



On the application of Ti/TiO₂/CuO n-p junction semiconductor: A case study of electrolyte, temperature and potential influence on CO₂ reduction



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HIGHLIGHTS

- Photoelectrochemical CO₂ reduction at an n-p Ti/TiO₂/CuO electrode.
- Formation of methanol, ethanol, and acetone as reduction products.
- Temperature, supporting electrolyte and potential influence in CO₂ reduction.
- A charge transfer and reaction scheme are presented to account for the product evolution.

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ABSTRACT

This work presents the use of photoelectrocatalysis (PEC) aiming at converting CO₂ into fuels such as methanol and ethanol. For the CO₂ conversion, Ti/TiO₂/CuO n-p junction semiconductor was chosen owing to its heterojunction benefits. The material was constructed using dip-coating technique and was found to present high porosity for both TiO₂ and CuO deposits. Photocurrent vs potential curves showed a relatively good electrode photoactivity for CO₂ dissolved in NaHCO₃ subjected to UV-Vis commercial irradiation. The CO₂ reduction process is found to be deeply affected by the type of electrolyte that, in essence, acts by supporting and generating different quantities of methanol, ethanol and acetone. Methanol is the preponderant fuel generated (91%) upon the reduction of CO₂ by photoelectrocatalysis operating at UV-Vis light and +0.20 V as bias potential in 0.1 mol L⁻¹ K₂SO₄ and UV-Vis light irradiation. Interestingly though, under 0.1 mol L⁻¹ NaHCO₃ pH 8 and applied potential of -0.6 V, we found it feasible to reach 97% for methanol following 2 h of reaction. The results primarily unravel an important contribution towards understanding the importance of the electrolyte when it comes to CO₂ reduction by photoelectrocatalysis and Ti/TiO₂/CuO electrode has clearly proven to be a promising material for the photoelectrochemical CO₂ reduction into methanol with high selectivity.

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1. Introduction

The current appalling growing concern for CO₂ levels on the planet has widely contributed to fueling a greater demand for methods capable of promoting the reuse of CO₂ mainly through its conversion into products with high added value [1]. The literature has reported several methods proposed with this objective in mind among them including biocatalysis [2,3], thermocatalysis [4,5], photocatalysis [6,7], electrocatalysis [8,9] and photoelectrocatalysis [10,11]. The methods based on artificial photosynthesis such as photocatalysis have attracted a wider interest as an approach

for the conversion of CO₂ using solar energy into useful fuels including methane, methanol, carbon monoxide, formic acid and formaldehyde [1,6,12,13]. Admittedly though, the method efficiency is found to be limited to easy recombination of charges generated during the process of semiconductor irradiation [14].

Photoelectrocatalysis is a widely known methodology that has been developed capable of effectively combining the photocatalysis technique with bias potential in order to minimize the photo-generated electron-hole pairs recombination, promoting a fast electron transfer to CO₂ while at the same time maximizing the yield [11,15–18]. All the results have shown that the electrode material has a significant influence on the CO₂ reduction performance and on the selectivity of the products generated.

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One of the main crucial challenges of photoelectrochemistry still lies in the development of materials with visible light activity, high stability and enhanced photoactivity; and as such it bears no difference when the target is CO₂ reduction [18]. With this in mind, some research studies have been conducted so as to improve the semiconductor properties where most of them have dealt with the junction of different oxides or metal/oxides types of semiconductors [16,17,19].

The literature reports the use of copper oxides as a good material for CO₂ reduction and alcohols formation [15,20–24], nonetheless, copper oxides have been typically found to suffer from photocorrosion [25,26], which compromises their stability when applied towards CO₂ reduction by means of photoelectrocatalysis [15]. Aimed at the improvement of copper oxides stability, some researchers have conducted studies coupling these oxides to other materials where they reported a great alteration in terms of the oxides stability [1,12,27].

In general, the coupling of TiO₂ to copper oxides may be a good option for improving the stability of the latter and as such has been applied in photocatalysis reactions [1,28–30]. Slamet and collaborators in their works have reported doping the TiO₂ Degussa-P25 with copper nitrate, generating different copper species (Cu⁰, Cu⁺ and Cu²⁺) which led to their conclusion that TiO₂/CuO is the better enhancement for the photoreduction of CO₂ and methanol formation [28,29]. Qin et al. [1] have studied the TiO₂/CuO composite for CO₂ reduction into methanol as sacrificial reagent and for methyl formate generation. Yuan and other collaborating researchers [30] prepared a copper (I) dye-sensitised TiO₂-based system aimed primarily at efficient light harvesting for photoconversion of CO₂ into methane (CH₄). These works have shown that this arrangement can be applied successfully towards improving the CO₂ reduction by photocatalysis.

It is noteworthy that the coupling of copper oxides to TiO₂ is justified given that TiO₂ is the most useful semiconductor applied in photoelectrocatalysis [31,32] owing to its low cost, non-toxicity and high catalytic stability besides the long lifespan of the photo-generated electron/hole pairs [33,34]. However, copper oxide application towards the direct conversion of CO₂ by photoelectrocatalysis is found to bear some restrictions. Even so, the coupling of TiO₂/CuO has yet not been tested in CO₂ reduction using photoelectrocatalysis, where the coupling of UV-Vis irradiation and bias potential is seen to be likely more effective a technique compared to photocatalysis.

