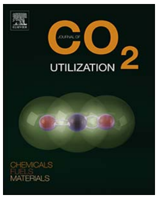
Journal of $CO_2$ Utilization 24 (2018) 81–88

Contents lists available at ScienceDirect

Journal of $CO_2$ Utilization

journal homepage: www.elsevier.com/locate/jcou



# Photoelectrocatalytic performance of nanostructured p-n junction $NtTiO_2$/NsCuO electrode in the selective conversion of $CO_2$ to methanol at low bias potentials

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## ARTICLE INFO

*Keywords:*
$CO_2$ reduction
Nanostructured $NtTiO_2$/NsCuO semiconductor
Methanol formation
p-n junction
Photoelectrocatalysis mechanism

## ABSTRACT

Aiming a selective reduction of $CO_2$ to methanol, a p-n junction semiconductor was constructed based on CuO nanospheres (NsCuO) deposited at $TiO_2$ nanotubes ($NtTiO_2$). The $NtTiO_2$/NsCuO material demonstrated smaller charge transfer resistance, smaller flat band potential and wider optical absorption when compared with $NtTiO_2$ and/or Ti/$TiO_2$ nanoparticles coated by higher size particles of CuO (Ti/$TiO_2$/CuO). The selective reduction of dissolved $CO_2$ to methanol was promoted at lower potential of +0.2 V and UV–vis irradiation in 0.1 mol $L^{-1}$ $K_2SO_4$ electrolyte pH 8 with 57% of faradaic efficiency. Even though the performance of the nanostructured material $NtTiO_2$/NsCuO was similar to the non-completely nanostructured material Ti/$TiO_2$/CuO (0.1 mmol $L^{-1}$ methanol), the conversion to methanol has been significantly increased when hydroxyls (0.62 mmol $L^{-1}$) and holes scavengers (0.71 mmol $L^{-1}$), such as p-nitrosodimethylaniline (RNO) or glucose, respectively, were added in the supporting electrolyte. It indicates that photogenerated electron/hole pairs are spatially separated on p-n junction electrodes, which produces effective electrons and long-life holes, influencing the products formed in the reaction. A schematic representation of the heterojunction effect on the photoelectrocatalytic $CO_2$ reduction is proposed under the semiconductor and each supporting electrolyte, which improves the knowledge about the subject.

## 1. Introduction

The pursuit for solution to global warming and use of fossil fuel has demanded great interest in the conversion of $CO_2$ to fuels [1–4]. The recent advances in the understanding of the role of photoelectrocatalytic devices, semiconductors and photoelectrocatalytic processes in the development of solar fuels from water and $CO_2$ is reviewed in the literature [5–9]. However, the great challenge is to design systems able to promote the capture of solar radiation and conversion of $CO_2$ into fuels that can be easily stored. On this basis, photoelectrocatalysis for $CO_2$ reduction has gained significant attention in the last five years due to its high efficiency and the high-value products generated [1–4,10], but it still offers lack of efficiency and low selective reactions to just one high-value product [11].

The photoelectrocatalytic conversion of dissolved $CO_2$ in aqueous solution is complex. A high efficiency can be obtained for catalyst with high ability to chemisorb and activate the $CO_2$ and it depends of (i) the semiconductor type used as photocathode [[3],12,13], (ii) the irregularities of the surface that can display different $CO_2$ adsorption modes [14], (iii) the supporting electrolyte [3], (iii) the pH of the solution [12], (iv) the applied potential [13], (v) the photoelectrocatalysis time [15], the photoelectrocatalytic reactor design [[3],15,17,18] and others.

Thermodynamically, the reduction of $CO_2$ takes place faster under semiconductor that presents conduction band edge more negative than the redox potential for $CO_2$ reduction and valence band edge lower than redox potential for water oxidation [11,16,17]. Nevertheless, p-type semiconductor commonly demands large potential, once their valence band potentials are not positive enough to oxidize water [18].

Semiconductors based on copper and copper oxides [1,[23],19] are good candidates for that and have shown great success for photoelectrocatalytic reduction of $CO_2$ to alcohols [[23],16,20,21]. Copper oxides have the ability to act simply as electron traps [22] and present good platform for $CO_2$ adsorption [23]. $Cu^{2+}$ ion has an unfilled 3d shell, making its reduction thermodynamically feasible. On the other hand, CuO absorbs light in the visible region [24,25], presents specific reductive characteristics [25,26] and can easily trap the electron generated on the other semiconductor surface [13,22]. But, they can show low stability under reductive conditions and light [27].

