



MOFs based on ZIF-8 deposited on TiO₂ nanotubes increase the surface adsorption of CO₂ and its photoelectrocatalytic reduction to alcohols in aqueous media



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ABSTRACT

This work describes, the decoration of Ti/TiO₂ nanotubes by nanoparticles of ZIF-8 (zeolite imidazole framework-8) grown using a layer-by-layer process. Morphological and crystallographic analyses showed that the TiO₂ nanotubes were coated with ZIF-8 nanoparticles around 50 nm in size. Curves of I_{ph} vs. E showed that the incorporation of ZIF-8 at Ti/TiO₂ electrodes increased the photocurrent and that the values were dramatically increased in solution saturated with CO₂. The CO₂ adsorbed on the ZIF-8 formed stable carbamates, as demonstrated by spectroscopic and voltammetric assays. Photoelectrocatalytic reduction of CO₂ at Ti/TiO₂NT-ZIF-8 electrodes resulted in formation of up to 10 mmol L⁻¹ of ethanol and 0.7 mmol L⁻¹ of methanol in 0.1 mol L⁻¹ Na₂SO₄, at E_{app} of +0.1 V, under UV–vis irradiation at room temperature. Our findings open up new applications of metal-organic frameworks (MOFs) in photoelectrocatalysis for the highly efficient preconcentration and conversion of CO₂ in aqueous media at ambient temperature.

1. Introduction

Energy production has progressively become a major global concern due to the depletion of natural resources and the problem of global warming. Therefore, it is essential to develop renewable energy sources that are environmentally friendly and economically viable. The conversion of CO₂ to value-added fuels or chemical products by direct use of sunlight is one of the most attractive processes, but ensuring selectivity remains a challenge [1–3].

CO₂ photoreduction involves multi-electron processes that can lead to a wide variety of products ranging from CO and CH₄ to higher hydrocarbons in the gas phase, and various oxygenates such as alcohols, aldehydes, and carboxylic acids in the liquid phase [1]. Consequently, there is increasing interest in the development of new catalytic materials that can increase performance for the conversion of CO₂ into these compounds. Metal-organic frameworks (MOFs) have been applied as an excellent alternative for the storage of fuels (hydrogen and methane) [4], the capture and preconcentration of carbon dioxide [5], and several applications in catalysis [6]. According to the official IUPAC definition, MOFs are coordination polymers with an open framework containing potential voids [7]. Members of this special class of coordination compounds are formed by the self-assembly of secondary

building units (SBUs) linked by strong metal-ligand covalent bonds, leading to the formation of infinite 3D networks with channels and cavities of regular size and shape [8,9]. They present permanent porosity, well-defined crystalline structure, very high surface area, and low density, and offer the possibility of functionalization of their pores [10]. Due to these properties, MOFs have shown promise for applications in areas including the storage and separation of gases [4,5,11], catalysis [6,12], chemical sensing [13], and biomedicine [8], among others [6].

In addition to carboxylate-based MOF materials, nonlinear N-based ditopic linkers can also be used for the construction of these types of porous coordination solids. A very important subclass of MOFs, the zeolitic imidazolate frameworks (ZIFs), has attracted interest mainly because these materials combine the advantages of the MOFs with the very high chemical and thermal stabilities of zeolites [14]. They are constructed from the coordination of tetrahedral divalent cations (Zn²⁺, Co²⁺, and Cd²⁺) with imidazole spacer ligands, whose frameworks resemble those of the zeolites. The Si–O–Si bond angle (145°) in silicate-based zeolites is close to the angle formed by imidazolates when bridging metal ions [15]. These robust materials have promising potential for use in a variety of practical applications, especially gas storage and separation [16] and catalysis [17].

The zinc-based compound [Zn(mIM)₂], where mIM = 2-

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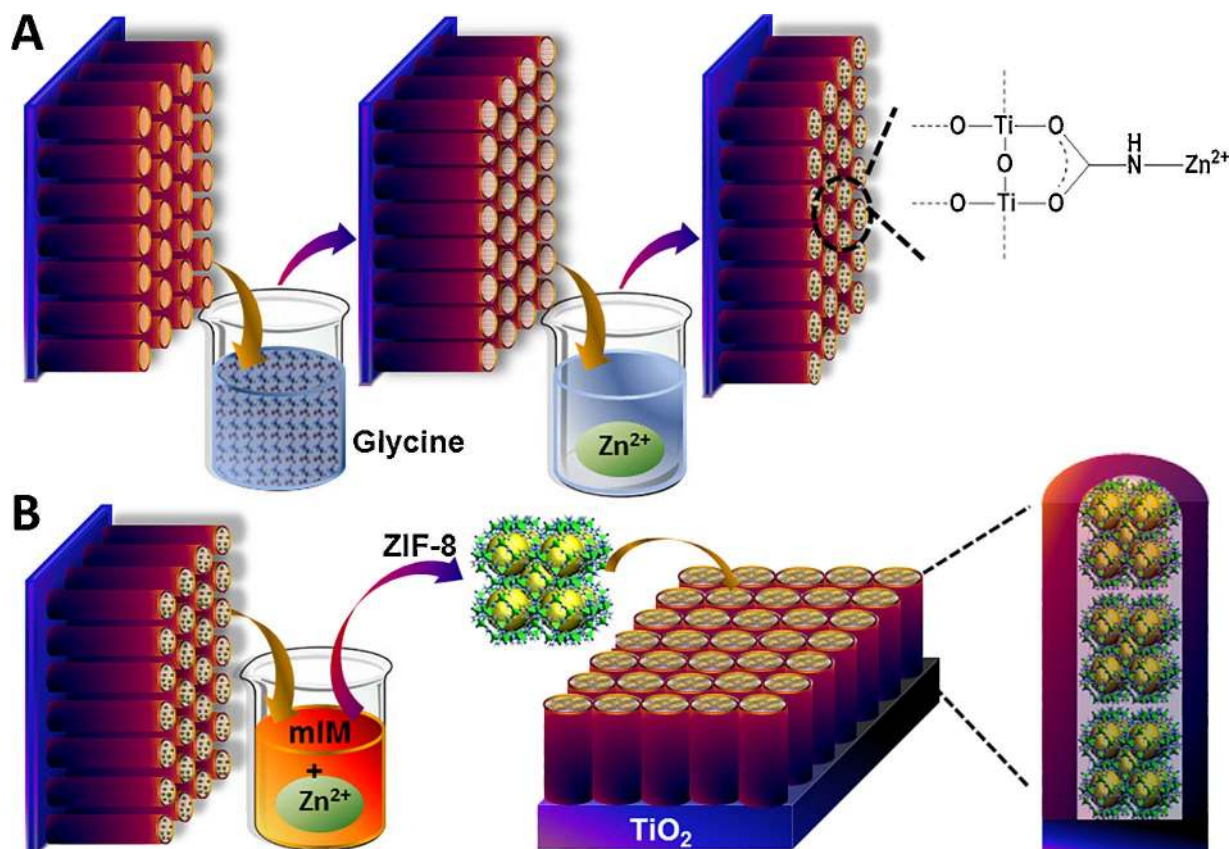


Fig. 1. ZIF-8 formation on Ti/TiO₂NT.

methylimidazole, denoted ZIF-8 [18], has been successfully used for CO₂ greenhouse gas adsorption, due to its excellent stability, very high surface area (1881 m² g⁻¹), and ease of synthesis, combined with highly selective CO₂ capture [19]. Since the aperture in ZIF-8 (with SOD topology) connecting large cavities (~1.5 nm) has a size of 0.34 nm, which is in the same range as the nominal kinetic diameter of CO₂ (0.33 nm), the known structural flexibility of this material is crucial for diffusion of the gas [12].

Therefore, given that ZIF-8 has been used for dioxide carbon capture, the present work investigates the integration of this very porous material with TiO₂ nanotubes in order to not only improve CO₂ uptake and activation (due to the basic sites on the imidazolate linkers), but also to improve catalyst efficiency in CO₂ transformation reactions. Recent studies have reported the use of some MOFs as co-catalysts in CO₂ photoreduction systems, in order to promote the transport of photoexcited electrons [20–24].