This paper, at its core, seeks to present the reduction of CO₂ dissolved in aqueous medium on Ti/TiO₂/CuO electrodes by photoelectrocatalysis aiming at alcohol formation. As TiO₂ is said to be a really stable and efficient semiconductor while Cu²⁺ stands to be a promising candidate when it comes to the reduction of CO₂ to alcohol, the coupling of TiO₂ and CuO seeks to investigate a new material for photoelectrocatalytic CO₂ reduction with the purpose of raising the degree of stability and understanding the influence it exerts on alcohol formation. The CO₂ reduction was analyzed under different supporting electrolyte types and the products formed were quantified using chromatographic techniques.

2. Experimental part

2.1. p-n Ti/TiO₂/CuO semiconductor

The p-n Ti/TiO₂/CuO semiconductor was prepared using titanium isopropoxide and dibasic copper carbonate as precursors of TiO₂ and CuO, respectively [35]. Both solutions were prepared with 8.4×10^{-2} mol L⁻¹ of metal. The semiconductor was obtained following the deposition of 6 thin films carried out by dip-coating

using a solution of TiO₂:CuO prepared in a proportion of 3:1 (v/v). The semiconductor was calcined after each deposition at 600 °C with heating rate of 1 °C min⁻¹ during 90 min. A Ti/TiO₂ semiconductor was prepared for comparison using the same procedure though without the dibasic copper carbonate in the solution. The morphological and structural characterization were carried out by X-ray diffraction (Siemens D5000), FEG-SEM images (Zeiss Supra 35) coupled to EDS analysis. The photocurrent response was evaluated by linear sweep voltammetry in NaHCO₃ 0.1 mol L⁻¹ at pH 8 with and without CO₂ using scan rate of 0.01 V s⁻¹ obtained in an Autolab PGSTAT 302.

2.2. Photoelectrocatalytic CO₂ reduction

The photoelectrochemical experiments were performed in 500 mL cylindrical two-compartments glass reactor equipped with a cooling system (5 °C). The Ti/TiO₂/CuO working electrode (2.5 × 2.5 cm) was irradiated with a commercial UV-Vis light obtained from a 125 W high pressure mercury lamp without the bulb vertically inserted in a central quartz glass tube. A saturated Ag/AgCl (KCl sat) electrode was used as reference, and the counter electrode was a Pt gauze (2 × 1 cm). The CO₂ reduction was accomplished by measuring the UV-Vis light and controlled-potential electrolysis carried out in +0.20 V and -0.60 V using different supporting electrolytes at pH 8 and 0.1 mol L⁻¹. The methanol, ethanol and acetone formation were identified and quantified by gas chromatograph instrument coupled to a flame ionization detector (GC-FID model 2010 Shimadzu) using the solid-phase micro-extraction technique (SPME) [15].

3. Results and discussion

3.1. Characterization of TiO₂/CuO p-n junction semiconductor

Fig. 1 shows the morphological characteristics of Ti/TiO₂/CuO obtained by FEG-SEM. The image shows the Ti substrate completely covered by two different nanoparticles sizes. The smaller particles are TiO₂ nanoparticles with high porosity and uniformity with size ranging from 13 to 25 nm. These particles are randomly coated by CuO particles with size ranging from 100 to 300 nm. The EDS analysis confirmed the Ti, Cu and O presence, as can be observed in Fig. 2a. According to the EDS analysis the weight by

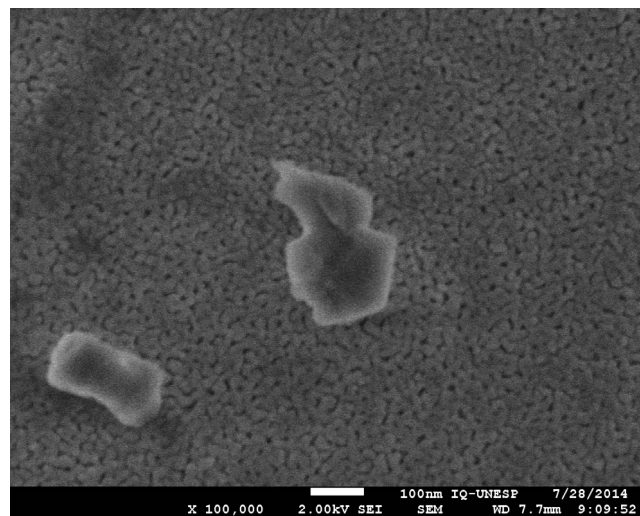


Fig. 1. FEG-SEM image of Ti/TiO₂-CuO p-n junction semiconductor prepared with sixty thin layers by dip coating of Ti plate in solution with 3:1 of TiO₂ and CuO precursors, respectively, calcined at 600 °C for 90 min in each deposition.

