</sub>/H<sub>2</sub>O ratio calculations.

Therefore, to boost the titania effectiveness in the CO<sub>2</sub> conversion, a new thin film reactor was developed. In this work, the photocatalyst was coated directly on the reactor surface. This option allowed to reduce the amount of catalyst from 400 mg to 10 mg and, most importantly, to expose all the employed catalyst to incident light: in this way the catalyst is more prone to provide the photocatalytic effect. Moreover, diffusion problems detected in previous works were avoided.

In Fig. 1 the comparison between the photoactivity obtained either with the fixed bed reactor or with the thin film reactor is reported. It is clear that methane formation increases enormously (from 0.03  $\mu\text{mol g}_{\text{cat}}^{-1}$  to 14.00  $\mu\text{mol g}_{\text{cat}}^{-1}$ ) when using a thin film reactor: this means that there are three order of magnitude of difference between the photocatalytic performances of the same catalyst in the same experimental conditions, but in the presence of the two different photocatalytic setups.

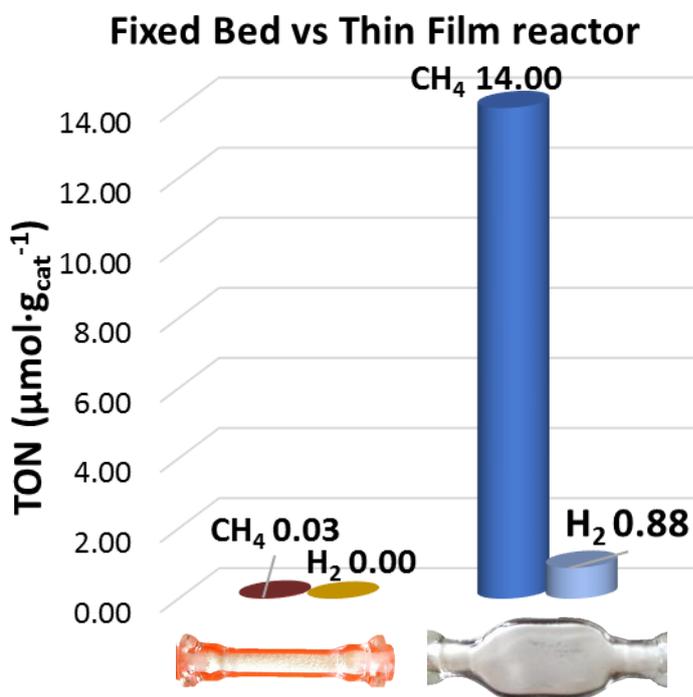


Fig. 1 Benchmark titania photocatalytic activity in fixed bed and thin film reactors.

It is worth noting that this result cannot be ascribed to the different amount of catalyst employed for each test. Indeed, the small amount of catalyst and the use of a thin film promote the adsorption of reagents on the active sites as well as the product desorption.

These steps need to be as fast as possible to make catalytic sites available for new carbon dioxide molecules to adsorb again. This means that within the thin film reactor the mass transport is facilitated compared to the fixed bed reactor, hence making products desorption easier and, as a consequence, their subsequent collection as well.

To sustain this statement, light harvesting is more efficient on thin film deposited catalyst: as a matter of fact, in this case quantum yield is 0.11 % to  $2.31 \cdot 10^{-4}$  %.

Finally, the photoactivity was so low when using the fixed bed reactor, that no other product was observed. On the contrary, the increased photoefficiency in the case of the thin film reactor would allow to observe any other products, namely hydrogen. Such molecule comes from the water splitting, that is a side reaction that might occur under the same experimental conditions.

### 3.2 Characterisation of the unpromoted $TiO_2$ photocatalyst

Preliminary to the investigation on the effect of the dopants, the morphological properties and photocatalytic activity of the unpromoted titania sample were studied.

In order to obtain efficient photocatalysts, the titania crystalline phase is an important parameter and anatase phase is highly suitable [78]. Aimed at finding the optimal calcination temperature to obtain  $TiO_2$  in the anatase form, TG/DTA analysis was performed on the uncalcined sample. The results are reported in Fig. 2.

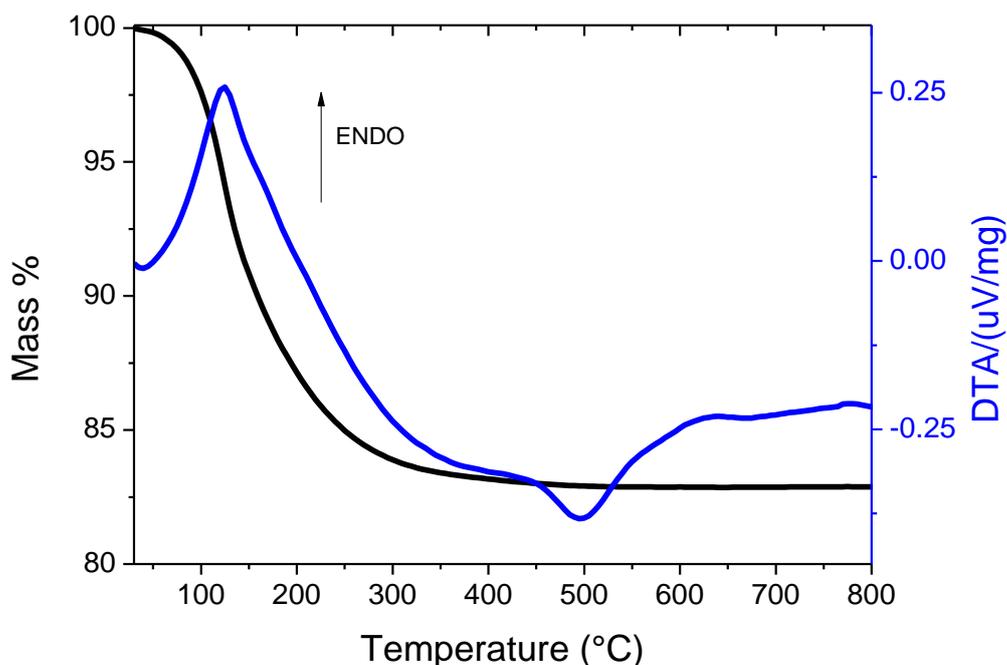


Fig. 2 Uncalcined titania TG/DTA analysis.