Photoelectrocatalysis is a technique that uses a semiconductor, such as TiO₂, which under irradiation higher than the band gap energy is capable of generating e⁻/h⁺ pairs that can be separated by means of a potential gradient established at the interface of the electrode (semiconductor) and the electrolyte [13,20–28]. The photoelectrocatalysis technique offers great versatility for use in the reduction of CO₂ to hydrocarbons with short and long carbon chains [32]. The electrons driven to the photocatalyst surface in a photoelectrocatalytic process [33] play a major role in the conversion of CO₂ to fuels or other chemical products. This is an attractive process, although remaining challenges include low dissolution of CO₂ in aqueous media and poor selectivity of the CO₂ reduction reaction [24,25,29–31,34–36].

In this context, Metal Organic Frameworks are used as a catalyst in systems for CO₂ conversion [37,38]. Some authors [24,39,40] have indicated that MOFs over graphitic carbon nitride nanotubes can convert CO₂ to a large variety of products, such as methane, methanol, formate, carbon monoxide by the photocatalysis, for instance.

Furthermore, in recent years Metal Organic Frameworks has being investigated in the electrochemical reduction of CO₂ [41–44], reaching different types of interesting products (formate, carbon monoxide, etc.). But, the use of MOFs in photoelectrocatalytic systems is scarce and the use of Ti/TiO₂ nanotubes as platforms for the deposition of thin films of catalytic ZIF-8 material seems an alternative for novel catalytic applications in the field of CO₂ conversion.

The development of Ti/TiO₂ nanotubes as platforms for the deposition of thin films of catalytic ZIF-8 material could lead to a variety of novel catalytic applications in the field of photoelectrocatalysis [45]. The use of this technique to reduce CO₂ is considered as the first report in the literature using this catalytic system. The present work reports, a new hybrid photocatalyst produced by growing thin films of ZIF-8 on Ti/TiO₂ nanotube electrodes. The aim was to develop a system able to increase CO₂ gas capture, with improved photoelectrocatalytic reduction to a fuel such as methanol. ZIF-8 was selected for this purpose due to its high surface area, excellent thermal and chemical stability, high capacity for the chemisorption and activation of CO₂ [20], and ability to mediate the reduction of CO₂ under UV irradiation at low applied potential. This work demonstrates that photoelectrocatalysis using a MOF-based Ti/TiO₂ composite has promising potential applications in the fields of energy conversion and environmental protection.

2. Materials and methods

2.1. Formation OF TiO₂ nanotube arrays

Organized self-assembled nanotubes of TiO₂ (TiO₂NT) were obtained by anodizing clean 10 cm² titanium foil samples (Realum, Brazil) that were polished with silicon carbide sandpaper of different roughness (220, 320, 400, 800, 1200, and 1500 grit), sonicated for 15 min in isopropanol, acetone, and ultrapure water, and dried in a flow of N₂ [13]. Anodizing was performed by immersing the foils (at room

temperature) in glycerol/water (90:10 v/v) containing 0.25% NH_4F (Sigma-Aldrich), for 50 h, in an electrochemical cell. A voltage of 30 V was provided using a DC power supply (Minipa MPL-1303), and a Ti/Ru DSA[®] (De Nora) was used as the counter electrode. The samples were subsequently rinsed with deionized water, dried in a nitrogen stream, and annealed at 450 °C for 1 h in air, using a heating rate of 2 °C min^{-1} .

2.2. Formation of ZIF-8 nanoparticles ON TiO₂ nanotube arrays

Firstly, the Ti/TiO₂NT electrode was immersed for 1 h in a 0.3 mol L⁻¹ aqueous glycine solution (Fig. 1), followed by washing with deionized water and drying at 50 °C for 2 h. After drying, the nanostructured TiO₂ material was immersed in a 0.1 mol L⁻¹ zinc(II) acetate solution for 20 min and then dried for 10 h at 50 °C. The reaction medium for formation of the MOF, using a metal:ligand molar ratio of 1:70, was prepared by weighing out 7.566 g (92.1 mmol) of 2-methylimidazole into a beaker and dissolving it in 26.66 mL of deionized water. The pretreated electrode was then immersed in this solution for 1 h, under stirring. Finally, a solution containing 0.390 g (1.3 mmol) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in 2.66 mL of deionized water was added, with stirring continued for 3 h.

2.3. Photoreactor

The stainless steel photochemical reactor (250 mL total volume, with 200 mL for solution and 50 mL for headspace) used in these experiments was constructed to maintain constant distances between the electrodes and the illumination source, hence ensuring the reproducibility of the measurements. The distance between each electrode was 1.0 cm, and a 20 cm² quartz window in the wall of the reactor was at a distance of 0.8 cm from the working electrode. The pressure of the system was controlled with a manometer. Gas and liquid samples were collected through a silicone septum, using a gastight syringe. The solution was stirred using a magnetic bar in the base of the reactor. All the measurements were made at a pressure of 1 atm. A schematic illustration of the reactor is provided in Fig. 2.

2.4. Photocatalytic and CO₂ reduction experiments

All the CO₂ reduction experiments were performed for a period of 3 h, employing the following techniques: photoelectrocatalysis (PEC), photocatalysis (PC), photolysis (PT), and electrolysis (ET). The PEC experiments were conducted at controlled potential, using TiO₂ nanotubes with and without ZIF-8 decoration as the working electrodes. The reference electrode was Ag/AgCl in 3.0 mol L⁻¹ KCl, and the counter

electrode was a DSA[®] plate. The working electrode was illuminated by UV–vis light using a 125 W mercury vapor lamp positioned at a 5.0 mm distance outside the reactor. The PC experiments used the same system, but only with the catalyst irradiated by UV–vis light. The PT and ET experiments used the same reactor system with and without UV–vis irradiation, respectively. Before each experiment, the 0.1 mol L⁻¹ Na₂SO₄ supporting electrolyte was saturated by bubbling CO₂ through the solution for 1 h, using a gas diffuser system to reduce the bubble size and improve the mass transfer of the gas. This solution was then added to the reactor, which was sealed to prevent loss of the gas. An approximately 50 mL headspace was provided for collection of the gaseous products generated in the catalytic reaction.

2.5. Identification and quantification of the products generated by CO₂ reduction

The products formed after CO₂ reduction were identified and quantified by gas chromatography with flame ionization detection (GC-FID), using a Shimadzu model 2010 instrument. For analysis of liquid samples, extraction of the products was performed by transferring a 0.5 mL aliquot of the photoelectrolyzed solution to a sealed 1.5 mL container and heating in a bath for 7 min at 65 °C. After this time, a 75 μm Carboxen/PDMS fiber (Supelco) was exposed to the vapors in the container for 5 min, followed by injection into the gas chromatograph. A Restec Stabilwax chromatographic column was used (30 m × 0.25 mm i.d.; 25 μm film thickness). The carrier gas was nitrogen, at a flow rate of 1.0 mL min^{-1} . The injector was operated in splitless mode at 250 °C, and the detector temperature was 260 °C. The column oven heating program was an initial temperature of 40 °C, followed by heating at 2 °C min^{-1} up to 46 °C, and then at 45 °C min^{-1} up to 170 °C, with the final temperature held for 3 min. Headspace analysis was performed by direct injection of aliquots collected with a gastight syringe. The concentrations of the products obtained in the SPME and headspace analyses were summed to give the total concentration of the products formed.

