



# Boosting the solar-light-driven methanol production through CO<sub>2</sub> photoreduction by loading Cu<sub>2</sub>O on TiO<sub>2</sub>-pillared K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>



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## ABSTRACT

The enhancement of the photoactivity of the layered semiconductor K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub> towards the greenhouse CO<sub>2</sub> gas photoreduction is reported in this work. Such improvement was due to the synergistic effect created by pillaring K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub> with TiO<sub>2</sub> pillars and the subsequent loading of Cu<sub>2</sub>O cocatalyst. A throughout characterization of the final nanocomposite and the intermediate materials was carried out in order to evaluate the structural and compositional features responsible for the increased photocatalytic activity. The layered precursor phase (K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>), the incorporation of anatase TiO<sub>2</sub> pillars and cuprite Cu<sub>2</sub>O nanoparticles were studied through X-ray diffractometry, electron microscopy analyses and X-ray photoelectron spectroscopy. All the successive reactions performed in the layered precursor led to the increment of its surface area, from 25 to 145 m<sup>2</sup> g<sup>-1</sup>, and mesoporosity (4.6 nm), as indicated by N<sub>2</sub> adsorption-desorption isotherms. The pillaring and the loading of Cu<sub>2</sub>O nanoparticles have red shifted the onset of the absorption band of the semiconductor, broadening the optical response of the final nanocomposite. All these modifications enhanced the activity of the photocatalyst, doubling the production of methanol compared to the pristine K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>.

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## 1. Introduction

The production of clean and renewable fuels has become one of the main quests of the modern civilization as a consequence of the concern caused by the rising of global energy demand and environmental issues [1–3]. The urgent need for alternative energy sources has directed a strong impulse into research of solar energy applied in the synthesis of solar fuels [4–6]. In this context, the exploitation of solar energy for the generation of hydrogen, via water splitting, and fuels such as methanol and methane, through the photocatalytic reduction of carbon dioxide, has been widely considered as one of the most feasible solution to fulfill the future energy demands of mankind [2,7–9].

Additionally, the global levels of carbon dioxide, a greenhouse gas, have reached worrisome concentrations, making urgent the development of effective solutions for CO<sub>2</sub> remediation [1]. Among many different approaches, an efficient way to mitigate or reduce the emission of CO<sub>2</sub> is using it as a feedstock in the production of valuable renewable fuels [10,11].

Carbon dioxide photoreduction is an appealing alternative for the substitution of the extensive use of non-renewable fossil fuels because it uses inexpensive and non-toxic reactants, such as water, and abundant energy source, such as sunlight, to convert CO<sub>2</sub> into useful chemicals. A power of approximately 120,000 TW of solar radiation is provided to the Earth every year, making the artificial photosynthesis process an outstanding affordable and environmentally friendly source of renewable energy [7]. Nevertheless, CO<sub>2</sub> photoreduction methods using semiconductors as photocatalysts still suffer from low conversion yields because of the fast electron-hole recombination and narrow light absorption range of the most well-known photocatalysts. Consequently, the development of new strategies to improve the yield of this process has been a constant aim of many research groups [2,7,9].

An efficient CO<sub>2</sub> photoreduction under solar radiation requires the use of visible-light-responsive photocatalysts, which can be achieved by the designing, modification and/or combination of nanostructured semiconductors to attain the desired tailored chemical-physical characteristics. Previous reports have achieved this goal by modifying the structures of the most studied photocatalysts, such as TiO<sub>2</sub> and SrTiO<sub>3</sub> [12–14].

Lamellar materials are known for their interesting chemical and structural versatility [15,16]. One of their most flexible

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characteristics is the basal distances, which make them suitable for several applications. The layered titanates  $\text{Na}_2\text{Ti}_3\text{O}_7$ ,  $\text{K}_2\text{Ti}_4\text{O}_9$ , and  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ , for example, have shown good physicochemical and photocatalytic properties that can be improved by the intercalation of photoactive species within their sheets, creating the so-called porous pillared structure [16–20]. The pillaring process is favorable because of the increase in the surface area and the integration of two semiconductors with suitable band gap energy levels. Thus, such heterojunction structure is important for charge transfer processes, enabling an increase in the photoactivity by promoting the spatial separation of photogenerated electrons and holes. Furthermore, the pore structure of the solid can be controlled by adjusting the conditions of the pillaring process [19,21–23].