According to the TG curve, the weight loss takes place in a single stage from 60 °C to 400 °C. The endothermic peak centred at 120 °C can be attributed to the loss of water. Moreover, an exothermic process without any weight loss is observed between 400 °C and 600 °C. In agreement with literature data [79], this process can be ascribed to the phase transition from amorphous to crystalline titania in the anatase phase.

Considering the TG/DTA results, it was proposed that the calcination at 400 °C could be an optimal compromise to retain relative high surface area of titania and, at the same time, to assure the transition from amorphous titania to crystalline anatase phase.

The calcined unpromoted titania sample was then tested in the CO<sub>2</sub> photoreduction. The results are reported in Fig. 3, where the comparison with those obtained for the commercial titania reference is shown.

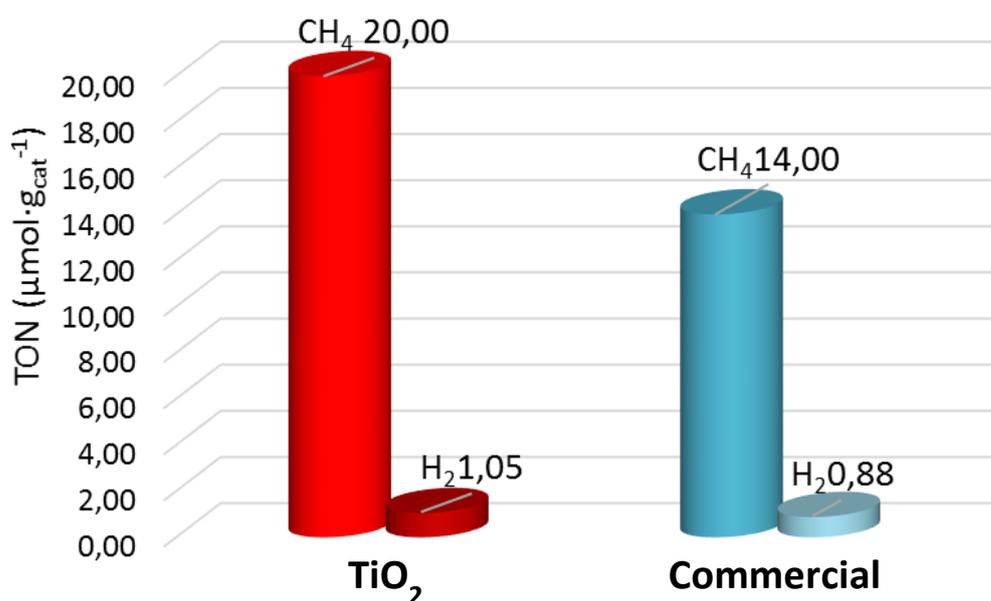


Fig. 3 Photoactivity tests in the CO<sub>2</sub> photoreduction performed on unpromoted TiO<sub>2</sub> (red columns) and commercial titania (blue columns).

First of all, it was observed that in the presence of both catalysts the only detected products are methane and hydrogen: the former derives from the CO<sub>2</sub> photoreduction and the latter comes from the water splitting. Moreover, the product distribution is definitely shifted towards methane: as a matter of fact, selectivity to methane is 95 % for both samples.

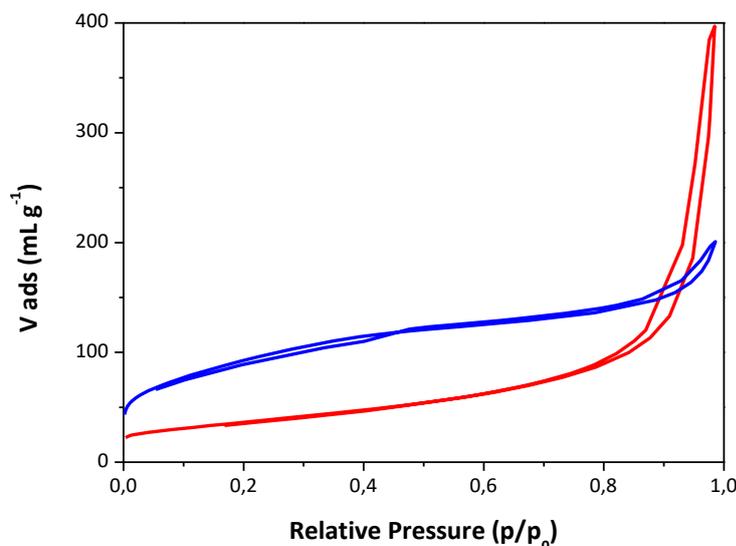
Interestingly, the unpromoted titania sample provides a considerably higher productivity towards methane than the commercial titania (20,00 μmol<sub>CH<sub>4</sub></sub>·g<sub>cat</sub><sup>-1</sup> by TiO<sub>2</sub> sample vs 14,00 μmol<sub>CH<sub>4</sub></sub>·g<sub>cat</sub><sup>-1</sup> by reference material), whereas the difference in hydrogen

productivity is small ( $1,05 \mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{cat}}^{-1}$  by  $\text{TiO}_2$  sample vs  $0,88 \mu\text{mol}_{\text{H}_2} \cdot \text{g}_{\text{cat}}^{-1}$  by reference material).

Both methane and hydrogen yields are comparable to those found in the literature, though the reaction conditions adopted within this study are considerably milder. In particular, either carbon dioxide pressure or irradiance are considerably lower than those reported in most of literature, in which the photon energetic input was extremely high [72,80,81].

Therefore, in order to understand the different behaviours observed in the reactivity tests and to establish structure-activity relationships, a deep physicochemical characterization was performed.