2.6. Characterization of THE photoelectrodes

Field emission gun scanning electron microscopy (FEG-SEM), using a JEOL 7500F microscope and Transmission electron microscopy (TEM) CM Super Twin 200 transmission electron microscope (TEM) (Philips/FEI, Eindhoven, Netherlands) operated at 200 kV. Samples were prepared by ultrasonically dispersing the catalyst into isopropyl alcohol, then placing a drop of this suspension onto a copper grid, were employed to analyze the morphologies of the tubular TiO₂ nanostructures, with and without decoration with ZIF-8 nanoparticles. The crystallinities of the synthesized materials were evaluated by X-ray diffraction (XRD), using a Siemens D5000 diffractometer with Cu-Kα radiation, controlled by DIFFRACplus XRD Commander software. The X-ray photoemission spectra was obtained with a Scienta Omicron ESCA + spectrometer system equipped with a E A125 hemispherical analyzer and a X m 1000 monochromated x-ray source in Al k α (1486.7 eV). It was used a Cn10 Omicron Charge neutralizer with an beam energy in 1.6 eV for charge effects compensation. The binding energy were calibrated using C 1s peak at 284.8 eV. Fourier transform infrared spectroscopy (FTIR) spectra were obtained using a Diamond ATR (attenuated total reflectance) accessory and a Bruker Vertex 70 spectrometer equipped with a DLaTGS detector, in the range 4000–400 cm^{-1} . DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) experiments were performed using the same equipment with an EasyDiff accessory (Pike Technology, Madison, WI, USA). In order to evaluate the interaction between carbon dioxide and the materials, samples of activated ZIF-8 and Ti/TiO₂-ZIF-8 composite were prepared for the FTIR-ATR and DRIFTS measurements by pressurizing the reaction chambers (illustrated in Figs. S1 and S2, respectively) for 24 h with ~5 atm of CO₂. Evaluation of the photoactivity and Mott-Schokty plot

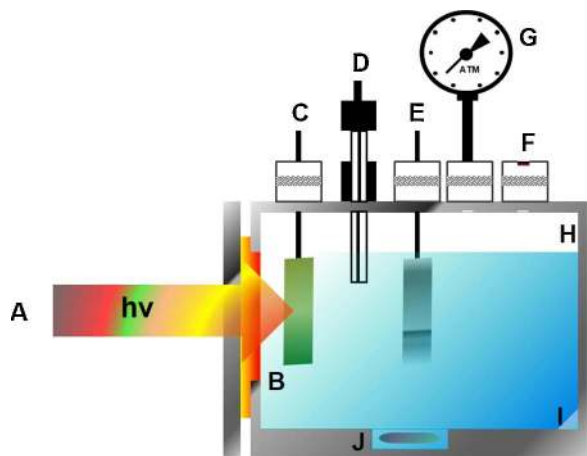


Fig. 2. Photoreactor used in all the experiments. (A) 125 W mercury vapor lamp; (B) quartz window; (C) working electrode; (D) reference electrode; (E) counter electrode; (F) septum; (G) manometer; (H) headspace; (I) supporting electrolyte; (J) magnetic bar.

of the electrodes and the photoelectrolysis employed an Autolab PGSTAT model 302 potentiostat/galvanostat, controlled using NOVA 1.10 software. The photocurrent was measured by linear scanning voltammetry, using the Ti/TiO₂NT with and without ZIF-8 nanoparticles as the working electrode, Ag/AgCl in 3.0 mol L⁻¹ KCl as the reference electrode, and a De Nora DSA[®] as the counter electrode, in an electrolyte of 0.1 mol L⁻¹ Na₂SO₄ (pH 6.8). The scan rate used was 10 mV s⁻¹. Mott-Schottky plots were analyzed using the impedance-potential mode in darkness at a fixed frequency of 3.0 Hz at potential ranged from -0.8 to 1.0 V vs Ag/AgCl in KCl 3 mol L⁻¹ and scan rate 50 mV s⁻¹. For CO₂ reduction, the electrochemical system was operated at constant potentials of -0.7 V and 0.1 V for 3 h. An Agilent Cary 60 UV-vis spectrophotometer was used to measure the absorption and diffuse reflectance spectra of the materials and to calculate the band gap of the catalyst.

Tauc graphs were used to estimate the band gap energies of the materials. This method consists of extrapolating the linear portion of a plot of $\alpha(h\nu)^{1/\gamma}$ as a function of $h\nu$ (eV), where the intercept at $\alpha = 0$ is the optical band gap (E_{bg} , in eV). In these expressions, α is the absorption coefficient, h is Planck's constant (J s), ν is the frequency (s⁻¹), and γ is the power coefficient, whose values can be 1/2, 3/2, 2, or 3, depending on the type of electronic transition: direct allowed, direct forbidden, indirect allowed, and indirect forbidden, respectively. The diffuse reflectance measurements were converted to equivalent absorption coefficients using the Kubelka-Munk (K-M) method.

3. Results and discussion

3.1. FEG-SEM and tem analysis

Fig. 3A–C show scanning electron microscopy images of TiO₂ nanotubes before and after coating with ZIF-8 by means of the layer-by-layer deposition process. The bare TiO₂NT electrode (Fig. 3A) showed the formation of tubes with diameters changing from 90 to 100 nm, thickness of from 20 to 30 nm, and length around 1.2 μ m [21,33]. The incorporation of ZIF-8 on the TiO₂ nanotubes (Fig. 3B and C) resulted in

agglomerates of nanoparticles formed by nucleation and growth, with an average size of 50–57 nm, distributed over the entire surface of the TiO₂ nanotubes, without complete blocking of the nanotubes by ZIF-8 molecules. Fig. 3D shows energy dispersive X-ray spectra for the same electrode. The EDS spectrum (Fig. 3D) revealed the presence of Ti, C, N, O and Zn related to the metal-organic complex synthesized on the Ti/TiO₂NT-ZIF-8 electrode. Fig. 3E–F shows the images obtained by TEM for Ti/TiO₂NT and Ti/TiO₂NT-ZIF-8, respectively, and it is possible to observe the presence of these ZIF-8 nanoparticles between and within the TiO₂ nanotubes.

The energy-dispersive X-ray spectroscopy (EDS) elemental mapping performed for the Ti/TiO₂NT-ZIF-8 catalyst is shown in Fig. 4. The presence of the Zn element uniformly throughout the analyzed sample is observed along with the other expected elements such as C, N, O and Ti.

3.2. XRD analysis

Powder X-ray diffractograms of simulated and synthesized ZIF-8 crystals are shown in Fig. 5, with the matching curves indicating formation of the ZIF-8 phase. The experimental ZIF-8 spectrum (Fig. 5B) exhibited sharp peaks, in excellent agreement with the simulated spectrum obtained using Mercurial software (Fig. 5A). The spectrum for a ZIF-8 single crystal, available from the Cambridge Crystallographic Data Centre database (file CCDC 602542), confirmed the crystallinity of the synthesized samples consisting of nano-sized crystals with nearly rhombic dodecahedron shapes [10,14]. Average sizes of these particles of between 50 and 57 nm were calculated using the Scherrer equation, in agreement with the values obtained from the FEG-SEM images.

3.3. X-ray photoelectron spectroscopy

Fig. 6A–F shows the spectra using the XPS technique to evaluate the composition and chemical states of Ti/TiO₂NT-ZIF-8 catalyst. A broad spectrum analyzed (Fig. 6 (Curve A) shows the prominent presence of the main peaks expected for this material. The high resolution XPS