The photoelectrocatalytic reduction of carbon dioxide is a multiple

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https://doi.org/10.1016/j.jcou.2017.12.008
Received 28 July 2017; Received in revised form 2 November 2017; Accepted 9 December 2017

step process, limited for the adsorption of $CO_2$ on the electrode surface. The steps are based on the transfer of multiple photogenerated electrons (conversion to methanol requires six electrons) and also the formation of hydrogen radical relevant to produce hydrocarbon from carbon dioxide [28]. The literature has reported that p-n junction semiconductors can be a good alternative to enhance the photoelectrocatalytic performance [15,13,29–32]. The heterojunction can enhance the separation of electron-hole pairs, since the charge transfer can be amplified by the Z-scheme mechanism [17,32], facilitating these multiple steps.

The arrangements of copper, copper oxides and $TiO_2$ have been investigated as effective way to improve the photoreduction of $CO_2$. A narrow band gaps ($E_{bg}$) and sufficient Fermi levels ($E_f$) are capable to reduce $CO_2$ to $CH_3OH$ ($E_0 \sim -0.4$ V *vs* NHE) in the CuO semiconductor ($E_{CB} \sim -1.75\sim$ and $E_{VB} \sim 0.25$ V *vs* NHE) [13]. The photoactivated electron in the $TiO_2$ conduction band (CB) ($E_{CB} \sim -0.25$ V and $E_{VB} \sim 3.0$ *vs* NHE) is not able to reduce $CO_2$–$CH_3OH$. Because of that, the coupling of two semiconductors (p and n-type) can minimize the recombination due the interaction with the electrons generated in the $TiO_2$ and holes generated in the valence band (VB) of CuO, a typically z-scheme mechanism [13,17,32]. In addition, holes generated in the VB of $TiO_2$ perform the water oxidation to H•, which is important to conversion of $CO_2$ into hydrocarbons and fuels. This $TiO_2$ and CuO union can increase the shift of light absorption to the visible light region ($E_{bgCuO} \sim 1.7$ eV and $E_{bgTiO2} \sim 3.2$ eV) [13,33] and improve the stability of the CuO catalyst [13,20,34].

Another effect that has presented photoelectrocatalytic upgrade is the use of nanostructured materials [31,17,35]. Among the several possibilities of nanostructures, nanotubes are shown to be the most promisor semiconductor type due to the large surface area and their good electronic transport of the photogenerated electron/hole pairs, reducing the recombination and increasing the efficiency in the process [36,37]. The literature also reports that nanoparticulated films deposited on semiconductor surface can improve the kinetic of holes reaction with electrolyte (due to higher penetration of electrolyte), change the material conductivity and also change the adsorption of analyte on the substrate [38,39].

The aim of the present work is to compare the effect of CuO nanospheres deposited at nanotubes $TiO_2$ electrode prepared by anodization with a non-nanostructured material, to improve photoelectrocatalytic performance in the selective conversion of $CO_2$ to methanol at low bias potentials (+0.20 V *vs.* Ag/AgCl for instance) and to understand the mechanism involved in the system. The heterojunction involving catalyst nanoparticle changed charge transfer resistance and separation efficiency at the contact interface semiconductor electrolyte when compared to composites of Ti/$TiO_2$/CuO without a complete nanostructure. These effects are supported by EIS, photocurrent voltage and also by the improvement of methanol formation analyzed by chromatographic techniques.

## 2. Experimental

### 2.1. Preparation of CuO nanospheres-decorated $TiO_2$ nanotubes electrode (Nt$TiO_2$/NsCuO)

$TiO_2$ nanotube arrays electrode was prepared by electrochemical anodization in aqueous solution [40]. A titanium plate with 4.0 $cm^2$ was polished using abrasive papers of successively finer roughness and then cleaned by applying three 15 min steps in sonication with acetone, isopropanol and ultrapure water. The cleaned plate was dried in a $N_2$ stream. Electrochemical anodization was performed in a two-electrode cell using a ruthenium foil as the counter electrode and 1.0 $mol\,L^{-1}$ $NaH_2PO_4$ + 0.3 wt.% HF as the supporting electrolyte. The applied potential was initially ramped from 0 to 20 V at 2 $V\,min^{-1}$ and then kept constant at 20 V for 2 h. After the anodization, the electrode was cleaned with ultrapure water, dried with a $N_2$ stream and annealed at 450 °C for 2 h.