The first investigated parameters were the specific surface area and the pore volume, crucial features for every heterogeneous catalyst [42]. The surface properties have been examined by means of nitrogen physisorption and the obtained adsorption/desorption isotherms are reported in Fig. 4.



**Fig. 4**  $\text{N}_2$  physisorption isotherms of unpromoted  $\text{TiO}_2$  (red curves) and commercial titania (blue curves).

The unpromoted  $\text{TiO}_2$  sample shows a type IV isotherm typical of mesoporous materials. The hysteresis loop is shifted towards high relative pressures (between 0,8 and 1  $p/p_0$ ), indicating a narrow distribution of pores, that is centred on 25 nm. Differently, the isotherm curves related to commercial titania are different, since they are characterized by a higher nitrogen adsorption at low relative pressures and a wider hysteresis loop, corresponding to a wider and non-homogeneous pore size distribution if

compared to unpromoted TiO<sub>2</sub>. Moreover, the commercial sample provides a higher surface area (217 m<sup>2</sup>·g<sup>-1</sup>) than the synthesised sample (110 m<sup>2</sup>·g<sup>-1</sup>). The comparison between the obtained specific surface areas and the photoactivity indicated that the commercial sample, despite possessing the highest surface area, shows the lowest photocatalytic activity. These findings suggested that a high surface area is not a crucial parameter in the adopted reaction conditions.

Then both crystallinity and crystal phase of the examined samples were studied by XRD analysis. The results are shown in Fig. 5.

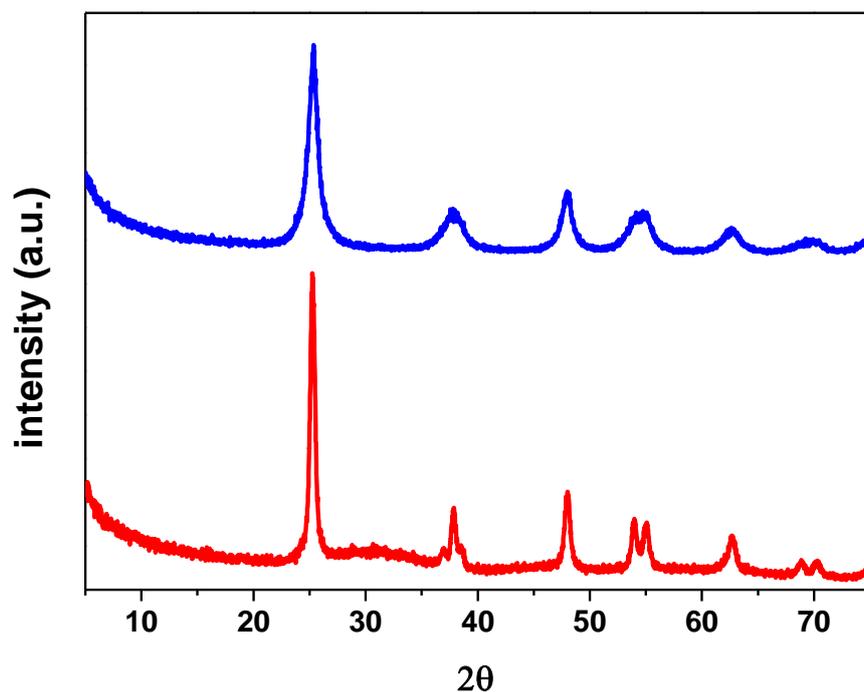


Fig. 5 XRD patterns of unpromoted TiO<sub>2</sub> (red curve) and commercial sample (blue curve).

In both cases the observed crystalline phase was anatase, i.e. the most suitable phase for photocatalytic purposes, as previously discussed [39]. The diffraction peaks related to the commercial sample are wider and less defined than those of the unpromoted TiO<sub>2</sub> photocatalyst. Such feature is an indication that the commercial sample is made of titania nanoparticles smaller than those present in the TiO<sub>2</sub> sample, in agreement with the N<sub>2</sub> physisorption measurements which provided a surface area (217 m<sup>2</sup>·g<sup>-1</sup>) for the commercial sample higher than that of the synthesised TiO<sub>2</sub> sample (110 m<sup>2</sup>·g<sup>-1</sup>).

In addition, the different width of the XRD peaks could also point out that a large fraction of the commercial sample is mainly made up of amorphous titania. Indeed, the commercial titania purchaser stated that only 40 wt. % of the reference material is

crystalline and in the anatase phase, whilst it was found that in the unpromoted TiO<sub>2</sub> the anatase phase is more than 95 wt. % of the sample and only a small fraction is amorphous. Therefore, the XRD evidences, along with the catalytic results (showed in Fig. 3), suggest that the sample crystallinity affects the CO<sub>2</sub> photoreduction activity, whereas it has no influence on the selectivity.

### 3.3 Effect of the promoters on the properties and activity of the TiO<sub>2</sub> photocatalysts

In order to further improve the effectiveness of the titania photocatalyst, two different promoters, i.e. CuO and Au, were introduced into the TiO<sub>2</sub> sample. In particular, the same amount (0,2 wt. % on metal base) of promoter was added, as confirmed by the FAAS analysis. Due to such low amount, the promoters were not detected by XRD analysis and it was found that the addition of the promoter has a negligible effect on the specific surface area, as demonstrated by N<sub>2</sub> physisorption results reported in Table 1.

Photocatalyst	BET Specific Surface Area (m <sup>2</sup> /g)
MIRKAT 211	217
TiO <sub>2</sub>	110
CuO-TiO <sub>2</sub>	100
Au-TiO <sub>2</sub>	100

**Table 1. Specific Surface Areas of the examined photocatalysts obtained by N<sub>2</sub> physisorption analyses.**

The nature of the promoters was then investigated and TPR analyses were resorted on to have information to on the oxidation state of copper and gold after insertion into the TiO<sub>2</sub> sample.