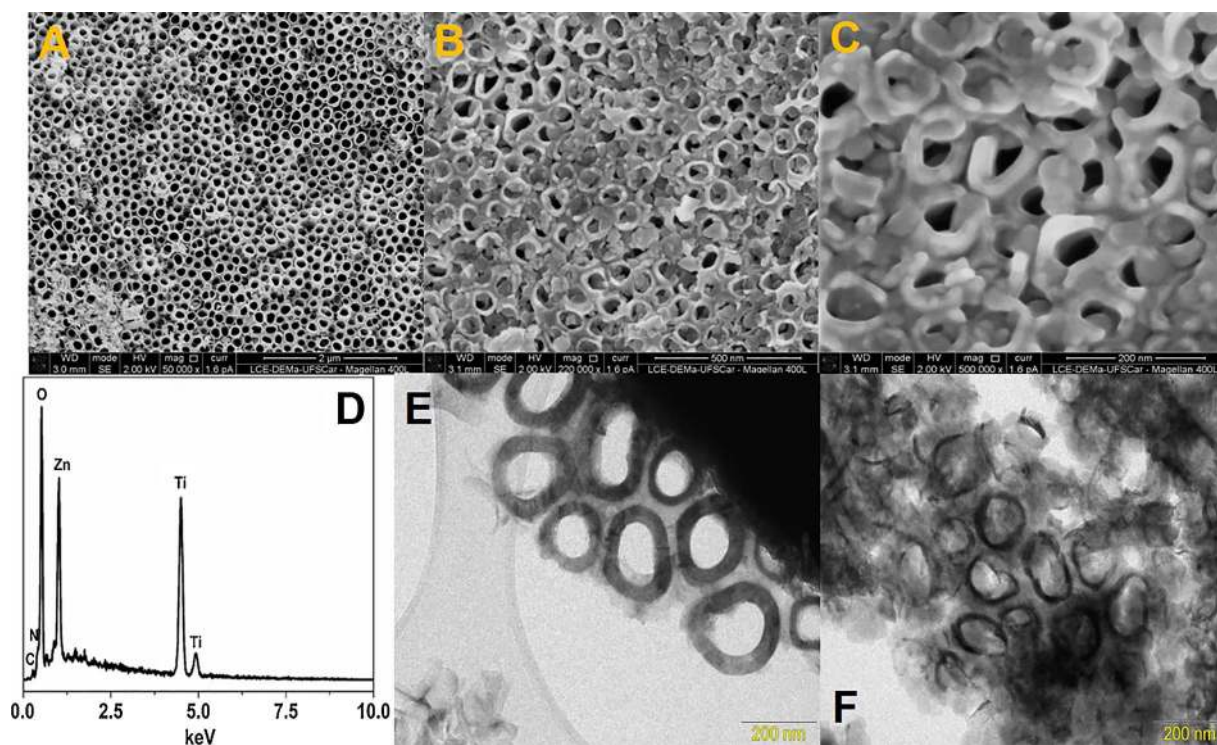


Fig. 3. Morphological characterization of ZIF-8 nanoparticles incorporated on TiO₂ nanotubes. A: FEG/SEM image of pure TiO₂ nanotubes; B and C: FEG/SEM images of nanoparticles of ZIF-8 incorporated on Ti/TiO₂NT, at two different magnifications; D SEM-EDS spectrum of Ti/TiO₂NT-ZIF-8; E: TEM of Ti/TiO₂ nanotube and (F) TEM of Ti/TiO₂NT-ZIF-8.

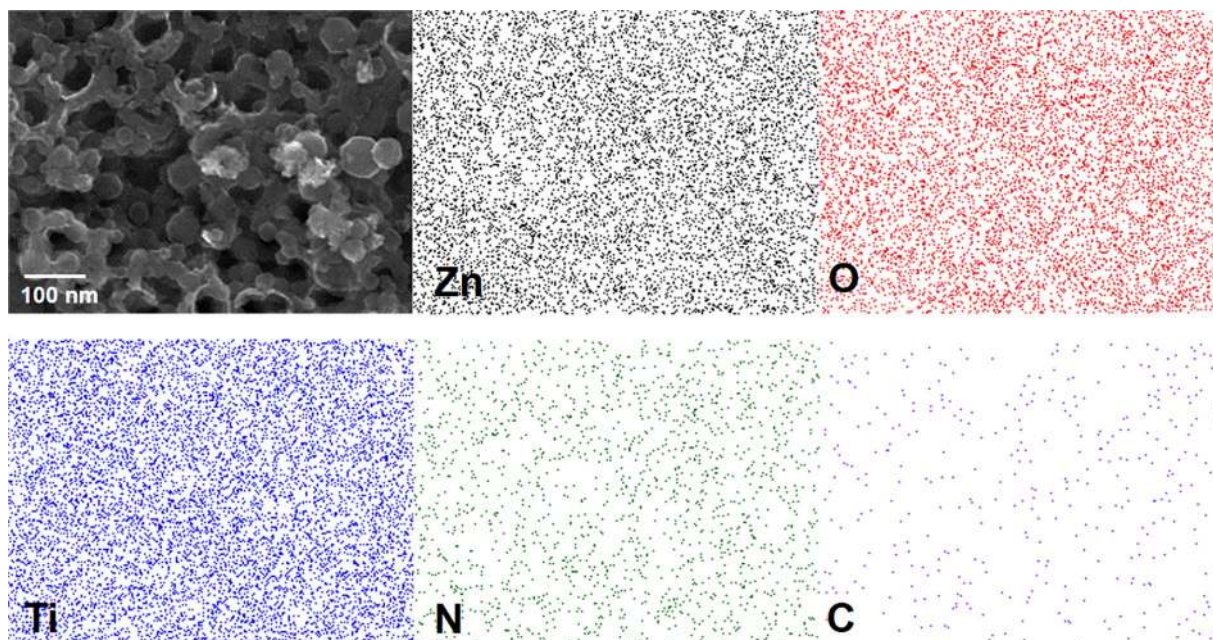


Fig. 4. EDX elemental mapping of Ti/TiO₂NT-ZIF-8.

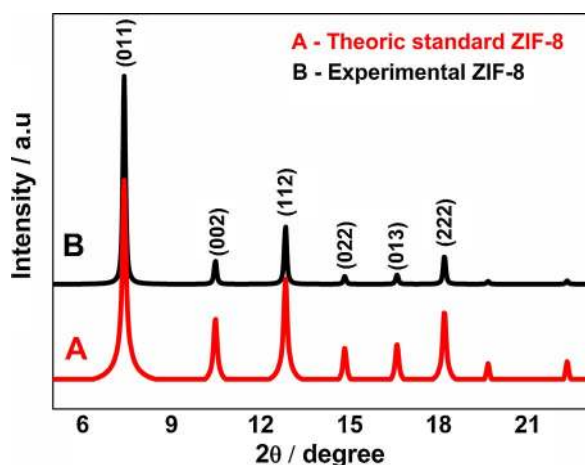


Fig. 5. XRD diffractograms of ZIF-8: (A) simulated; (B) experimental.

spectra for each element analyzed is shown by Fig. 6 (Curves B–F) to: Zn 2p; Ti 2p; N 1s; O 1s and C 1s, respectively. According to these analyzes the presence of the main elements in their respective states were observed as shown in each individual spectrum and when compared with similar values presented in the literature, present a very significant similarity. The Ti 2p and O 1s peaks for TiO₂ nanotubes indicate that there is no complete coating of the entire surface by the ZIF-8 nanoparticles [46–48].

3.4. UV–vis analysis

The absorption spectra of the synthesized materials are shown in Fig. 7A. The spectrum for ZIF-8 (black curve) showed no absorption in the visible region, while bands in the UV region, at 225 and 307 nm, could be attributed to absorption of the 2-methylimidazole linker. From comparison of the spectra for Ti/TiO₂NT and Ti/TiO₂NT-ZIF-8, it can be seen that the absorption increased for the latter, indicative of effective interaction between the TiO₂ nanotubes and the ZIF-8 nanoparticles and consequent diversification of the options for photoelectrode activation. Calculations using the Kubelka-Munk equation indicated that the addition of ZIF-8 resulted in a shift of the band gap potential from

3.2 to 2.8 eV as shown in Fig. 7B.

3.5. Infrared spectroscopy

FTIR-ATR and DRIFTS experiments were carried out in order to investigate CO₂ capture by ZIF-8. Fig. S3 shows FTIR-ATR spectra of the activated MOF before (red) and after (black) CO₂ exposure. The main vibrational modes of the carbon dioxide molecule, associated with the $\nu_{as}C=O$ ν_3 , ν_1 , and ν_2 bending bands, are found in the gas phase CO₂ spectrum at 2349, 1388, and 667 cm⁻¹, respectively [49], as can be observed in Fig. S3 (see also Table S1). The spectrum obtained for ZIF-8 after exposure to the carbon dioxide atmosphere showed the corresponding bands at 2339/2360, 1382, and 672 cm⁻¹, in addition to typical CO₂ combination bands ($\nu_3 + \nu_1$ and $\nu_3 + 2\nu_2$) near 3700 and 3600 cm⁻¹, respectively. The presence of two bands in the C=O anti-symmetric stretching region (at 2339 and 2360 cm⁻¹) could be explained by the presence of two distinct CO₂ interaction sites (see the DRIFTS results). The characteristic FTIR-ATR bands of ZIF-8 are also provided in Table S1 [50].