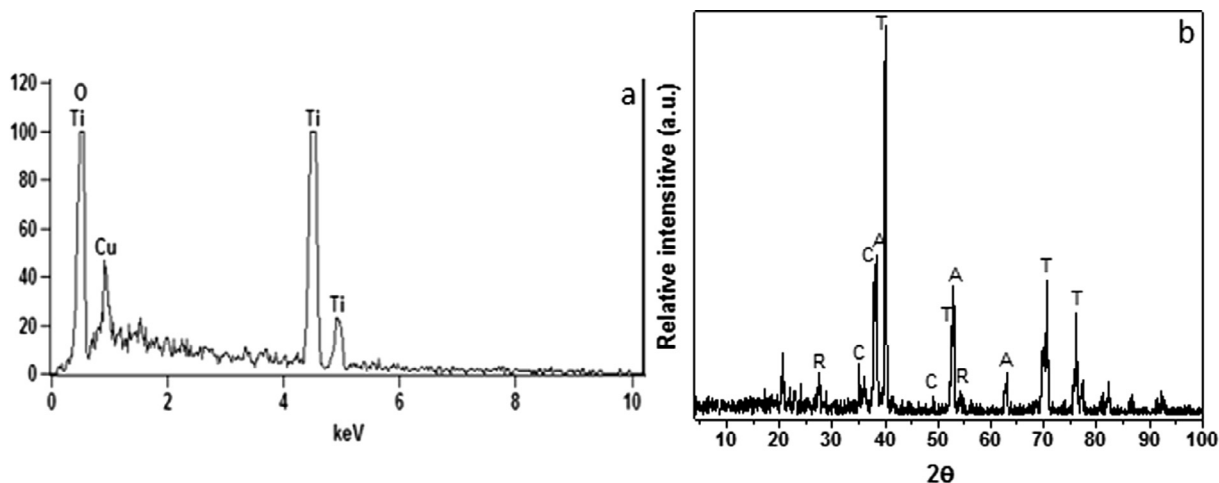


Fig. 2. a) EDS analysis and b) XRD diffractogram, where R and A represent, respectively, the rutile and anatase phases of TiO_2 , T represents the metallic titanium used as substrate and C being the CuO of $\text{Ti/TiO}_2\text{-CuO}$ heterojunction semiconductor.

percentage of which element present in the electrode surface was 39.0% of oxygen, 55.5% of titanium and 5.50% of copper. Therefore, the actual weight ratio of CuO is 10% in relation to TiO_2 . The anatase TiO_2 phase formation ($2\theta = 38.2, 54.2$ and 63) and the CuO presence ($2\theta = 35.4, 38.7, 82.6$ and 86.8) as well as the Ti ($2\theta = 40, 52, 70$ and 76) and the rutile TiO_2 phase ($2\theta = 27.5$ and 54.4) were confirmed by X-ray diffraction presented in Fig. 2b.

Fig. 3 illustrates the reflectance spectrum obtained for the $\text{Ti/TiO}_2\text{/CuO}$ semiconductor at the UV–Visible region. The wide optical absorption of the new material is found to be markedly different from the TiO_2 semiconductor that presents optical absorption in the ultraviolet region [32] and from the CuO semiconductor whose optical absorption is seen in the visible region [1]. The coupling of $\text{Ti/TiO}_2\text{/CuO}$ p-n junction can thus be seen to promote better use of radiation coming from a commercial lamp (UV–Vis) for instance or solar irradiation. Furthermore, the inset of Fig. 3 presents the band gap energy for the material obtained by Tauc's graphic [36] using Kubelka-Munk function, according to the Eq. (1) below:

$$\alpha = (1 - R)^{1/\gamma} / 2R \quad (1)$$

where α is the material absorptivity and R being the reflectance. The γ was assumed as two (indirect electronic transition allowed)

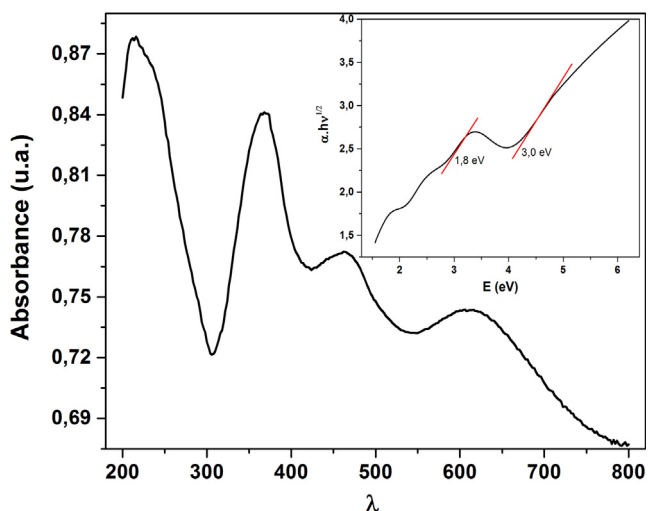


Fig. 3. Diffuse reflectance analysis in UV–vis region with an insert of $\alpha h\nu^{1/2}$ vs E graphic for band gap determination.

once this is the electronic transition more suitably indicated for both the TiO_2 [37] and CuO semiconductors [38]. The $\text{Ti/TiO}_2\text{/CuO}$ p-n junction semiconductor presents two values of band gap: 3.0 eV relative to TiO_2 contribution [39] and 1.8 relative to CuO contribution [38]. It is worth pointing out that for the fact that two band gap values have been obtained clearly perhaps substantively reinforces the affirmation that the material exhibits feature of a heterojunction with distinct influences of each semiconductor.

Fig. 4 illustrates the $\text{Ti/TiO}_2\text{/CuO}$ photocurrent response compared to a Ti/TiO_2 semiconductor without copper oxide deposition under dark, irradiation and dissolved CO_2 . A shifting of 400 mV is observed for CO_2 reduction when TiO_2 semiconductor is modified with CuO and exposed to UV–Vis light (Fig. 4a). This behavior is indicative of the role played by CuO in improving the electron trap when coupled to TiO_2 .