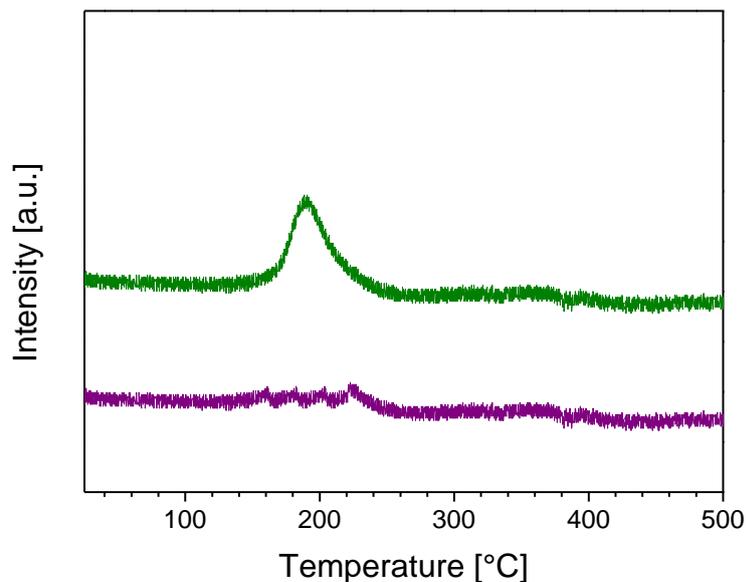


Figure 6. TPR analyses of CuO-TiO<sub>2</sub> sample (green curve) and Au-TiO<sub>2</sub> sample (violet curve).

TPR measurements revealed that copper is present as Cu(II), due to a single hydrogen consumption at 180 °C ascribable to Cu(II) reduction to Cu(0) (Figure 6, green curve), whereas gold is in its ground state, since no hydrogen consumption was observed (violet curve in the same Figure).

The diffuse reflectance UV-Vis-NIR spectra of the CuO-TiO<sub>2</sub> (green curve) and Au-TiO<sub>2</sub> (violet curve) photocatalysts are shown in Fig. 7.

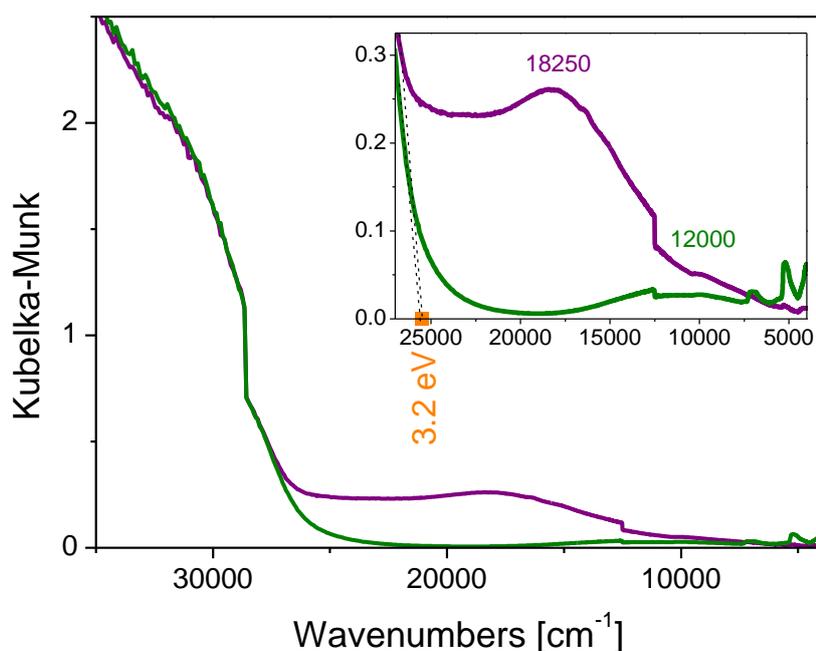


Fig. 7 Diffuse reflectance UV-Vis-NIR spectra of the CuO-TiO<sub>2</sub> (green curve) and Au-TiO<sub>2</sub> (violet curve) photocatalysts. Inset: zoom of the spectra in the Vis-NIR region.

The presence of the promoters does not seem to modify the titania electronic properties, since the absorption in the UV region was comparable and no significant modification in the band gap value was observed: a value corresponding to 3,2 eV (orange point in the inset of Fig. 7), which is the typical value for titania in the anatase form, was obtained in both cases. On the contrary, some differences were observed in the Vis-NIR region, as shown in the inset of Fig.6. In particular, a broad absorption centred at 18250  $\text{cm}^{-1}$  and due to the plasmonic resonance of gold nanoparticles [82,83], was observed for the Au-TiO<sub>2</sub> sample. Differently, a weak absorption centred at 12000  $\text{cm}^{-1}$ , assigned to d-d transition in Cu(II) species, was detected and ascribed to the presence of copper oxide nanoparticles [84,85] on the CuO-TiO<sub>2</sub> photocatalyst. Even if the presence of the promoters did not affect the titania band gap value, the presence of such species is aimed at reducing the electron-hole recombination by modifying the interaction between the titania surface and light.

After having considered the chemical nature of the promoters, the Au-TiO<sub>2</sub> and the CuO-TiO<sub>2</sub> samples were tested in the CO<sub>2</sub> photoreduction. The results are reported in Fig. 7 with those already obtained for the unpromoted TiO<sub>2</sub> sample.

