

Synergetic Electrocatalytic Effects of Cu₂O-TiO₂ Heterostructures in a Solar Driven PEC Device for CO₂ Reduction to >C1 Chemicals

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A solar driven photo-electro-catalytic (PEC) device for CO₂ reduction/water oxidation is here presented. The electrodes are engineered to be used in the *n*-type configuration, without using precious metals or rare/expensive raw materials. Specifically, the photoanode for water oxidation is made of TiO₂ nanotube arrays prepared via controlled anodic oxidation, while Cu₂O-TiO₂ heterostructures, synthesised by ultrasonicated assisted co-precipitation and then spray-coated over a carbon-based gas diffusion layer (GDL), are used as electrocathode materials for CO₂ reduction. All the tests are performed without applying external bias or adding sacrificial donors, in a compact homemade PEC reactor in comparison with a conventional slurry photoreactor. The catalytic performances are evaluated in terms of formic acid and acetic acid production, the latter involving the formation of C-C bond. The effect of the presence of TiO₂ is investigated in comparison with a bare cuprous oxide (Cu₂O) film. Results for the bare Cu₂O/GDL electrode (no TiO₂) show 31.8 and 80.6 μmol h⁻¹ g_{Cu}⁻¹ as formic acid and acetic acid production rates, respectively. Cu₂O-TiO₂/GDL electrode, instead, shows more than one order of magnitude higher productivity (0.69 and 2.59 mmol h⁻¹ g_{Cu}⁻¹, respectively). The Faradaic efficiency (FE) to acetic acid is much higher for Cu₂O-TiO₂/GDL electrodes (61.9 %) considering the higher number of electrons involved for acetic acid with respect to formic acid (8 vs. 2). This behaviour can be ascribed to the synergetic electrocatalytic effects of the as-formed Cu₂O-TiO₂ heterostructures, favouring the formation of C-C bond for the sustainable production of >C1 chemicals and fuels.

1. Introduction

Carbon dioxide (CO₂) reduction by using sunlight has attracted more and more attention in the scientific community in the last years (Nitopi et al., 2019). In general, “solar energy exploitation” in its wide meaning is not only related to the direct exposure to solar radiation, but includes a wide range of renewable energy sources like wind, photovoltaic, hydropower, etc. However, a direct use of solar energy by photo-electro-catalytic (PEC) approach represents a more attractive long-term solution (Iqbal et al., 2018). A device capable of directly converting sunlight and CO₂ into chemicals in one-step process may reduce the loss of energy, thus resulting to an increase of overall efficiency (Ding et al., 2020).

The development of a device for the conversion of CO₂ and H₂O into >C1 valuable products by using solar energy represents a great challenge for the next future (Giusi et al., 2020). However, the realization of an efficient PEC system must go through the preparation of robust and low-cost electrodes and devices, because a rapid and efficient electrocatalytic reaction requires not only an active catalytic material, but also a proper electrode and cell design (Ampelli, 2020).

Many aspects should be taken into account in electrode and cell design for CO₂ reduction: i) light harvesting and charge separation, ii) electron transfer and mass diffusion, iii) yield and type of products formed (Wang Y. et al., 2020). The correct choice of materials for the electrode preparation, and their assembling in a proper

reactor configuration are the key to enhance the photo-conversion efficiency (Genovese et al., 2013). For these reasons, a PEC device should have a compact design to decrease the volume of the electrolytes, two separate chambers for anodic and cathodic half-reactions, and high robustness for continuous flow operation (Ampelli et al., 2019).

Regarding the kind of materials, the photoanode should be resistant to photo-corrosion and have a proper nanoarchitecture to improve the electron transport and minimize electron-hole charge recombination (Tavella et al., 2017). The electrocathode, instead, should be designed to minimize side-reactions (i.e., hydrogen evolution) and to address CO₂ reduction process towards the formation of the more desired >C1 products (Marepally et al., 2017a). Among the electrodes investigated so far in literature for CO₂ reduction, copper-based materials have been the most active (Mais et al., 2019).

In this context, the combination of titania (TiO₂) nanotube arrays as the photoanode with Cu₂O nanoparticles (also mixed with TiO₂ P25) coated on a gas diffusion layer as the electrocathode, was here investigated in a compact homemade PEC device for CO₂ reduction, in comparison with conventional slurry reactors.