After annealing, the $TiO_2$ nanotubes were decorated with CuO nanospheres by dip coating using an adapted methodology [41]. The decorated semiconductor was obtained following two depositions of copper oxide by dip coating. The solution used for the dip coating was prepared with dibasic copper carbonate ($8.4 \times 10^{-2}$ $mol\,L^{-1}$ of metal) as a copper oxide precursor, citric acid and ethylene glycol in a metal molar ratio of 1:4:16, respectively. The semiconductor was annealed after each deposition at 450 °C for 2 h.

The Ti/$TiO_2$/CuO semiconductor without nanostructure was obtained by dip coating of six layer with copper oxide and titanium oxide precursors following by annealing after each deposition [13,41]. This material results of characterization and $CO_2$ reduction under different potential and supporting electrolytes was publish recently by the authors [13]. The Ti/$TiO_2$/CuO electrode presents 10% in weight of CuO semiconductor [13], three times higher than is coating in the Nt$TiO_2$/NsCuO.

### 2.2. Characterization of (Nt$TiO_2$/NsCuO)

The prepared semiconductor was characterized structurally and morphologically by X-ray diffraction (XRD) on a Siemens D5000 diffractometer with Cu Kα radiation and Field Emission Gun-Scanning Electron Microscopes (FEG-SEM) on a JEOL 7500F Microscope coupled to energy-dispersive X-ray spectroscopy analysis (EDS). An UV/Vis/NIR spectrometer (PerkinElmer Lambda 1050) with an Integrating Sphere-150 mm UV/Vis/NIR (InGaAs) module for diffuse reflectance measurements was used to obtain the optical band gap.

The electronic charge transfer was analyzed by electrochemical impedance spectroscopy (EIS) in an Autolab PGSTAT 302N potentiostat with Nova 1.11.2 software (Metrohm Autolab B.V.). The measurements were performed using a Ag/AgCl reference electrode and a Pt counter electrode in 5.0 $mmol\,L^{-1}$ $Fe(CN)_6^{3-/4-}$ prepared in 0.1 $mol\,L^{-1}$ KCl as supporting electrolyte. The frequency employed range from 10 kHz to 0.03 Hz, with a 5 mV rms sinusoidal modulation at 0.22 V.

The photocurrent response was evaluated by linear sweep voltammetry in 0.1 $mol\,L^{-1}$ $NaHCO_3$ at pH 8 with and without $CO_2$ using at scan rate of 0.01 $V\,s^{-1}$ using an Autolab PGSTAT 302.

### 2.3. $CO_2$ Reduction by photoelectrocatalysis

The photoelectrocatalytic reduction of $CO_2$ was performed in a two compartments reactor of 200 mL in each compartment (Fig. 1), separated by a nafion® proton exchange membrane (6). An electrode of Nt$TiO_2$/NsCuO acting as photocathode (working electrode) (1) was positioned in a compartment receiving the incidence of light system (UV–vis light from a commercial 125 W high pressure mercury lamp without the bulb with I = 9.23 $W\,m^{-2}$) through a quartz window (7). An Ag/AgCl reference electrode (2) was also inserted in the same compartment where, $CO_2$ was also bubbled (1.0 $mL\,min^{-1}$) (3) continuously during 45 min to reach saturation and maintained during all the experiment. A Pt grid was used as a counter electrode (4) and the

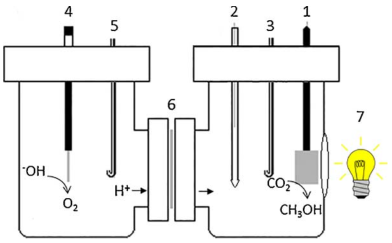

**Fig. 1.** Scheme of the two compartments photoelectrocatalytic reactor used for $CO_2$ reduction. 1) photocathode, 2) reference electrode (Ag/AgCl), 3) $CO_2$ bubbling, 4) counter electrode (Pt grid), 5) gas bubbling, 6) nafion® proton exchange membrane and, 7) UV–vis light incidence by a quartz window.