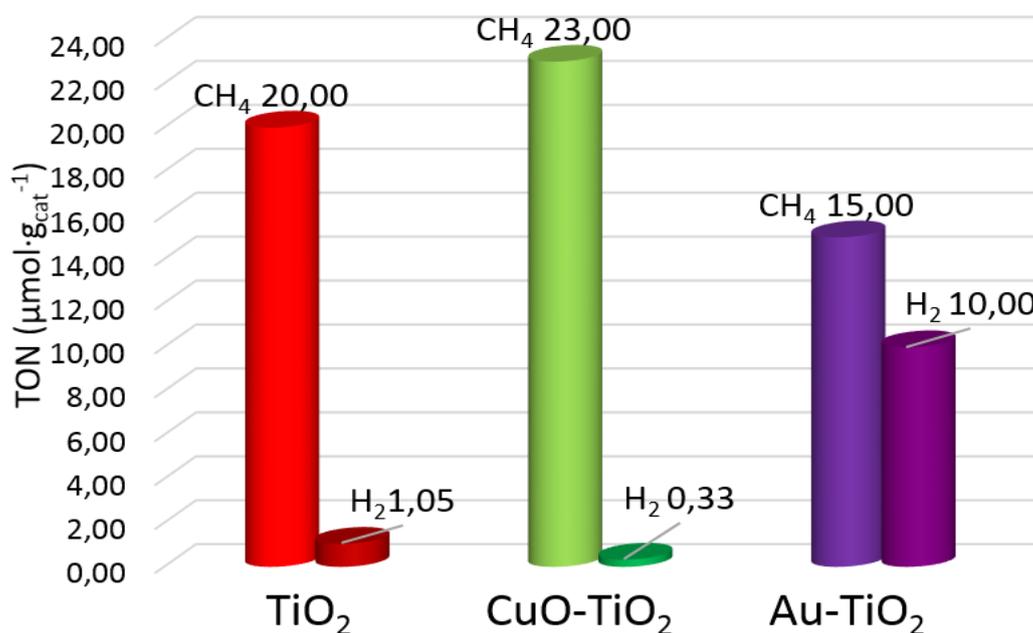


Fig. 8 Photoactivity tests in the CO<sub>2</sub> photoreduction performed on unpromoted TiO<sub>2</sub> (red columns), CuO-TiO<sub>2</sub> (green columns) and Au-TiO<sub>2</sub> (violet columns) catalysts.

As previously observed for the TiO<sub>2</sub> photocatalysts (Fig. 3), the selectivity as for the nature of the formed species did not varied upon the promoter insertion, since the detected products were methane and hydrogen also in this case. However, the presence

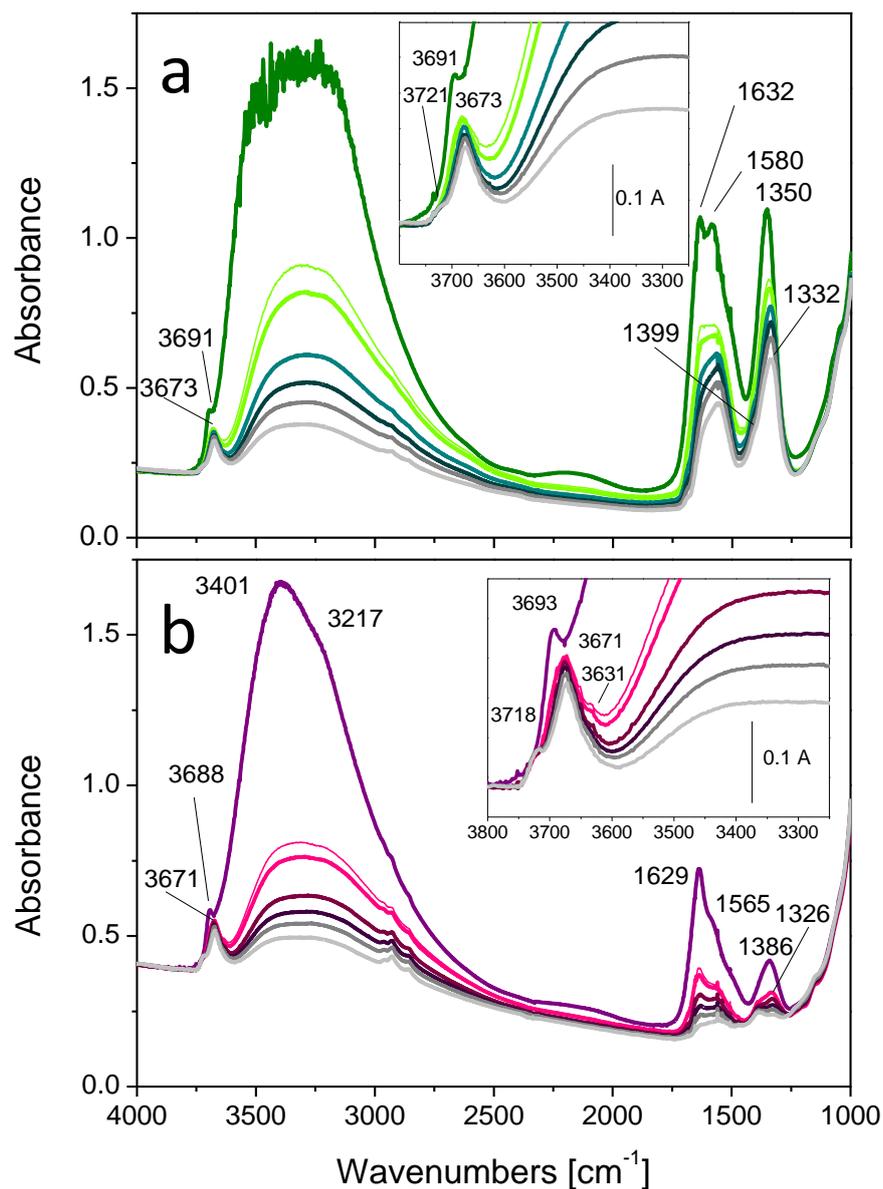
of CuO and Au promoters influenced the activity as well as the selectivity in the CO<sub>2</sub> photoreduction. In particular, if compared to the undoped sample, the promotion by CuO slightly increased the catalyst photoactivity toward the formation of methane (from 20,00 to 23,00  $\mu\text{mol}_{\text{CH}_4}\cdot\text{g}_{\text{cat}}^{-1}$ ) and, at the same time, it suppressed the hydrogen production by water splitting. Indeed, the selectivity to methane increased from 95 % for the undoped TiO<sub>2</sub> sample to 98 % for the CuO-TiO<sub>2</sub> sample. Differently, the sample containing Au nanoparticles gave the lowest methane production (15,00  $\mu\text{mol}_{\text{CH}_4}\cdot\text{g}_{\text{cat}}^{-1}$ ), whereas the production of hydrogen was considerably higher (10,00  $\mu\text{mol}_{\text{H}_2}\cdot\text{g}_{\text{cat}}^{-1}$ ), leading to a 60 % selectivity to methane. Considering light harvesting for CO<sub>2</sub> photoreduction, copper introduction increases quantum yield from  $4.75\cdot 10^{-4}$  % for the undoped sample to 5.48· for CuO-TiO<sub>2</sub> sample, whilst it decreases to  $3.56\cdot 10^{-4}$  % for Au-TiO<sub>2</sub> sample.