2. Experimental

2.1 TiO₂ nanotube arrays

Titania nanotube arrays (TiO₂ NTs) were prepared by controlled anodic oxidation technique, starting from metallic Ti discs (99.98% purity, 0.025 mm thickness, supplied by Alfa-Aesar) (Ampelli et al., 2017). The Ti discs were anodized in a two-electrode cell under the application of a constant voltage (50 V) for 45 min. The electrolyte consists of ethylene glycol with 2 % distilled H₂O and 0.33 % NH₄F. After the synthesis, the samples were rinsed with water and annealed at 450 °C in air for 3 h in order to obtain crystallization into the anatase phase (Perini et al., 2021).

The main advantage of adopting this technique is related to the possibility of tailoring the morphology of TiO₂ as “a priori” design for light-harvesting and catalytic applications (Tesler et al., 2020).

2.2 Cu₂O nanocubes

A facile wet precipitation process was used to synthesize cuprous oxide (Cu₂O) nanocubes (Liu et al. 2016). In brief, CuCl₂·2H₂O (0.85 g) was dissolved in distilled water (500 mL) under stirring at 60°C. After dissolution, 2 M NaOH (50 mL) was added and the resulting solution was stirred for 30 min. Then, 0.6 M ascorbic acid (50 mL) was slowly added and the temperature set to 60° C. The formation of an orange Cu₂O precipitate was obtained in 3 h. The as-obtained precipitate, after cooling at room temperature, was collected by centrifugation and dried in a vacuum oven at 60°C overnight.

2.3 Cu₂O-TiO₂ P25

Cuprous oxide / titania (Cu₂O/TiO₂, Cu loading ≈5) catalyst was prepared by an ultra-sonication assisted precipitation method. Copper acetate (0.3 g) was dissolved in 25 mL of ethanol forming a blue solution. Then, an appropriate amount of commercial TiO₂ (Degussa P25) was added under ultrasonication. The resulting suspension was heated up to 60 °C; then, 0.4 M glucose solution (25 mL) and 0.3 M NaOH (30 mL) were added. The solution was stirred for 30 min at 60 °C, and then it was cooled naturally to room temperature, collected by centrifugation, and washed with distilled water to remove the impurity. The resulting powder was dried under vacuum at 60 °C overnight.

2.4 Electrocathode preparation

The electrocathode materials (bare Cu₂O nanocubes or Cu₂O/TiO₂) were deposited in the form of a stable ink over a carbon-based gas diffusion layer (GDL, Sigracet® 29BCE, supplied by Ion Power) pre-heated to allow the evaporation of the solvent, by spray-coating technique. The ink (an organic solvent suspension of the catalytic powder) was prepared as follows: the powder was mixed with isopropanol (50 mL) and Nafion 5 wt. % perfluorinated solution (50 µL) under stirring for 20-30 min. The as-obtained stable suspension was sprayed on the GDL with a loading of 1 mg cm⁻².

2.5 Membrane-electrode assembly (MEA)

The electrodes were compacted by hot-pressing a proton exchange membrane (Nafion® NR212) to form a membrane-electrode assembly (MEA). This type of assembly is widely used in fuel cells and allows efficient transport of protons (H⁺) between the two catalytic layers, also physically separating the two half-cell compartments.

2.6 PEC device

The experimental apparatus for the photo-electrocatalytic tests consists of a solar simulator and a photoreactor. A Xe-arc lamp (Lot Oriel, 300 W) equipped with a set of lenses for light collection and focusing, and a water filter to eliminate the infrared radiation, was used as the light source. The solar-driven reactor is made of Plexiglas and equipped with a quartz window. It has a compact two-electrode configuration with separate compartments for the two half-reactions of CO₂ reduction and water oxidation. In comparison with the conventional photocatalytic reactors, this photo-device was designed to be more compact and better suited for a delocalized energy production (de Brito et al., 2019).

1 M NaOH aqueous solution (40 mL) was used as the anolyte, while 40 mL of 0.1 M KHCO₃ aqueous solution (saturated with a continuous flow of CO₂) were used as the catholyte. The irradiated area is about 5 cm². The liquid catholyte containing the products was analysed by Gas Chromatography-Mass Spectrometry (GC-MS, column Stabilwax, He carrier gas, detection limit around 1–5 ppm) to check the formation of methanol, ethanol, and other alcohols, and by Ion Chromatography (IC, column organic acids, detection limit around 0.1–1 ppm) to detect formic acid and acetic acid. The presence of products in the gas reactor outlet stream (H₂, CH₄, CO, C₂H₄, C₂H₆) was checked directly on-line by a Gas Chromatograph (MicroGC GCX Pollution Analytic Equipment), having a sensitivity of 1–2 ppm.