The adsorption of CO₂ was confirmed by DRIFTS spectroscopy, which is an important tool for obtaining information about the nature of the interactions between the adsorbed CO₂ molecules and the framework [51]. The DRIFTS spectra of the framework before and after loading using 5 atm of CO₂ showed evidence of host-guest interactions (Fig. 8). CO₂ is a linear molecule with high polarizability, and after interaction with the MOF, the corresponding band assigned to the ν_3 vibrational mode (at 2349 cm⁻¹) was shifted to 2360 cm⁻¹. Satellite peaks at 2367/2354 and 2365/2357 cm⁻¹ in the DRIFTS spectrum revealed the presence of more than one interaction site. It has been reported that in addition to the adsorption of carbon dioxide guest molecules in the pores of ZIF-8 (where the diameter of the hexagonal channels is around 0.34 nm) [52], the organic linkers also provide important CO₂ interaction sites [53]. The spectroscopic results obtained here were consistent with the previous findings, since an absorption band at around 1600 cm⁻¹ in the spectrum of ZIF-8 loaded with the gas (see Fig. S3) was assigned to the C=C stretching mode of the imidazole ring and was not present in the spectrum for the empty framework. This observation confirmed the interaction between CO₂ and the MOF at the specific site of the imidazole linker. There was also evidence of the formation of carbamate species from the interaction between CO₂ and

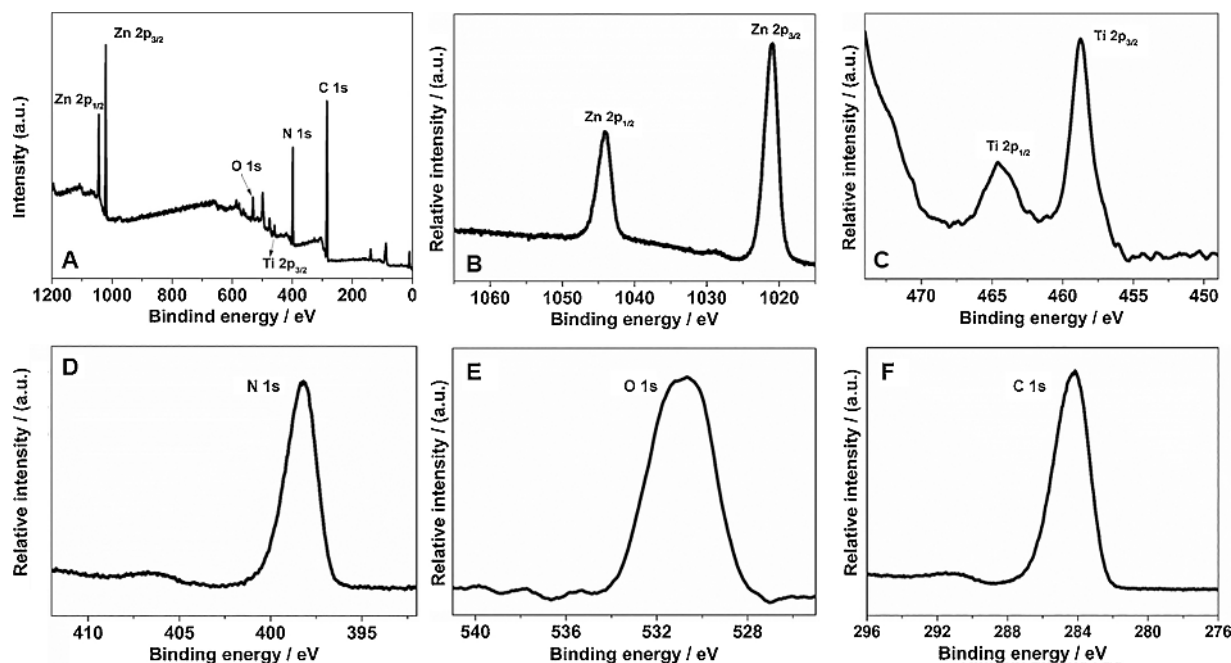


Fig. 6. XPS survey spectra of the sample Ti/TiO₂NT-ZIF-8 (A) and the corresponding high resolution XPS spectra of: (B) Zn 2p; (C) Ti 2p; (D) N 1s; (E) O 1s and (F) C 1s.

2-methylimidazole molecules at the surfaces of the ZIF-8 particles [54]. For example, the presence of a band at 1334 cm⁻¹ in the FTIR-ATR spectra for CO₂ adsorbed onto the ZIF-8 and ZIF-8/TiO₂NT materials (see Table S1) was in good agreement with the value reported by Long et al. [55] and could be attributed to the C–N vibrational mode of carbamate species.

Based on the high CO₂ capture capacity of the ZIF-8 [19] and DRIFTS spectroscopic results, it can be suggested that there still seems to be a significant interaction between CO₂ molecules and the ZIF-8/TiO₂ NT composite. The comparative analysis between the FTIR-ATR spectra shown in Fig. S4 once again confirms the successful growth of ZIF-8 on the TiO₂ nanotubes. Furthermore, the spectrum for CO₂ adsorbed on the ZIF-8/TiO₂NT composite also showed the C–N band characteristic of the formation of carbamate species (at 1334 cm⁻¹) (Fig. S4).

3.6. Photoactivity and electrical properties of the electrodes

The behaviors of the curves of the photocurrent plotted against potential obtained for the Ti/TiO₂NT electrode in 0.1 mol L⁻¹ Na₂SO₄ were compared with those for Ti/TiO₂NT-ZIF-8 in 0.1 mol L⁻¹ Na₂SO₄ in the presence and absence of saturated CO₂ in the electrolyte (Fig. 9X) while Fig. 9Y shows Mott-Schottky plots examined by the same electrodes.

Since Ti/TiO₂NT is an n-type semiconductor, electron-hole pairs are

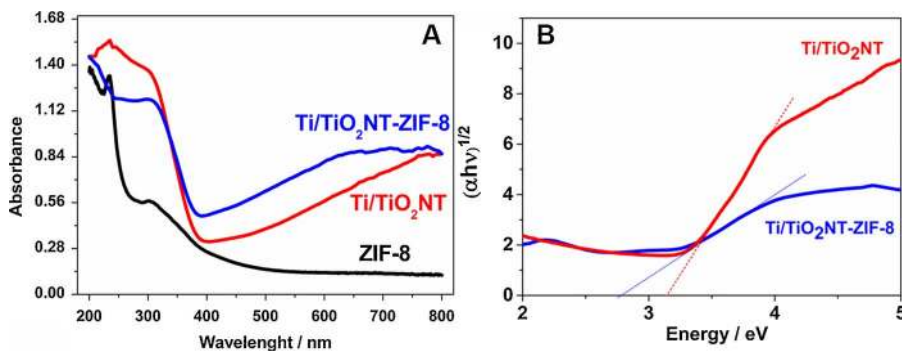


Fig. 7. UV-vis absorption spectra of ZIF-8, TiO₂NT, and TiO₂NT-ZIF-8 (A) and Tauc plot of Ti/TiO₂NT and Ti/TiO₂NT-ZIF-8 (B).