The above results demonstrated that the introduction of CuO on the TiO<sub>2</sub> catalyst favoured the CO<sub>2</sub> photoreduction and, on the contrary, the presence of Au nanoparticles increased the activity in the water splitting reaction. It must be considered that the reaction takes place only if the interaction between carbon dioxide and water occurs at the photoexcited catalytic surface [23]. Therefore, if only water is adsorbed at the surface, only water splitting reaction happens, since the CO<sub>2</sub> molecule is more difficultly adsorbed than water on the surface of titania [86]. To overcome this issue, the reaction has been performed in the presence of large excess of CO<sub>2</sub>, even though the water splitting reaction was not completely suppressed. The catalytic data indicate that the introduction of gold nanoparticles on the TiO<sub>2</sub> surface seems to increase the hydrophilicity of the photocatalyst and, as a consequence the capability of Au-TiO<sub>2</sub> to adsorb CO<sub>2</sub> was diminished. Carneiro *et al.* reported that gold nanoparticles are able to modify hydroxyl groups population on titania [87]. Hence, it can be proposed that the different surface properties of CuO-TiO<sub>2</sub> and Au-TiO<sub>2</sub> play a key role in the reaction, as revealed by the different photocatalytic behaviour displayed by the two photocatalysts.

### *3.4 Influence of the surface and electronic properties on the photoactivity of CuO-TiO<sub>2</sub> and Au-TiO<sub>2</sub>*

In order to explain the different behaviour displayed by the two promoted catalysts during the CO<sub>2</sub> photoreduction, FTIR measurement were performed on both CuO-TiO<sub>2</sub> and Au-TiO<sub>2</sub> samples.

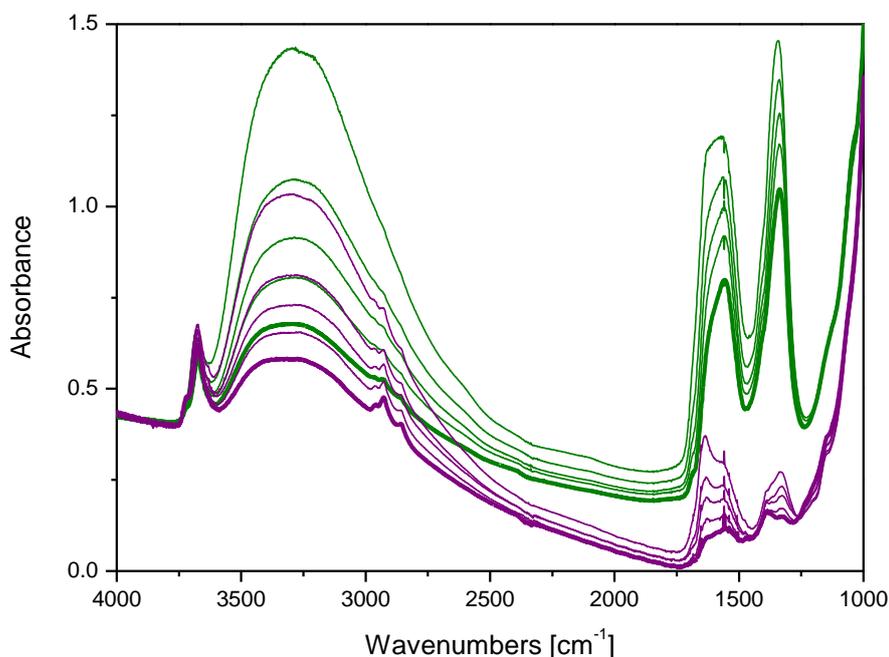
The FTIR absorbance spectra collected on CuO-TiO<sub>2</sub> and Au-TiO<sub>2</sub> samples upon outgassing from r.t. up to 150 °C are reported in Fig. 8. As specified in the experimental section, the spectra have been normalised to the density of the pellets. Therefore, the intensity of the absorption bands can be taken as a measure of the amount of adsorbed species and of their stability to the outgassing at increasing temperature on the two photocatalysts. The intense absorption centred at about 3400 cm<sup>-1</sup> and the peak at 1632-1629 cm<sup>-1</sup> observed on both CuO-TiO<sub>2</sub> and Au-TiO<sub>2</sub> are due to the stretching and bending modes, respectively, of OH groups related to the presence of adsorbed molecular water (navy curves). The largest fraction of such molecules is easily removed upon degassing the samples at r.t. for 30 min (bold blue curves); however, a monolayer of hydroxyl groups and water molecules is still present [88] and gradually decreases upon outgassing at increasing temperature, up to 150 °C (red curves), as confirmed by the peak at 3673(3671) cm<sup>-1</sup> with a weak shoulder at 3721(3718) cm<sup>-1</sup>, due to the stretching mode of two types of free hydroxyl groups [89,90] (see the insets in Fig. 8). These features give an idea of the behaviour of the catalyst at the surface during the CO<sub>2</sub> photoreduction, that is performed at room temperature in the presence of water. However if compared with CuO-TiO<sub>2</sub>, the Au-TiO<sub>2</sub> photocatalyst possesses a more hydrophilic surface since the intensity of the bands due to the presence of adsorbed water molecules is much higher than those related to carbonate species and observed at lower frequencies ( $\nu < 1600$  cm<sup>-1</sup>) that will be discussed in detail afterwards.