3. Results and Discussion

3.1 X-Ray diffraction crystallography

The crystallographic structure and the purity of the electrocathode materials (Cu₂O and Cu₂O-TiO₂) were investigated by X-ray Diffraction (XRD), as shown in Figure 1. The well-defined peaks prove the crystallinity of the two samples. The following peaks belong to cuprous oxide: 29.7, 36.6, 42.5, 52.5, 61.6, 73.7, and 77.5 ° referring to the planes (110), (111), (200), (211), (220), (311), and (222), respectively. XRD spectrum of Cu₂O-TiO₂ sample (black line) evidences the presence of the characteristic peaks of the two main components (Cu₂O and TiO₂). The TiO₂ phase distribution in the sample also reflects the P25 Degussa distribution, consisting in anatase and rutile in 3:1 ratio.

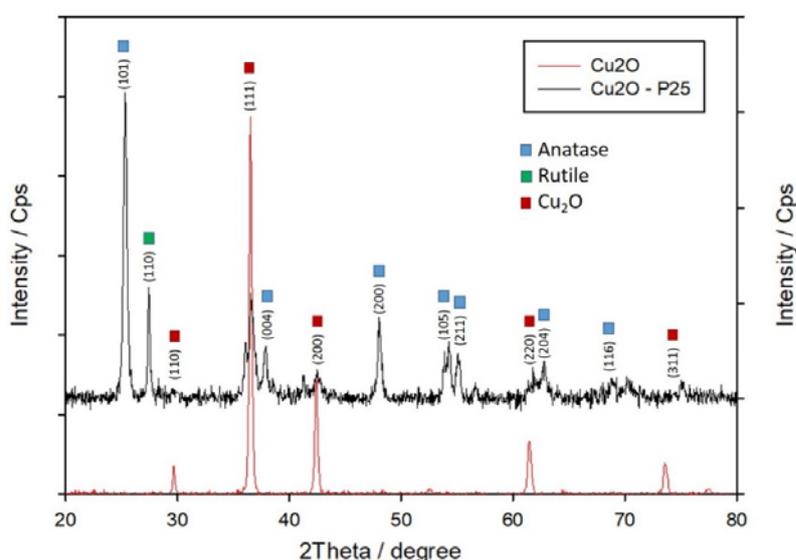


Figure 1: XRD patterns of Cu₂O (red line) and Cu₂O-TiO₂ (black line). Anatase and rutile TiO₂, and Cu₂O phases are highlighted.

3.2 Morphology analysis

Figures 2a and b show the Scanning Electron Microscopy (SEM) images of Cu₂O and Cu₂O-TiO₂ samples synthesized by wet precipitation and ultra-sonication assisted precipitation methods, respectively. Particularly, Cu₂O prepared by wet precipitation evidences a nanocube-shape morphology, with aggregates having a size of about 170–200 nm, while for Cu₂O-TiO₂ prepared by ultra-sonication assisted precipitation, the particle size

of the aggregates is larger, ranging from 400 to 700 nm. More in detail, a structure composed by spheroidal Cu_2O aggregates, deriving from the intergrowth of many nanocube crystals along different directions, in combination with a porous TiO_2 substrate, can be observed.

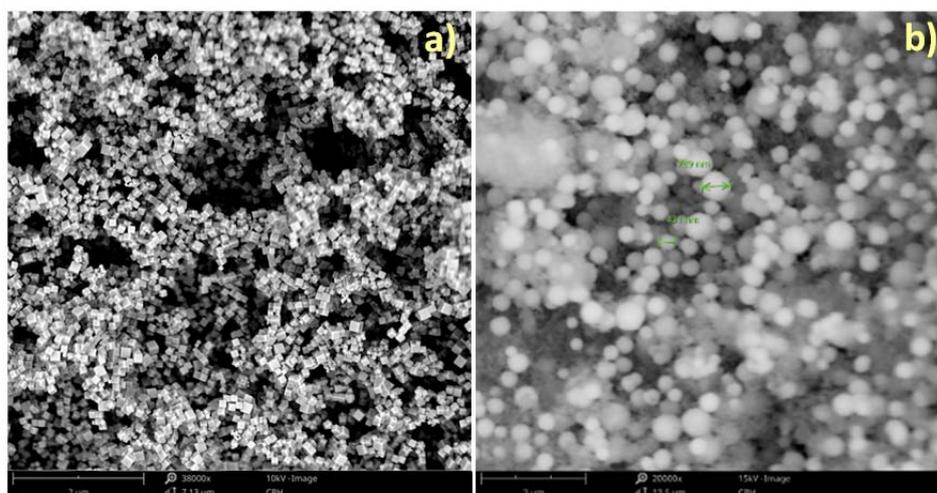


Figure 2. SEM images of a) Cu_2O nanocubes synthesized by wet-precipitation method and b) $\text{Cu}_2\text{O}/\text{TiO}_2$ obtained through ultra-sonication assisted wet precipitation method.