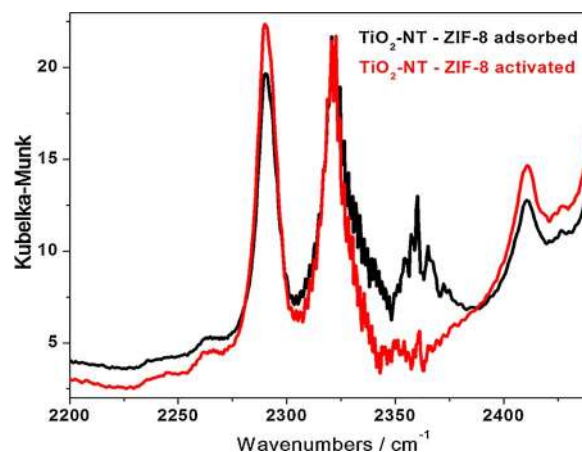


Fig. 8. DRIFTS spectra of ZIF-8 before (red) and after (black) exposure to CO₂, acquired at ambient temperature. The spectra are plotted in Kubelka-Munk units. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

only generated at the electrode surface when it is irradiated by light with energy greater than that of the band gap ($\lambda < 380$ nm). Curve 9X (A) shows the behavior of the electrodes in the dark, with no charge carriers being generated during the potential scan, as expected. A bias

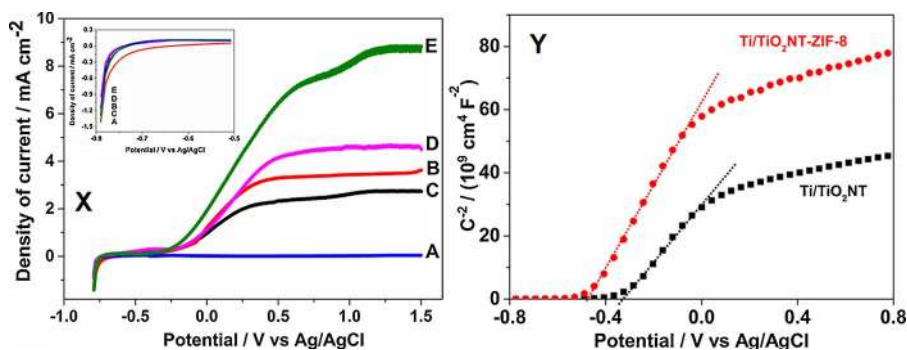
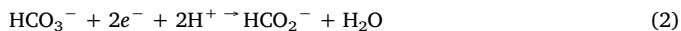
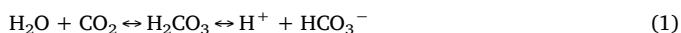


Fig. 9. (X) Linear scanning voltammograms of the electrodes: (A) both electrodes in the dark; (B) Ti/TiO₂NT without CO₂; (C) Ti/TiO₂NT with CO₂; (D) Ti/TiO₂NT-ZIF-8 without CO₂; (E) Ti/TiO₂NT-ZIF-8 with CO₂. Conditions: $\nu = 10 \text{ mV s}^{-1}$; $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$; pH 6.8 (without CO₂); pH 4.5 (with CO₂); illumination using a 125 W high pressure Hg vapor lamp and (Y) Mott-Schottky plot collected at 3.0 Hz for Ti/TiO₂NT and Ti/TiO₂NT-ZIF-8.

potential more positive than the flat band potential produces a bending of the conduction band, causing greater charge separation (e^-/h^+), with holes being driven to the electrode surface. This generates hydroxyl radicals from water oxidation at $E > E_{fb}$ [33]. The E_{fb} (flat band potential) for Ti/TiO₂ under these conditions is around $-0.35 \text{ V vs. Ag/AgCl}$ [56–60], therefore there are an increasing of the photocurrent (curve B). But the photocurrent increased by 33% for Ti/TiO₂NT-ZIF-8 (curve D), and at negative bias potential there is no significant change in the photocurrent, showing that there was ineffective charge separation (shown in the insert of Fig. 9X) for both electrodes. These results showed that ZIF-8 could act as an electron trap, improving separation of the charge carriers [57].

In the presence of CO₂, there was a decrease of 25% in the photocurrent for Ti/TiO₂ (curve C), which could be attributed mainly to equilibrium processes of CO₂ in aqueous solution (Eqs. (1) and (2)). It is known that the presence of acid carbonate in solution can trap photo-generated electrons and decrease the separation of charges formed during the process [42–44].



The effect of CO₂ on the Ti/TiO₂NT-ZIF-8 is shown in Fig. 9X (curves D and E). The photocurrent increased by 97% when the modified electrode was used in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ saturated with CO₂. This suggested that the effective interaction of CO₂ with the ZIF-8 nanoparticles incorporated into the TiO₂NT increased CO₂ capture in the selective MOF, as demonstrated in the DRIFTS experiments. The high efficiency of capture of CO₂ molecules could be attributed to the formation of carbamate compounds, as shown in Scheme 1 [16]. Vimont et al. [61] proposed that this reaction can lead to the formation of similar complexes for a class of structures containing reduced nitrogenated sites of imidazolate groups. Imidazole compounds can act as electron acceptors, and in a system containing Ti/TiO₂ activated by UV–vis irradiation, they could behave as mediators of electron donation, as well as improve the absorption of UV–vis radiation (Fig. 7). Therefore, the greater number of electrons photogenerated from this interaction dramatically increased the photocurrent. Hence, the CO₂ dissolved in the supporting electrolyte could adsorb strongly onto the ZIF-8 complex, due to the presence of the nitrogenated sites of the imidazolate groups, forming carbamates that could be reduced during the photoelectrocatalysis.

The IR spectroscopy results (Fig. 8) provided further evidence of carbamate formation when CO₂ was mainly preconcentrated on the ZIF-8 surface. A similar finding was reported by McDonald et al. [15] for a MOF with nitrogenous clusters. Knofel et al. [16] used infrared spectroscopy to investigate nitrogenous modifying groups and reported the formation of carbamyl compounds as major products. All these studies highlighted the greater effectiveness of interaction of CO₂ with nitrogen groups than with Ti cations or OH groups. Therefore, these species were more liable to be reduced by the electrons photogenerated on the surface of the Ti/TiO₂ catalyst decorated with ZIF-8, following

activation under UV–vis light and with an applied potential.

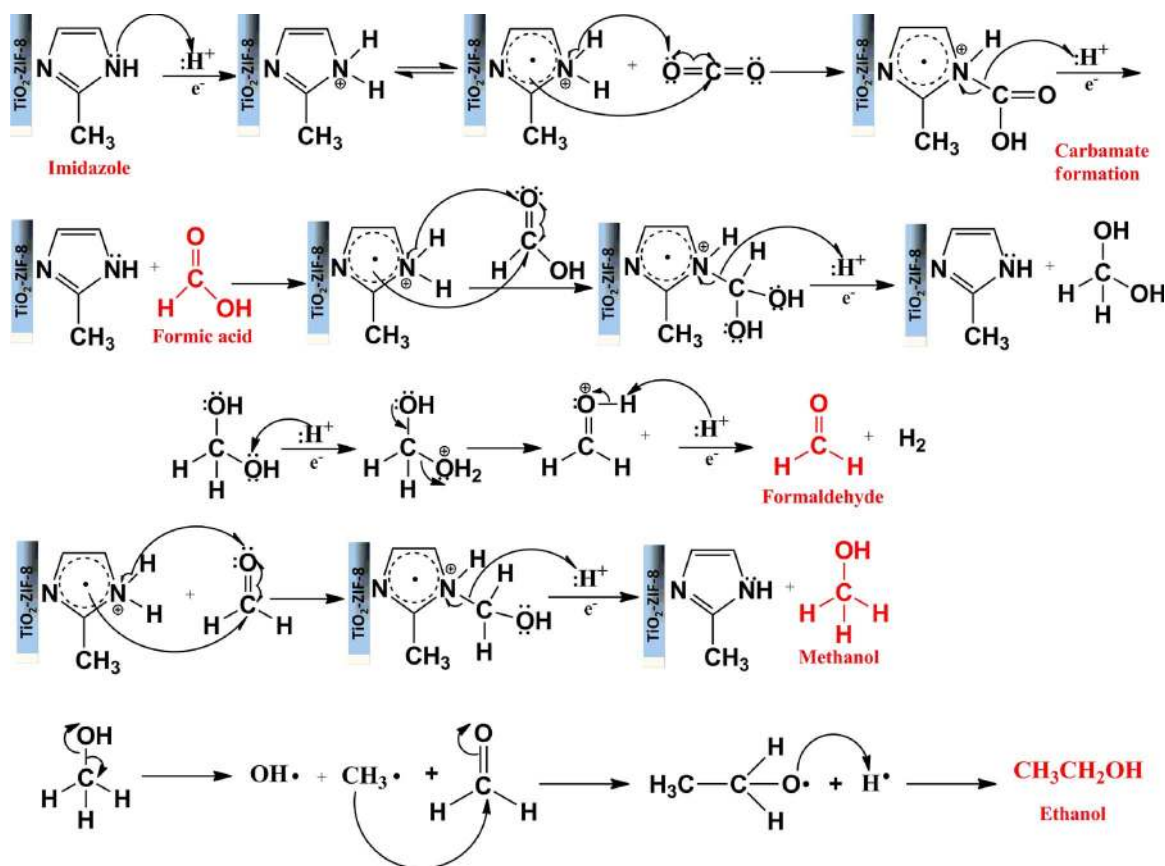
Mott-Schottky plots of the Ti/TiO₂NT and Ti/TiO₂NT-ZIF-8 electrodes were studied to evaluate the positioning of their respective electronic bands structures. As shown in Fig. 9Y, both curves showed positive slopes in Mott-Schottky plots at a frequency of 3.0 Hz, which is the typical n-type semiconductor behavior [48]. So, their flat band potentials are comparable to the conduction band potential. From the obtained curves it was possible to calculate the flat band potential of Ti/TiO₂NT and Ti/TiO₂NT-ZIF-8 at -0.35 V and -0.50 V versus Ag/AgCl at pH 6.8, respectively. Thus, combining the band gap values obtained from the optical analysis of each material (Fig. 7B) it was possible to estimate the position of the energy bands of the materials produced (Fig. S5). From these values it is highlighted that the potential of the conduction band is thermodynamically favorable to promote the reduction of CO₂ to several products, such as: CO₂/CH₄: -0.24 V ; CO₂/CH₃OH: -0.35 V and CO₂/CH₃CH₂OH: -0.33 V versus Ag/AgCl pH 7.0 [62].