**Fig. 8** FTIR absorbance spectra of CuO-TiO<sub>2</sub> (section a) and Au-TiO<sub>2</sub> (section b) in air (olive/purple curves), under 10 min (fine green/pink curves) and 30 min (bold green/pink curves) outgassing at r.t., at 80 °C (cyan/wine curves), at 100 °C (dark cyan/wine curves), at 120 °C (dark grey curves) and at 150 °C (light grey curves).

In addition, a careful comparison among the spectra obtained on the two photocatalysts reveals interestingly that at frequencies lower than 2500 cm<sup>-1</sup>, the addition of gold produced a modification in the spectra, ascribed to the erosion of an electronic absorption, occurring at all the temperatures here considered (violet curves vs green curves in Fig. 9). It is worth noting that the appearance of an electronic absorption is related to the presence of free electrons in the titania CB: its erosion is the consequence of the population of new energetic levels created when gold nanoparticles are introduced. In this case, the Schottky barrier between the metal nanoparticles and the oxide hinders electron flow to TiO<sub>2</sub>, effectively behaving as an electron trap. This

phenomenon is more pronounced in the case of Au-TiO<sub>2</sub> (violet curves) than in the case of CuO-TiO<sub>2</sub> (green curves) and it is also in agreement with the DRUV-Vis results that point out a small difference in the titania band gap of the two samples (see Fig. 8, inset).



**Fig. 9** Comparison among the normalised FTIR absorbance spectra of CuO-TiO<sub>2</sub> (green curves) and Au-TiO<sub>2</sub> (violet curves) reported in Fig. 8. Spectra normalised to the pellet density.

Therefore, the above findings indicate that in the case of the gold-doped titania photocatalyst, a less negative titania CB can be hypothesised, resulting in a less effective CO<sub>2</sub> reduction [8]. Indeed, gold insertion modified the electronic circulation, but it has a detrimental effect on the activity and selectivity displayed by titania in the CO<sub>2</sub> photoreduction if compared to CuO-promoted titania.

### *3.5 Interaction with CO<sub>2</sub> at room temperature: surface reactivity*

The adsorption of CO<sub>2</sub> at r.t. was carried out on both samples with the aim to investigate the interaction between the reactant and the catalytic surfaces and the results are reported in Fig. 10, section a. Before the analyses, the samples were simply outgassed from r.t. up to 150°C for 10 minutes and then the temperature was decreased again to r.t. under outgassing. This procedure guaranteed to remove the large fraction of water molecules adsorbed at the surface, leaving only some residual of hydroxyl groups and adsorbed water molecules, as shown in section a. In addition, a number of bands is produced on the CuO-TiO<sub>2</sub> (green curves) and Au-TiO<sub>2</sub> (violet curves) photocatalysts in

the 2400-2250  $\text{cm}^{-1}$  and 1800-1000  $\text{cm}^{-1}$  ranges (highlighted by dashed frames and enlarged in sections b and c, respectively) upon the inlet of 15 mbar  $\text{CO}_2$  at room temperature (bold curves).