Owing to the advantages of pillared composites in promoting the separation of charge carriers, this work reports the multi-step synthesis of a ternary pillared mesoporous titanium-based semiconductor and its useful application in photocatalytic  $\text{CO}_2$  reduction. The lamellar semiconductor  $\text{K}_2\text{Ti}_4\text{O}_9$  was pillared with  $\text{TiO}_2$  (semiconducting pillars) by following a method of exfoliation of its protonic version ( $\text{H}_2\text{Ti}_4\text{O}_9$ ) with tetrabutylammonium hydroxide into individual nanosheets, and restacking in the presence of anatase  $\text{TiO}_2$  nanosol coordinated with acetylacetone. This method, developed by Choy et al. [19], eases the access of guest species into the interlayer space of the host lattice without steric hindrance and was adopted because the interlayer space of the titanate host does not undergo enough swelling due to the high charge of its layers, which prevents an effective intercalation of  $\text{TiO}_2$  sol particles through simpler pillaring methods [19,21].

Even though the pillaring process improves the photocatalytic activity of  $\text{K}_2\text{Ti}_4\text{O}_9$  due to the coupling with  $\text{TiO}_2$  nanopillars, the resulting material is still limited to UV absorption, which only corresponds to 3–5% of the solar spectrum [17,24]. To circumvent this drawback,  $\text{Cu}_2\text{O}$  nanoparticles were deposited on the surface of the mesoporous solid.

Copper oxides ( $\text{Cu}_2\text{O}$  and  $\text{CuO}$ ) have been applied as cocatalysts coupled with classical photocatalysts, leading to notable enhancements in the photocatalytic yields [25–27].  $\text{Cu}_2\text{O}$  is a semiconductor with a narrow band gap of 2.0–2.2 eV. Its loading on the surfaces of other photoactive semiconductors has proven to generate highly active photocatalysts because of the extension of the absorption range of the resulting heterostructures [26–29]. In addition, such connection between the  $\text{Cu}_2\text{O}$  semiconductor with  $\text{K}_2\text{Ti}_4\text{O}_9$  and  $\text{TiO}_2$  may lead to suitable alignment of energy band edges that further favors the electron mobility under illumination [26,30].

The loading of  $\text{Cu}_2\text{O}$  nanoparticles as cocatalysts on the mesoporous structure prepared in this work remarkably improved the catalytic performance of the conversion of  $\text{CO}_2$  to methanol. The structural and compositional features of the solids were fully explored to unveil the characteristics responsible for such activity enhancement. To the best of our knowledge, this is the first time a multi-component pillared structure is applied in the production of methanol from  $\text{CO}_2$  photoreduction, especially a  $\text{Cu}_2\text{O}$ -decorated  $\text{TiO}_2$ -pillared tetratitanate. The combination of three different species conducted to an intensification of light harvesting, surface charge separation and electron mobility.

## 2. Experimental

### 2.1. Chemicals

Potassium carbonate,  $\geq 99\%$  (Aldrich) and titanium(IV) oxide, anatase  $\geq 99.99\%$  (Aldrich) were used for the synthesis of pristine  $\text{K}_2\text{Ti}_4\text{O}_9$ . Titanium(IV) isopropoxide, 97% (Aldrich), tetrabutylammonium hydroxide 30-hydrate,  $\geq 99.0\%$  (Aldrich), and

acetylacetone P. A. (Merck) were employed for the pillaring of the layered material. Copper(II) acetate monohydrate (Vetec) and ethylene glycol P. A. (Reagen) were used for the *in-situ* synthesis of  $\text{Cu}_2\text{O}$  nanoparticles. All other chemicals, such as ethanol P. A. (Synth), hydrochloric acid P. A. (Synth) and nitric acid P. A. (Synth) were high-grade reagents and were used as purchased without prior purification. The titanium dioxide (P25) used in the photocatalytic tests was a high-grade reagent purchased from Evonik, Brazil. Deionized water used in the syntheses and photocatalytic tests was purified to 18.2 M $\Omega$ cm resistivity using an ultra-pure Milli-Q Millipore system.