3.3 CO_2 reduction tests

The performances of $\text{Cu}_2\text{O}/\text{GDL}$ and $\text{Cu}_2\text{O}-\text{TiO}_2/\text{GDL}$ electrodes in the process of CO_2 reduction were evaluated using the solar-driven compact PEC device described in the experimental part. The tests were carried out using an *n*-type photo-active thin film of ordered arrays of titania nanotubes (grown by anodic oxidation on a perforated Ti foil) in the anodic part. The procedure of working of the PEC system was the following: the electrons generated by irradiation of the TiO_2 nanotubes were collected through the Ti layer remained not-oxidized after the anodization, and transported to the cathodic part of the cell through an external circuit; the protons, which were generated from water oxidation in the anode, first diffused along the TiO_2 nanotubes and then migrated through the Nafion membrane towards the cathodic part of the PEC cell to reduce CO_2 over Cu_2O or $\text{Cu}_2\text{O}-\text{TiO}_2$ electrocatalysts. The two electrolyte aqueous solutions (NaOH and KHCO_3) circulated continuously through each cell compartment and an outer reservoir.

Before each test, the aqueous KHCO_3 solution was saturated with CO_2 for 30 min in order to stabilize the pH, which corresponds to a value of 6.8 for 0.1 M KHCO_3 concentration. A continuous CO_2 flow was maintained during the irradiation tests (20 mL min^{-1}). This operation allowed to create a sort of buffer $\text{CO}_2/\text{KHCO}_3$, guaranteeing a relative high concentration of CO_2 in solution. However, the diffusion of CO_2 through the Helmholtz double layer remains a great issue for CO_2 reduction in liquid systems, and a different gas-phase approach (without using an electrolyte in the cathode compartment) would be highly desirable (Marepally et al., 2017b). Note that the reaction was driven only by light irradiation, using a solar simulator and without adding any external current or electrical bias. The behaviour of the electrodes was investigated in the photo-electrocatalytic device for 4 h of irradiation, monitoring the formation of both gas and liquid products. The main products were formic acid, acetic acid and hydrogen. Other products of CO_2 reduction, such as methanol, ethanol, isopropanol, methyl formate, acetone, methane and carbon monoxide, were analysed, but they were absent or formed only in traces in all tests. The production rates of formic acid and acetic acid obtained with $\text{Cu}_2\text{O}/\text{GDL}$ and $\text{Cu}_2\text{O}-\text{TiO}_2/\text{GDL}$ electrodes are reported in Table 1. The bare $\text{Cu}_2\text{O}/\text{GDL}$ electrode (no TiO_2) showed 31.8 and $80.6 \mu\text{mol h}^{-1} \text{ g}_{\text{Cu}}^{-1}$ of formic acid and acetic acid production rates, respectively. $\text{Cu}_2\text{O}-\text{TiO}_2/\text{GDL}$ electrode, instead, showed more than one order of magnitude higher productivity (0.69 and $2.59 \text{ mmol h}^{-1} \text{ g}_{\text{Cu}}^{-1}$ as formic acid and acetic acid production rates, respectively). This can be ascribed to the synergetic electrocatalytic effects of the as-formed $\text{Cu}_2\text{O}-\text{TiO}_2$ heterostructures.

Table 1: Production rates obtained with $\text{Cu}_2\text{O}/\text{GDL}$ and $\text{Cu}_2\text{O}-\text{TiO}_2/\text{GDL}$ as electrocathodes and TiO_2 nanotube arrays as photoanode.

Sample	Formic acid $\text{mmol g}_{\text{Cu}}^{-1} \text{h}^{-1}$	Acetic acid $\text{mmol g}_{\text{Cu}}^{-1} \text{h}^{-1}$
$\text{Cu}_2\text{O}/\text{GDL}$	0.0318	0.0806
$\text{Cu}_2\text{O}-\text{TiO}_2/\text{GDL}$	0.69	2.59

As the GDL support is not inert, a blank experiment without spraying Cu_2O or $\text{Cu}_2\text{O}-\text{TiO}_2$ on the GDL was also performed. In this case, only very low amounts of formic acid and acetic acid were detected (about 20 times less than the electrode containing Cu_2O). A further blank experiment without CO_2 in the supporting electrolyte was also made, evidencing the formation of only formic acid as carbon product, but with a much lower productivity (a thousand times lower) than in presence of CO_2 , which is to ascribe to the conversion of small amounts CO_2 released from KHCO_3 solution. A low amount of carbon products was also detected in the anode part, likely due to cross-over of anions (formate and acetate) through the Nafion membrane, evidencing that the behaviour of this kind of membrane is far from ideal.