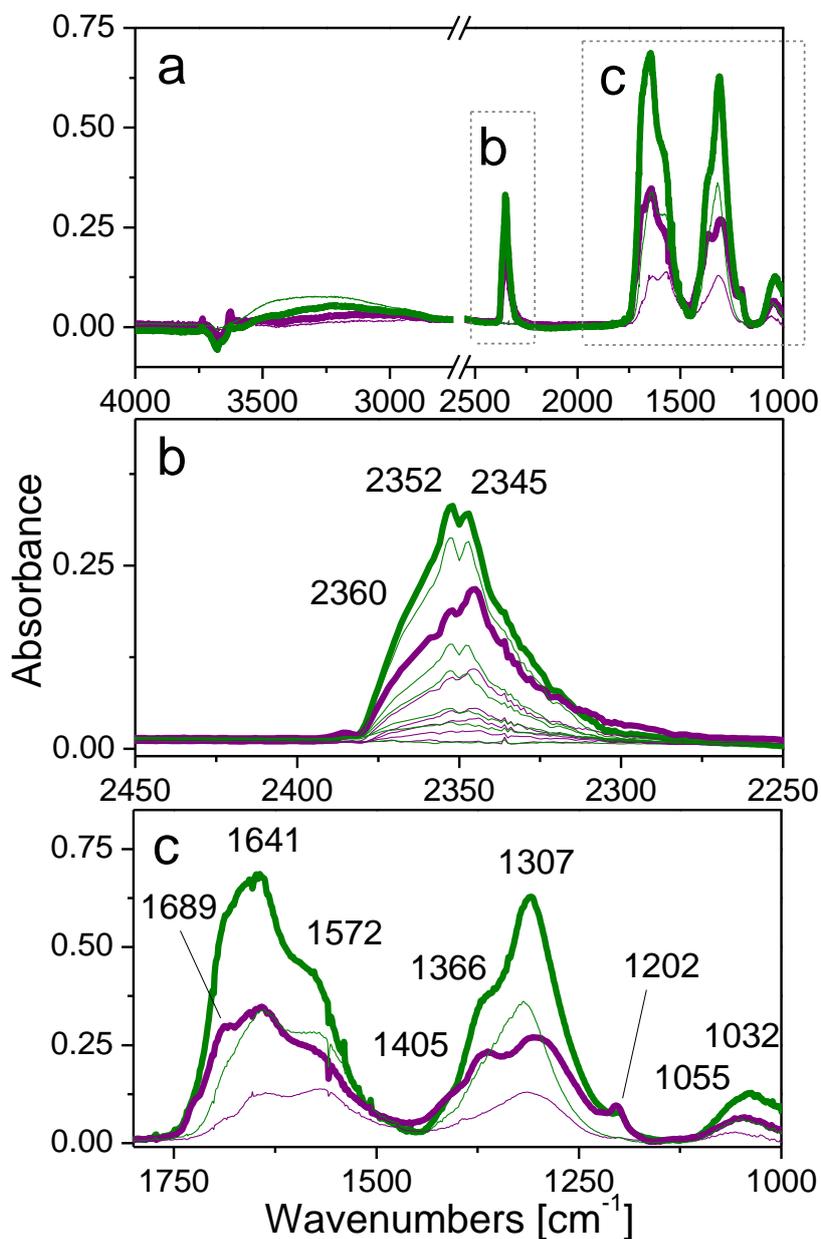


Fig 10. Section a: FTIR difference spectra collected on  $\text{CuO-TiO}_2$  (green curves) and  $\text{Au-TiO}_2$  (violet curves) after the inlet of 15 mbar  $\text{CO}_2$  at r.t. (bold curves) and subsequent outgassing at the same temperature for 30 minutes (fine curves). Section b: zoom on the 2450-2250  $\text{cm}^{-1}$  spectral range in which the spectra collected at decreasing  $\text{CO}_2$  pressure and under outgassing at r.t. (fine curves). Section c: zoom on the 1800-1000  $\text{cm}^{-1}$  spectral range.

A quite asymmetric absorption with two components at 2345 and 2352  $\text{cm}^{-1}$ , with a broad shoulder at about 2360  $\text{cm}^{-1}$ , due to carbon dioxide molecules linearly adsorbed on  $\text{Ti}^{4+}$  sites, is observed (section b, bold curves) and it is gradually depleted when

decreasing the CO<sub>2</sub> pressure and after outgassing at r.t. (fine curves). The intensity of the absorption observed in the case of CuO-TiO<sub>2</sub> (green curves) is higher than that related to Au-TiO<sub>2</sub>, pointing out a larger amount of linearly adsorbed CO<sub>2</sub> formed on CuO-doped titania. Moreover, the shift of the  $\Sigma_u^+$  band of adsorbed CO<sub>2</sub> molecules with respect to the gas phase (2343 cm<sup>-1</sup>) increases with the Lewis acid strength of the cationic sites [91]. Therefore, the presence of two defined peaks indicate that the CO<sub>2</sub> molecules are adsorbed on surface Ti<sup>4+</sup> ions with different Lewis acid strength. At the same time, bands due to carbonate-like species produced by the reaction of linearly adsorbed CO<sub>2</sub> with O<sub>2</sub><sup>-</sup> basic sites are produced (section c, bold curves) on both samples with different relative intensity. The production of carbonate-like species points out the presence of surface Ti<sup>4+</sup>-O<sup>2-</sup> couples in which the basic O atom is able to react with the C atom from CO<sub>2</sub>. More in detail, bands at 1641, 1307 and 1032 cm<sup>-1</sup>, and at 1572, 1366 and about 1045 cm<sup>-1</sup> are observed. These absorptions are assigned to two different (chelate and/or bridged) bidentate carbonate species [92]. From these findings, it can be inferred that several kind of sites, i.e. those able to coordinate molecular CO<sub>2</sub> and those producing bidentate carbonate species are present on the titania surface. All these sites are more abundant on CuO-TiO<sub>2</sub> than on Au-TiO<sub>2</sub>. Moreover, on the CuO-TiO<sub>2</sub> catalyst the produced species are slightly more stable to the outgassing at r.t. than on Au-TiO<sub>2</sub>, as revealed by the comparison between the initial intensity (bold curves) and final intensity (fine curves) of the bands related to each sample.

Finally, bands at 1689, 1405 and 1202 cm<sup>-1</sup>, with almost the same intensity for both samples, due to bicarbonate species produced by reaction of CO<sub>2</sub> with some basic -OH groups, are observed [92, 93]. A component at about 1730 cm<sup>-1</sup>, more evident in the case of Au-TiO<sub>2</sub> and tentatively assigned to carboxylate species is also detected [94].

FTIR spectra of adsorbed CO<sub>2</sub> definitely showed that the surface of the CuO-TiO<sub>2</sub> photocatalyst is more efficient in adsorbing and reacting with the molecule, resulting in a more valuable interaction between the CO<sub>2</sub> molecules and the photocatalytic surface [51], which represents the first step of carbon dioxide photoreduction.

From all the experimental findings, it is possible to state that surface properties affect reactants adsorption (particularly for CO<sub>2</sub>, the least adsorbable reactant) and, as a consequence materials activity and selectivity in CO<sub>2</sub> photoreduction.

## Conclusions

The development of an efficient technology for carbon dioxide conversion into solar fuel relies on an integrated and interdisciplinary “catalysis by design” approach covering different expertise areas, such as fundamental science and applied engineering. In this paper, two main carbon dioxide photoreduction drawbacks, namely light harvesting and process selectivity, were investigated.

Light harvesting was enormously implemented by reactor design: the choice of a thin film reactor enhanced methane enormously, leading to comparable results with those found in literature, despite considerably milder conditions, particularly in terms of irradiance.

On the contrary, the material design was fundamental to develop an opportunely designed catalytic system to control the selectivity to the desired product, i.e. methane. Modification of electronic and surface properties allowed to reach this goal. On one side, the enhanced charge separation observed for Au-TiO<sub>2</sub> seems to negatively affect the activity, resulting in a less negative CB, thus less efficient in CO<sub>2</sub> photoreduction.

On the other side, CO<sub>2</sub> adsorption on catalytic surface represents a critical step that still deserves as much attention as developing greener and highly active catalysts. The CuO-TiO<sub>2</sub> photocatalyst matches all these requirements, proving to be more active and selective than the Au-TiO<sub>2</sub> material. The reasons for the enhanced photoactivity can be related to the presence and the abundance of surface sites able to efficiently adsorb and react with the CO<sub>2</sub> reactant.

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## **Captions**

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