### 2.2. Synthesis of $\text{K}_2\text{Ti}_4\text{O}_9$

The layered solid  $\text{K}_2\text{Ti}_4\text{O}_9$  was synthesized through a solid-state reaction. A mixture of potassium carbonate ( $\text{K}_2\text{CO}_3$ ) and titanium dioxide ( $\text{TiO}_2$  – anatase phase) in a molar ratio of 1:3.5 was suspended in acetone (20 wt%), to lower the friction force between the particulate solids, and sonicated for 10 min. The suspension was wet-ground in an agate mortar, dried, and the white powdered mixture, transferred to an alumina crucible, was heated at 800 °C for 20 h, under a heating rate of 10 °C min<sup>-1</sup>. After cooling, the solid was removed from the crucible, ground, suspended in acetone (20 wt%), sonicated for 10 min, wet-ground and submitted again to the same thermal treatment. The final solid ( $\text{K}_2\text{Ti}_4\text{O}_9$ ) was washed three times with deionized water, and dried at 100 °C in an oven, under vacuum for 8 h [31].

### 2.3. Pillaring

The corresponding titanate protonic form ( $\text{H}_2\text{Ti}_4\text{O}_9$ ) was prepared by stirring the synthesized  $\text{K}_2\text{Ti}_4\text{O}_9$  in HCl 1 mol L<sup>-1</sup> aqueous solution at room temperature for 3 days. During this period, the suspension was centrifuged and the acidic solution was replaced by a fresh one every day. The product was centrifuged, washed with deionized water and dried at 100 °C under vacuum for 8 h. Subsequently, 5.0 g (14.8 mmol) of the layered protonic titanate was exfoliated into single titanate nanosheets by suspending it with 11.8 g (14.8 mmol) of tetrabutylammonium hydroxide (TBAOH) in 250 mL of deionized water. The formed suspension was sonicated at room temperature for 2 h.

In a separate container, a monodispersed  $\text{TiO}_2$  nanosol was prepared by the dropwise addition of a mixture of 28.8 g (0.101 mol) of titanium isopropoxide and 19.9 g (0.198 mol) of acetylacetone to 180 mL of a 0.015 mol L<sup>-1</sup>  $\text{HNO}_3$  aqueous solution under vigorous stirring and then peptized for 8 h at 60 °C. This prepared  $\text{TiO}_2$  nanosol was added dropwise into the exfoliated layered titanate solution and stirred at 60 °C for 24 h.

The resulting powder was centrifuged, washed with a mixed solution of deionized water and ethanol (1:1, v/v) to remove the excess of  $\text{TiO}_2$  nanosol, and dried at 60 °C under vacuum for 8 h. Lastly, in order to complete the pillaring process, the obtained material was heated at 300 °C for 2 h with a heating rate of 1 °C min<sup>-1</sup> [19]. The as-prepared porous pillared solid was named  $\text{TiO}_2/\text{Ti}_4\text{O}_9$ .

### 2.4. Incorporation of $\text{Cu}_2\text{O}$ nanoparticles

First, 1.0 g of  $\text{TiO}_2/\text{Ti}_4\text{O}_9$  was suspended in a solution containing 0.139 g (0.70 mmol) of copper(II) acetate dissolved in 200 mL of ethanol. This mixture was sonicated for 2 h and, subsequently, magnetically stirred for 4 h at 25 °C to ensure the complete adsorption of  $\text{Cu}^{2+}$  onto the surface of the porous structure. The solid was centrifuged, washed four times with pure ethanol, and dried under vacuum at 60 °C for 8 h. At this point, the mesoporous

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