Fig. 4b shows the curves obtained for the $\text{Ti/TiO}_2\text{/CuO}$ p-n junction semiconductor under dark (line I) and under UV–Vis irradiation (line II). The curves can be seen to undergo a steep shift towards a less negative potential when the semiconductor is activated by light, indicating that the electrons and holes pairs (e^-/h^+) are created inside both TiO_2 and CuO, amplifying the charge on the electrode surface. In the presence of CO_2 , the curve is found to shift to less negative onset potential (from -0.80 to -0.50 V vs Ag/AgCl) in the cathodic region with the same photocurrent value while a high current peak is seen in the anodic region (from 0.03 to 0.1 mA cm^{-2}). This outcome may be attributed to the CO_2 acting as electron scavenger in the $\text{Ti/TiO}_2\text{/CuO}$ n-p junction electrode [1] (curve III, Fig. 4b). The current rises to maximum at potential around -0.65 V region, where a defined peak is observed, suggesting that the semiconductor is likely to be a good strategy vis-à-vis the promotion of CO_2 reduction.

Taking into account the previous results of diffuse reflectance spectra (Fig. 3) and the studies of Liu et al. [27] and Morales-Guio et al. [40], a schematic relative band position diagram of both TiO_2 and CuO has been presented in Fig. 5. The diagram depicts the potential redox necessary to reduce CO_2 to CH_3OH (~ -0.4 V) as well as the potential through which the reduction of CuO to Cu_2O (~ 0.2 V) occurs both in relation to hydrogen reference electrode [26]. The $\text{TiO}_2\text{/CuO}$ configuration presented in the band edges of the two oxides leads to a vector transference of photogenerated electrons from the TiO_2 to CuO particles. During the UV–Vis irradiation of the $\text{TiO}_2\text{/CuO}$ surface, a generation of electron hole pairs (e^-/h^+) charges in TiO_2 is found to occur. By so doing, the reduction of CO_2 on the $\text{TiO}_2\text{/CuO}$ surface may be said to take place via two

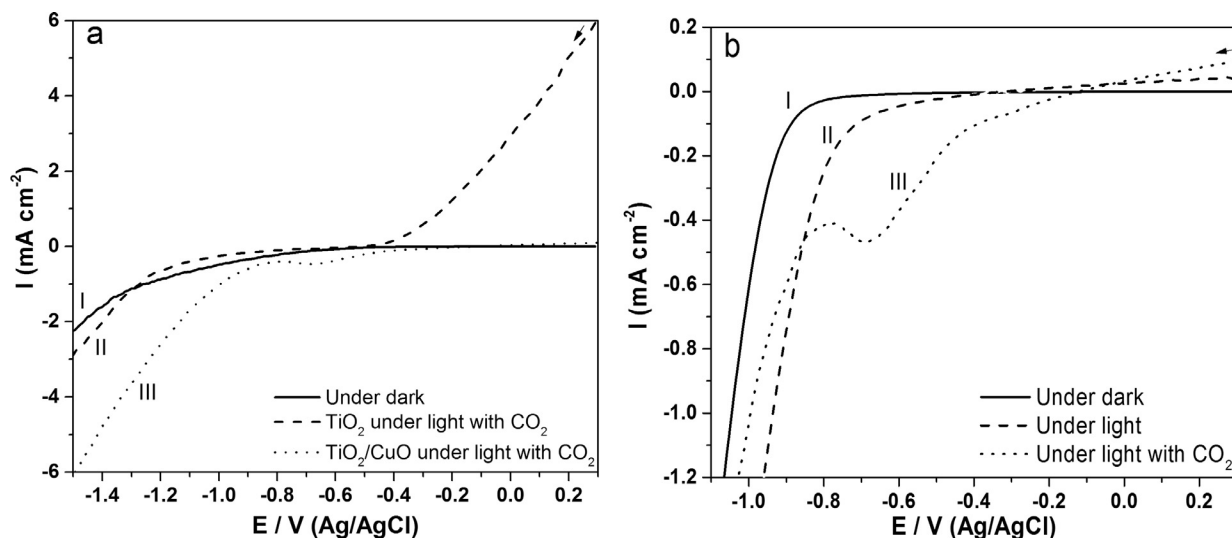


Fig. 4. a) Photocurrent vs potential in 0.1 mol L⁻¹ NaHCO₃ saturated with CO₂ obtained for TiO₂ semiconductor under dark (line I) and under UV-Vis light (line II) and TiO₂/CuO p-n junction semiconductor under UV-Vis irradiation (line III). b) photocurrent vs potential of the TiO₂/CuO n-p junction semiconductor under dark (line I), under UV-Vis light (line II) and under UV-Vis light with 0.1 mol L⁻¹ NaHCO₃ saturated with CO₂ (line III).