3.7. Photoelectrocatalytic reduction of CO₂ at Ti/TiO₂NT-ZIF-8

Firstly, the performance of the Ti/TiO₂NT and Ti/TiO₂NT-ZIF-8 electrodes was evaluated for reduction of CO₂ during 60 min of photoelectrocatalysis in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ (pH 4.5) saturated with CO₂, under UV–vis irradiation and with an applied potential of $-0.7 \text{ V vs. Ag/AgCl}$. The main products formed in the process were methanol and ethanol (Fig. 10A and B). Other products such as acetone and formic acid were generated, but at very low concentrations that were below the quantification limits. The photoreduction of CO₂ to methanol and ethanol at the Ti/TiO₂NT electrode was very low, this behavior can be attributed to the low capacity of Ti⁴⁺ species to adsorb CO₂ in their structure, as described by Bhattacharyya et al. [63]. There was low CO₂ adsorption at the TiO₂ surface, and the Fermi energy level and formal potential of CO₂/CH₃OH were not sufficiently aligned for electron transfer [64]. The same performance of CO₂ reduction using the nanotubular TiO₂ electrodes were recorded evaluating the other conditions of analysis.

When the Ti/TiO₂NT-ZIF-8 catalyst was used, the conversion of CO₂ to methanol and ethanol increased almost 20-fold and 430-fold, respectively (Fig. 10A), demonstrating the remarkable effect of the complex on the conversion of CO₂ to ethanol fuel. This could be explained by the efficient preconcentration of CO₂ on the electrode modified with ZIF-8 by interaction with the nitrogenated sites of the imidazolate groups in the ZIF-8 complex (Scheme 1), as confirmed by the IR spectroscopy analyses (Fig. 8). Fig. 10B illustrates the effect of photoelectrocatalysis times ranging from 0 to 3 h, using the Ti/TiO₂NT-ZIF-8 electrode. The methanol concentration remained almost constant throughout the catalysis, while there was a substantial progressive increase of the ethanol concentration between 1 and 3 h of photoelectrocatalysis.

The influence of the bias potential applied in the photoelectrocatalytic system was evaluated using photoreduction at -0.7 V and $+0.1 \text{ V vs. Ag/AgCl}$, under UV–vis irradiation. The results (Fig. 11)



Scheme 1. Proposed mechanism for alcohol formation using Ti/TiO₂NT-ZIF-8 electrodes operated under UV–vis irradiation and with application of an external potential.

showed that the main products were methanol and ethanol, with a potential of +0.1 V providing 42.5% and 20% higher yields, respectively, which could be attributed to better separation of the electron/hole charges. The bending of the conduction bands was more effective at +0.1 V, favoring the transfer of photogenerated electrons towards the ZIF-8 on the surface of the electrode, where CO₂ was pre-concentrated in the form of carbamyl compounds.

3.8. Comparison of photoelectrocatalysis, photocatalysis, photolysis, and electrolysis FOR CO₂ reduction at ZIF-8

In order to evaluate the relative importance of applied potential and UV–vis irradiation in the process of CO₂ reduction to alcohols at Ti/TiO₂NT-ZIF-8, photoelectrocatalysis was carried out for 3 h in 0.1 mol L⁻¹ Na₂SO₄ (pH 4.5) saturated with CO₂, using an applied voltage of +0.1 V and UV–vis irradiation. The results were compared with photocatalytic reduction (using Ti/TiO₂NT-ZIF-8 in 0.1 mol L⁻¹

Na₂SO₄ (pH 4.5), with UV–vis irradiation), photolytic reduction (in 0.1 mol L⁻¹ Na₂SO₄ (pH 4.5), with UV–vis irradiation), and electrochemical reduction (using Ti/TiO₂NT-ZIF-8 in 0.1 mol L⁻¹ Na₂SO₄ (pH 4.5), with an applied voltage of +0.1 V). The same tests were performed using Ti/TiO₂NT however, the concentration of all products found were below the quantification limit of the technique. The results are shown in Fig. 12.

The results obtained for the photolysis and electrolysis processes showed that there was no generation of any of the products analyzed during the three hours of treatment, demonstrating the importance of the Ti/TiO₂NT-ZIF-8 catalyst in inducing the reduction.

For the PEC and PC processes revealed excellent performance of the former in the formation of methanol (Fig. 12A) and ethanol (B). The conversions of CO₂ to methanol and ethanol using PEC were 75.8% and 52.7% higher, respectively, compared to use of PC. This suggested that in the reduction reactions, the bias potential reduced the effects of charge recombination by providing the photogenerated electrons

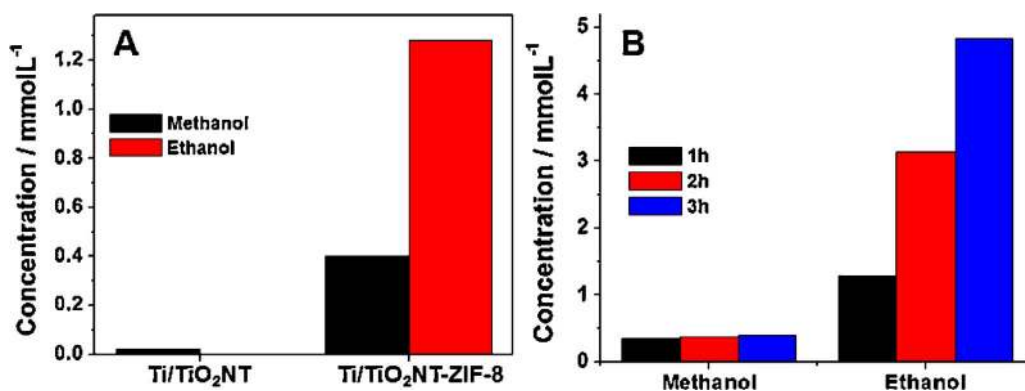


Fig. 10. Concentrations of methanol and ethanol generated in the photoelectrocatalytic processes at -0.7 V vs. Ag/AgCl, in 0.1 mol L⁻¹ Na₂SO₄ (pH 4.5), using (A) the Ti/TiO₂NT and Ti/TiO₂NT-ZIF-8 electrodes for 1 h, and (B) the Ti/TiO₂NT-ZIF-8 electrode for different times.