Figure 3 shows a plot of Faradaic Efficiency (FE) to formic acid and acetic acid. The values of current density are also plotted in the same graph. A much higher FE to acetic acid was observed for $\text{Cu}_2\text{O}-\text{TiO}_2/\text{GDL}$ electrode (61.9 %) with respect to the bare $\text{Cu}_2\text{O}/\text{GDL}$ (18.9 %), indicating that the presence of TiO_2 favoured the formation of C-C bond, as also recently demonstrated for the photocatalytic reduction of CO_2 in a gas flow-through reactor (Giusti et al., 2020). Note that a higher number of electrons is needed for the formation of acetic acid than formic acid (8 vs. 2). Moreover, a stable current density of $142.1 \mu\text{A cm}^{-2}$ was obtained using $\text{Cu}_2\text{O}/\text{GDL}$ electrode, while the current density was lower for $\text{Cu}_2\text{O}-\text{TiO}_2/\text{GDL}$ electrode ($70.1 \mu\text{A cm}^{-2}$). The cathode performances were stable for at least 24 h.

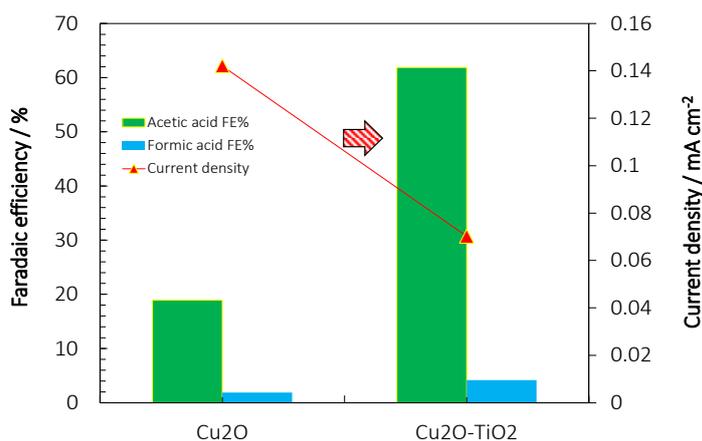


Figure 3: Faradaic efficiency (FE) and current density for CO_2 reduction tests with $\text{Cu}_2\text{O}/\text{GDL}$ and $\text{Cu}_2\text{O}-\text{TiO}_2/\text{GDL}$ electrodes.

Table 2 shows instead a comparison of productivity obtained in the solar-driven PEC device (using $\text{Cu}_2\text{O}/\text{GDL}$ electrode) with results obtained using a conventional photo-reactor working in liquid phase (with Cu_2O powder in slurry) irradiated by the same solar simulator. The productivity was much higher (of about one order of magnitude) in the solar-driven PEC reactor, as well as the selectivity to acetic acid, highlighting the importance of electrode and cell design to improve performances of CO_2 reduction towards the sustainable production of $>\text{C}1$ chemicals and fuels.

Table 2: Production rates in the solar-driven PEC device in comparison with a conventional slurry photoreactor, with Cu_2O as electrocatalyst.

Reactor type	Acetic acid $\mu\text{mol g}_{\text{Cu}}^{-1} \text{h}^{-1}$	Formic acid $\mu\text{mol g}_{\text{Cu}}^{-1} \text{h}^{-1}$
PEC	81	32
Slurry	3.1	3.7

4. Conclusions

This study has analysed the synthesis, characterization, and application of Cu₂O/GDL and Cu₂O-TiO₂/GDL electrodes in the photo-electro-catalytic reduction of CO₂ (in combination with TiO₂ nanotube arrays as photoanode for water oxidation) in a compact-design solar-driven PEC cell without application of any external potential/current and without sacrificial agents. Both electrodes were made using only earth-abundant materials and low-cost preparation procedures suitable for scale up. High Faradaic efficiency (FE) to acetic acid was obtained especially for Cu₂O-TiO₂/GDL electrodes (61.9 %), evidencing that the synergetic catalytic effects of the as-formed Cu₂O-TiO₂ heterostructure favoured the formation of C-C bond, thus improving the production of the more desired >C1 products. Results also showed that a rapid and efficient electrocatalytic reaction requires not only an active catalytic material, but also a proper electrode and cell design.

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