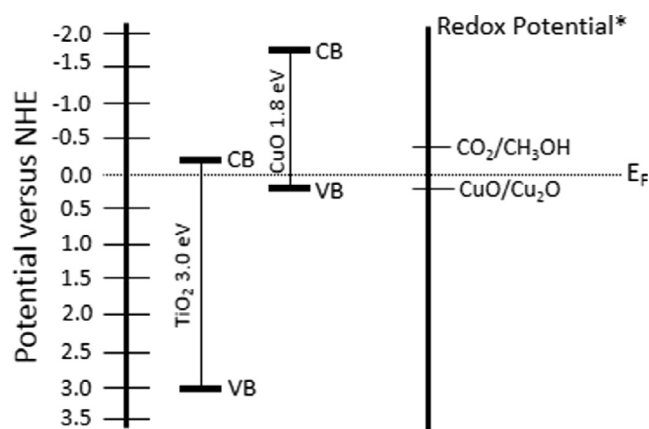


Fig. 5. Energy-band diagram of TiO₂/CuO p-n junction semiconductor. Semiconductor band edges and redox potential are presented versus NHE at *pH 7 in aqueous solution, 25 °C and 1 atm (VB = valence band, CB = conduction band and E_F = Fermi energy).

modes. At a higher potential such as -0.6 V, CO₂ reduction is likely to happen directly through the migration of excited e⁻ in the conduction band to the CO₂. However, the excited e⁻ in the conduction band of TiO₂ could also migrate onto the surface and be trapped by the CuO, leading to the formation of Cu⁺ while undergoing oxidation back to Cu²⁺, thereby reducing the CO₂ to CO₂^{-•}. This way, the recombination is hindered by both the photoexcited electrons and holes on grounds of their spatial separation. This can contribute towards improving the electrons on the TiO₂/CuO p-n junction semiconductor surface as verified previously [29,41].

3.2. Photoelectrocatalytic CO₂ reduction

The photoreduction of CO₂ is a multistep process involving adsorption, electron transfers and subsequent reactions [42]. There has been a fundamental consensus on the proposition that the CO₂^{-•} radical is the main intermediate, followed in turn by electron addition/protonation reactions [23]. Thus, based on what has been reported in the literature, further experiments were carried out testing PEC performance in order to reduce CO₂ in varying potentials, pH and supporting electrolyte.

3.2.1. Potential effect

Fig. 6 shows the products generation when the Ti/TiO₂/CuO n-p junction semiconductor is acting as photocathode after 2 h of photoelectrolysis carried out in 0.1 mol L⁻¹ NaHCO₃ pH 8 saturated with CO₂ and applied potential ranging from -0.60 V to +0.20 V. The results indicate that methanol is the preponderant compound formed in both +0.20 V and in -0.60 V. In the case of CO₂ reduction at +0.20 V, the CO₂ could be indirectly reduced concomitantly when the Cu₂O formed is reoxidized to CuO. This behavior essentially corroborates with the results presented in Fig. 4b which presents a shift to more negative onset potential around -0.60 V, culminating in a higher increase in the current value around +0.20 V both in the presence of dissolved CO₂.

The semiconductor promotes the generation of the electron (e⁻)/hole (h⁺) pair when subjected to irradiation with energy higher than the band gap (Eq. (2)), confirmed by the photocurrent vs potential (Fig. 4). According to Chiang, Amal and Tran [41], CuO has an unfilled 3d shell responsible for its thermodynamically

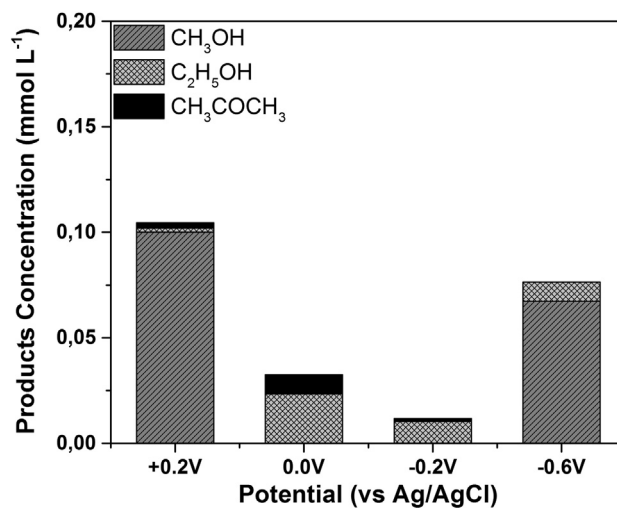
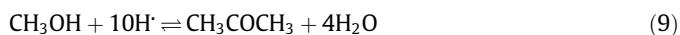
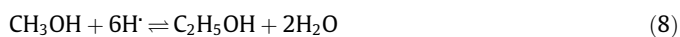
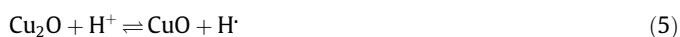
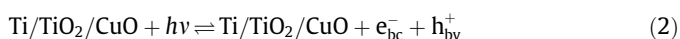


Fig. 6. Evaluation of the products CH₃OH (gray) C₂H₅OH (light gray) and CH₃COCH₃ (black) formed by photoelectrocatalytic CO₂ reduction in 0.10 mol L⁻¹ NaHCO₃ at pH 8 and 20 °C applying different potentials and UV-Vis light (125 W).

favorable reduction, thus making it an excellent electron trap on the TiO₂ surface (Eq. (3)). Tseng and coworkers [43] presented in their manuscript a fluorescence studied in order to prove that electrons generated in the TiO₂ are transferred to CuO. This electron needs to be consumed fast, otherwise the Ti/TiO₂/CuO surface will be transformed into an accumulator of charges [41] (Eq. (5)). Thus, the e⁻ generated on the TiO₂ surface is trapped by the Cu²⁺ species while the latter is consequently reduced to Cu⁺ [26,28]. Slamet et al. [29] have reported that Cu⁺ are the best adsorption sites for CO₂ in a paper they published previously. Hence, the CO₂ reduction occurs on Cu⁺ sites where this species undergoes a further reoxidation to Cu²⁺ (Eq. (6)). The same process is found to occur in the photoelectrocatalytic CO₂ reduction under +0.20 V owing to the fact that the reduction of CuO to Cu₂O is largely favored in this potential [26,41]. As a result of this behavior, the reduction of CO₂ under p-n junction Ti/TiO₂/CuO using any of the two potentials and UV-Vis light ensure a better life cycle of the semiconductor, rendering it possible to conduct over 30 experiments at a time with the same electrode without any noticeably significant efficiency loss. The photogenerated hole on the semiconductor surface is responsible for the water oxidation with ·OH and H⁺ formation (Eq. (4)) deemed indispensable for the new products formation (Eqs. (7), (8) and (9)). This mechanism ensures a high stability for the TiO₂/CuO semiconductor and is represented in Fig. 7.