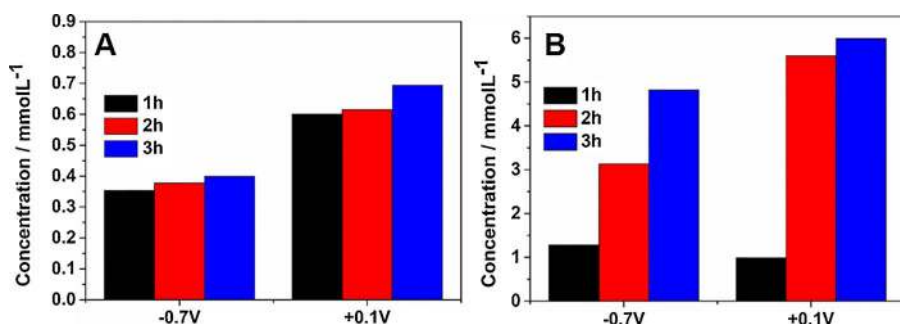


Fig. 11. Concentrations of methanol (A) and ethanol (B) generated in the photoelectrocatalytic processes with bias potentials of -0.7 V and $+0.1$ V vs. Ag/AgCl, in 0.1 mol L^{-1} Na_2SO_4 (pH 4.5), using Ti/TiO₂NT-ZIF-8 electrodes for 3 h.

captured by the linker. These effects were also evaluated by Li et al. using ZIF-8 as a model compound for the evaluation of these deleterious effects in photocatalytic reactions, where a smaller recombination is observed in the presence of more thicker layers of this MOF [65]. The CO₂ preconcentrated in the form of carbamates enhanced the use of these available electrons by rapid electronic transfer, consequently increasing the concentrations of the photogenerated products. Specific faradaic efficiencies of 16% for methanol and 84% for ethanol were calculated at the end of three hours of PEC treatment. The separate electrolysis and photolysis processes did not lead to the generation of any products, even after 3 h of treatment.

The stability of the Ti/TiO₂NT-ZIF-8 photoelectrode was determined comparing curves of the photocurrent vs potential obtained after a series of experiments over 50 h. The values showed differences that did not exceed $20 \pm 2\%$. SEM images and IR spectrum of the electrode after 50 h of use are shown in Fig. S6 and Fig. S7. As can be observed, there was a significant decrease in the intensity of the CO₂ bands (at 2338 and 2359 cm^{-1}) as well the appearance of an intense band at 1727 cm^{-1} and a negative peak centered at 3330 cm^{-1} , assigned to $\nu\text{C}=\text{O}$ and $\nu\text{N}-\text{H}$ of the carbamate species, respectively [66]. This behavior suggest that carbamate species are still be formed on the electrode surface in the presence of CO₂.

As shown in the representative process provided in Scheme 1, the photoelectrochemical reductions of CO₂ to methanol and ethanol differed slightly and involved the reduction of carbamates formed on the Ti/TiO₂NT-ZIF-8 electrode. The method was highly successful in transferring electrons generated from photoactivation by UV-vis light and an applied potential, able to reduce subsequently the carbamate to ethanol as a major product after transfer of 12 electrons and 12 protons. The presence of ZIF-8 nanoparticles on TiO₂ nanotubes provided a significant reduction in the band gap values of this material with a change in the potential of the conduction band making it more thermodynamically favorable the conversion of CO₂ to the photogenerated products.

In agreement with literature [67] and our findings the Scheme 1 resumes the CO₂ reduction mechanism at Ti/TiO₂NT-ZIF-8 electrode illuminated by UV-vis light and under $+0.1$ V. The photoactivation of the electrode firstly produced highly reactive imidazole radicals [18,19], which interacted with the CO₂ present in solution, leading to the formation of carbamate compounds after preconcentration of the

dissolved gases on the surface of the Ti/TiO₂NT-ZIF-8 electrode. These reactions occurred intensively throughout the experiment, with the electrons generated being attracted to the surfaces of the ZIF-8 nanoparticles and promoting the reduction to form methanol and ethanol in measurable concentrations. Our results indicate that the presence of nitrogenous groups in the ZIF-8 seems to be fundamental to selectively promote the reduction of CO₂ to methanol [67,68]. Thus, the first reduction step could be the pre-protonation of carbamate via H⁺ abstraction and formic acid formation (Scheme 1). From the positioning of the calculated energy bands (Fig. S5), it is clear that the ZIF-8 coating Ti/TiO₂ increases the conduction band to higher energy levels, which can be favored with a slight advantage on conversion of CO₂/ethanol due to the lower potential needed to promote the conversion from CO₂ [68]. But, probably the mechanism involves formation of formic acid, formaldehyde as unstable intermediate in the process and culminates in the formation of methanol and ethanol as main products. Our results corroborate with the formation of carbamates after the interaction of CO₂ dissolved in solution with the imidazoles groups of ZIF-8 favors the reduction to methanol as highlighted by Seshadri et al. [69] at overpotentials of only 0.2 V. According to these authors, this reaction occurs almost directly to methanol with very low concentrations of formic acid being formed during the reaction. The electron flow in the photoelectrocatalysis certainly is higher and the product reaches new reductive species such ethanol.

4. Conclusions

A MOF-based hybrid chemical system was produced by growing nanoparticles on Ti/TiO₂NT and was used as a photoelectrocatalyst for CO₂ reduction reactions in aqueous solution. FTIR spectroscopy analyses showed that host-guest interactions depended on the pore structure as well as the chemical nature of the MOF linker. The composite was constructed by the deposition of ZIF-8 nanoparticles on TiO₂ nanotubes and provided efficient photoelectrocatalytic conversion of CO₂ into methanol and ethanol fuels. The zinc-based MOF therefore acted not only in CO₂ adsorption/activation, but also as a co-catalyst, since it transferred the excited electrons for the photoelectrocatalytic reduction. We believe that the findings of this study constitute an important contribution to research on promising MOF-based catalysts for CO₂ photoelectroconversion, particularly concerning the interactions

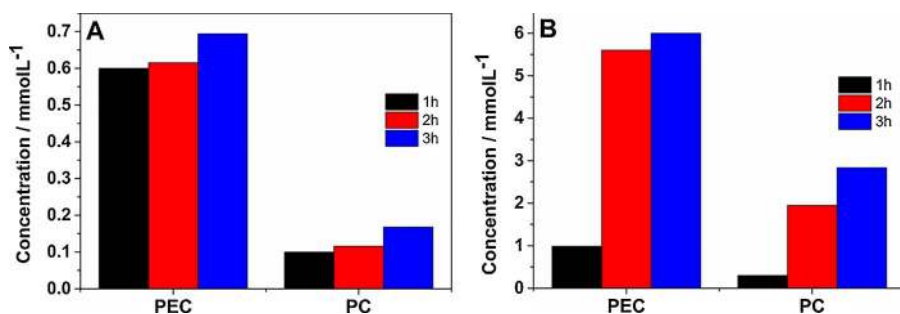


Fig. 12. Formation of methanol (A) and ethanol (B) using different techniques. Conditions: PEC (Ti/TiO₂NT-ZIF-8 in 0.1 mol L^{-1} Na_2SO_4 (pH 4.5), $E = +0.1$ V, UV-vis irradiation); PC (Ti/TiO₂NT-ZIF-8 in 0.1 mol L^{-1} Na_2SO_4 (pH 4.5), UV-vis irradiation). Illumination using a 125 W high pressure Hg vapor lamp.

between semiconductors and MOFs. It was very important to conclude that this is the first report on photoelectroreduction of CO₂ using MOFs as catalyst. In addition, a new perspective for researchers is opening, because of the real possibility to convert the more important greenhouse gas and very stable carbon dioxide into fuels through photoelectrocatalytic processes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.apcatb.2017.12.013>.

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