The reduction CO₂ under Ti/TiO₂ semiconductor was also performed. However, there is no satisfactory performance and none product able to be quantified was detected. In fact, this behavior was expected due the expected performance of the material in the presence or absence of CO₂. Ti/TiO₂ semiconductor is a good material to promote oxidation under anodic potential when

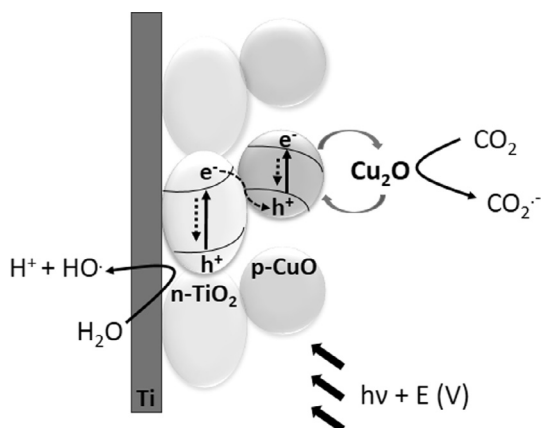


Fig. 7. Charge transfer illustrative mechanism of the p-n junction Ti/TiO₂/CuO semiconductor for the indirect CO₂ reduction.

irradiated by UV/Vis light. Although, the literature reports a review indicating why should not perform a CO₂ reduction under titanium dioxide [7].

3.2.2. Temperature effect

Further studies were conducted for CO₂ reduction dissolved in 0.10 mol L⁻¹ NaHCO₃ pH 8 at Ti/TiO₂/CuO irradiated by UV-Vis, with applied potential of -0.60 V and +0.20 V, under controlled temperature of 5, 20 and 35 °C using a cooling device. The products quantified after 2 h of treatment in each case are depicted in Fig. 8.

For both maxima potential applied, photoelectrocatalytic CO₂ reduction is obtained at lower temperature such as 5 °C. This can be attributed to the higher solubility of CO₂ at low temperature, as reported by Kaneco et al. [44] and Chaplin and Wragg [45]. It is, nonetheless, worth pointing out as shown in Fig. 8a, that at an applied potential of +0.20 V one can observe the formation of methanol and ethanol almost in the same concentration (0.10 mmol L⁻¹) while under -0.60 V (Fig. 8b) the methanol formed seems to be preponderant reaching three times higher (0.32 mmol L⁻¹). These results clearly indicate a better performance of the photoelectrocatalytic reactor pointing to 97% of selectivity, which thereby suggests that the method is relatively more selective for methanol formation.

The different oxidative state of the compound formed may be associated with the ease encountered at generating OH· radical during the process [14,46] or at the adsorption effectiveness of CO₂ on the electrode surface during photoelectrolysis. It has widely become a known fact that the semiconductor material has the ability to exert a significant influence on the products type formed by CO₂ reduction [20]. In addition, the adsorption of CO₂ on the electrode surface can take place in different ways on the semiconductor surface when polarized with +0.20 V or -0.60 V [47].

Under +0.20 V potential, the Ti/TiO₂/CuO electrode is positively charged, which contributes towards keeping the intermediate generated after the CO₂ reduction (CO₂^{-·}) adsorbed on its surface, thanks to the opposite charges of the two. Consequently, the subsequent steps of the products formation also occur, possibly, with the intermediate adsorbed on the electrode surface.

On the other hand, under -0.60 V potential, the CO₂^{-·} intermediate is weakly adsorbed on the electrode surface charged negatively. The similar charges encountered render the adsorption difficult on the Ti/TiO₂/CuO surface. The reaction between the intermediate radical and the reactive species present in the medium (H· for example) which are responsible for the products formation [48] occurs in the reaction medium, and not on the electrode surface.

This behavior provides a plausible elucidation concerning the results obtained upon applying photoelectrocatalytic CO₂ reduction using UV-Vis light in 0.10 mol L⁻¹ NaHCO₃ pH 8 at 5 °C under -0.60 V and +0.20 V (Fig. 8). The photoelectrocatalysis under +0.20 V presented the formation of 0.10 mmol L⁻¹ methanol and 0.09 mmol L⁻¹ ethanol, while under -0.60 V the formation was practically selective for methanol forming a concentration of 0.32 mmol L⁻¹.

A mechanism that seeks to explain how the CO₂ reduction using photoelectrocatalysis and Ti/TiO₂/CuO p-n junction semiconductor forms the three different products quantified in this work is presented in Fig. 9. This mechanism was proposed based on some recent works published in the literature [6,16,49,50], where all the authors agree that the products formation occurs via protons and electrons transfers using Cu₂O as mediator. Methanol is the product identified in relatively greater quantities in this work likewise in other studies reported in the literature [17,19,26,51]. This fact coupled with the time of the reduction studies [16,23] lead us to believe that ethanol and acetone are the products generated through methanol consumption, as demonstrated in the proposed mechanism.

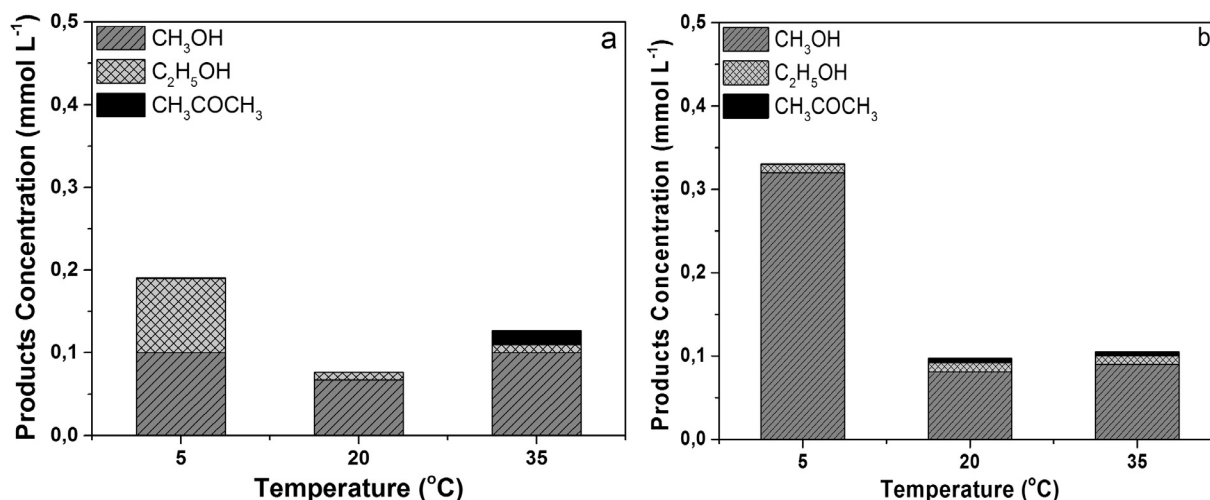


Fig. 8. Products CH_3OH (gray) $\text{C}_2\text{H}_5\text{OH}$ (light gray) and CH_3COCH_3 (black) formed by photoelectrocatalytic CO_2 reduction after 2 h of reaction in $0.10 \text{ mol L}^{-1} \text{ NaHCO}_3$ at pH 8 with varying temperatures and UV-Vis light (125 W) under potential of a) $+0.20 \text{ V}$ and b) -0.60 V .

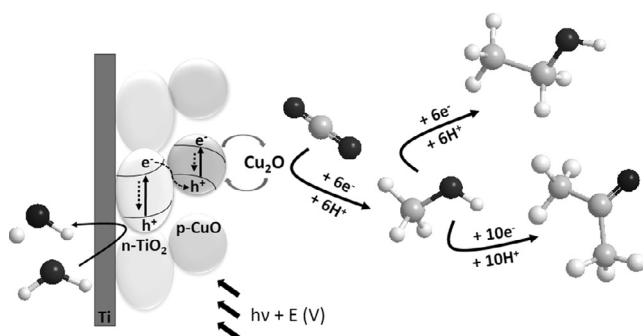


Fig. 9. Mechanism proposed for CO_2 reduction by photoelectrocatalysis and methanol, ethanol and acetone formation using $\text{Ti}/\text{TiO}_2/\text{CuO}$ p-n junction semiconductor.

3.2.3. Effect of supporting electrolyte

Besides the effect of temperature on the photoelectrocatalytic reaction, the solubility of CO_2 as well as the adsorptive properties on the electrode surface could be altered in different electrolytes [45]. With the aim of investigating this effect, the CO_2 conversion in methanol or ethanol was tested using NaHCO_3 , KHCO_3 , NaCl ,

KCl , Na_2SO_4 and K_2SO_4 in a concentration of 0.10 mol L^{-1} , pH 8 and under $+0.20 \text{ V}$ and -0.60 V bias potential and UV-Vis irradiation in order to evaluate different cations and anions. The products obtained after 2 h of photoelectrocatalysis are presented in Fig. 10.

Comparing the products obtained under the different supporting electrolytes in both potentials, it is remarkably clear that the quantities and the types of products obtained in each case are different. Interestingly, comparing the results of each supporting electrolyte employed in both potentials applied, we could observe a considerable difference in terms of the products type and concentration, which undoubtedly proves the influence of the potential applied on the semiconductor. According to Sato et al. [52], the use of carbonates and bicarbonate of sodium or potassium has been widely reported in the literature owing to the fact that the supporting electrolyte is not adsorbed on the semiconductor surface besides the maintenance of the species equilibrium seen to occur in the medium. However, by these results we can say that the aforementioned affirmation needs to be linked to the potential applied in the semiconductor. For instance, when the potentials -0.60 V and $+0.20 \text{ V}$ were applied in the semiconductor, the best supporting electrolytes obtained for the reduction were K_2SO_4

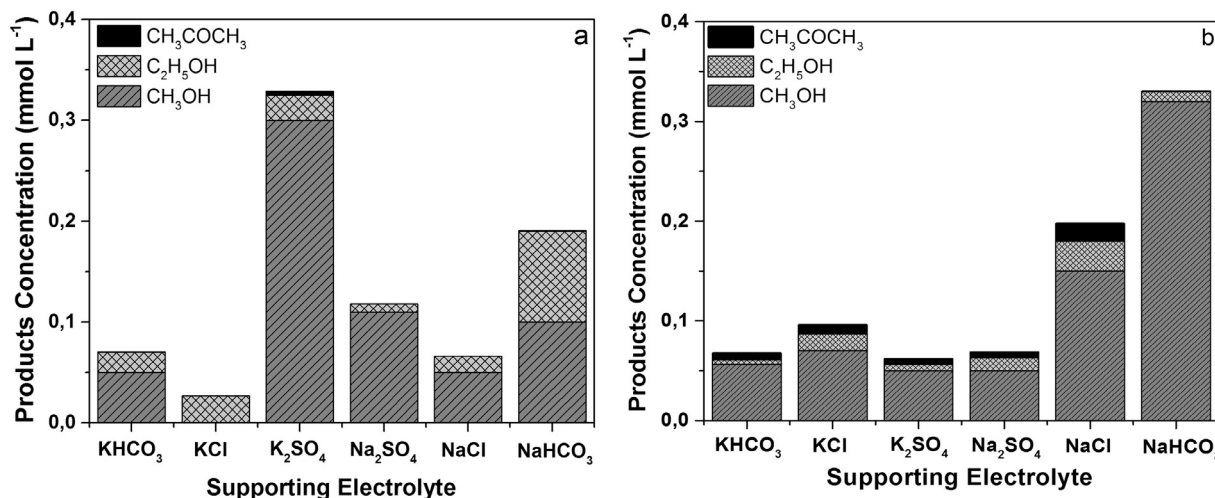


Fig. 10. Products CH_3OH (gray) $\text{C}_2\text{H}_5\text{OH}$ (light gray) and CH_3COCH_3 (black) obtained with photoelectrocatalytic reduction of CO_2 carried out in a) $+0.20 \text{ V}$ and b) -0.60 V during 2 h using different supporting electrolytes: NaHCO_3 , KHCO_3 , NaCl , KCl , Na_2SO_4 and K_2SO_4 , all of them at pH 8 and 0.10 mol L^{-1} .

and NaHCO_3 respectively, an outcome in line with that reported by Sato et al. [52].

Concerning the reduction occurring under +0.20 V (Fig. 10a), despite methanol being the product obtained in higher concentration, ethanol was the only product quantified using KCl as supporting electrolyte, while ethanol and methanol concentration were practically the same when NaHCO_3 was used. A higher products concentration was obtained when K_2SO_4 was used, with 91% of methanol formation, 7% of ethanol formation and only 2% of acetone. Analyzing the reaction performed at -0.60 V (Fig. 9b), the methanol formation can be seen to be preponderant regardless of the supporting electrolyte employed. However, the methanol concentration is seen to undergo some variation depending on the supporting electrolyte type employed likewise the acetone concentration, though that was not observed when NaHCO_3 was employed. Supporting electrolyte with the cations Na^+ presented higher products formation after 2 h of reaction compared to the cations K^+ . In the anions case, the influence found was seen to be less significant. The supporting electrolytes KHCO_3 , K_2SO_4 and Na_2SO_4 presented a very similar yield for the products generation under CO_2 reduction at -0.60 V. Furthermore, the higher products formation was obtained using 0.10 mol L^{-1} NaHCO_3 at pH 8 after 2 h, exhibiting only methanol and ethanol formation, with 97% of selectivity for methanol.

4. Conclusion

An efficient $\text{Ti/TiO}_2/\text{CuO}$ n-p junction semiconductor was constructed owing to its heterojunction benefits using dip-coating technique. The material obtained presented high porosity for both TiO_2 and CuO deposits, and photoactivity behavior with a typical characteristic of an n-p junction semiconductor. The semiconductor presented a good response for CO_2 reduction showing a system with high efficient electron-hole pairs separation, where CO_2 acts as preferential electron scavenger. The shifting observed for CO_2 reduction when TiO_2 semiconductor is modified with CuO and exposed to UV-Vis light proves that CuO enhances the TiO_2 capacity of CO_2 reduction.

The $\text{Ti/TiO}_2/\text{CuO}$ electrode was applied in the photoelectrocatalytic CO_2 reduction study and the results show a remarkable behavior when conducted under 0.10 mol L^{-1} NaHCO_3 pH 8, UV irradiation at +0.20 V and -0.60 V. A practically selective methanol formation (97%) was obtained under 0.10 mol L^{-1} NaHCO_3 at pH 8 under applied potential of -0.60 V. A charge transfer and reduction mechanism were presented to illustrate how the photoelectrocatalytic CO_2 reduction using a heterojunction semiconductor works. When the TiO_2 is subjected to light irradiation, the electrons generated on its surface are found trapped by the Cu^{2+} species, and the Cu^{2+} species are consequently reduced to Cu^+ species. The CO_2 reduction occurs on the Cu^+ sites further reoxidizing the Cu^+ species to Cu^{2+} . Primarily as a result of this behavior, a better life cycle of the heterojunction $\text{Ti/TiO}_2/\text{CuO}$ semiconductor was obtained once nearly 30 experiments of CO_2 reduction were remarkably accomplished with a single electrode. These results lead us to a plausible conclusion that the electrode stands to be a promising material for photoelectrochemical reduction purposes.

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