



# Photocatalytic reduction of CO<sub>2</sub> to hydrocarbons using bio-templated porous TiO<sub>2</sub> architectures under UV and visible light

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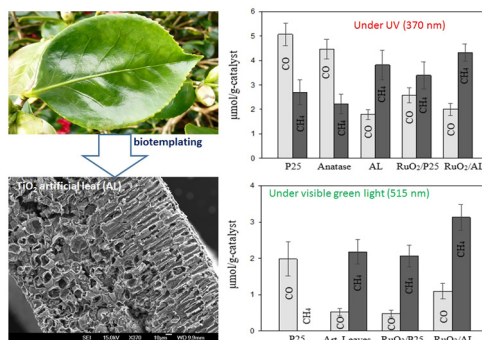
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## HIGHLIGHTS

- Bio-templated TiO<sub>2</sub> has mesoporous structure replicating pores in green leaves.
- The porous TiO<sub>2</sub> showed higher visible light photocatalytic activity than P25 TiO<sub>2</sub>.
- Bio-templated TiO<sub>2</sub> outperformed P25 TiO<sub>2</sub> in CO<sub>2</sub> reduction and ethanol reforming.
- Significant effect of morphology on the photocatalytic activity was demonstrated.
- Deposition of RuO<sub>2</sub> improved photocatalytic activity under UV and visible light.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

Artificial TiO<sub>2</sub> leaves with the morphology replicating that of *Camellia* tree leaves were synthesized through a multi-step bio-templating approach. Scanning and transmission electron microscopy images of the final products indicated that proposed method successfully replicates the highly porous structure of the leaf photosystem, down to the thylakoids. The hierarchical pore network and morphology of the bio-templated TiO<sub>2</sub> catalyst were demonstrated to be critical factors in successful photocatalytic reduction of CO<sub>2</sub> under UV (370 nm) and visible (515 nm) light. The artificial TiO<sub>2</sub> leaves increased the selectivity towards methane in CO<sub>2</sub> photoreduction compared with benchmark commercial catalyst under UV light. The new TiO<sub>2</sub> structures also outperformed the P25 titania by more than 1.35 times in terms of total product yield (CO + CH<sub>4</sub>) of under visible light. We hypothesized that modifying the morphology of the catalyst can alter the pathway and efficiency of photocatalytic reactions. Deposition of ruthenium dioxide on the surface of the new TiO<sub>2</sub> architecture showed further improvement in photocatalytic activity under both UV and visible light. The photocatalytic reduction of CO<sub>2</sub> coupled with the oxidative water splitting was also validated by kinetic modelling. The experimental data exhibited a very good fit to the pseudo first order kinetics. The understanding of the morphological contribution of the photocatalyst revealed in this study can help to augment the efficiency and selectivity of CO<sub>2</sub> photoreduction.

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## 1. Introduction

Sustainable processes for efficient conversion of solar energy to fuels has been heavily researched in recent years. Natural photosynthesis, which plays a fundamental role in the life cycle of nature, provides a promising blueprint for such system design. Green leaves capture CO<sub>2</sub> and convert it into chemicals via photosynthesis using solar energy. In chemical parlance, artificial photosynthesis is the conversion of water and carbon dioxide into hydrocarbons and oxygen [1,2]. Conducting photoreduction of CO<sub>2</sub> in stirred batch reactors, which involve gas and liquid phases in the presence of heterogeneous catalyst, is the most economical and convenient way to meet CO<sub>2</sub> abatement targets, especially for developing countries [3]. However, the performance of this photocatalytic system highly depends on the operating conditions; for example, the gas-phase partial pressure CO<sub>2</sub> affects the solubility of CO<sub>2</sub> in water [4]. Other operating conditions (pH, temperature, stirring rate, light wavelength and intensity etc.) are also influential. For instance, although higher temperatures may speed-up reactions corresponding to the rate determining steps of the process, the increase in temperature could often show overall detrimental effect on the photocatalytic CO<sub>2</sub> reduction due to the low CO<sub>2</sub> solubility in water [5]. The volume of the reacting phase should be optimized to fulfil perfect mixing and to overcome mass transfer limitations in slurry reactors [6,7]. High concentration of catalyst may cause undesirable effects of light scattering or poor penetration. Ballari et al. [6,7] showed that the catalyst loading should be below 1 g L<sup>-1</sup> in order to achieve efficient light penetration. Furthermore, the use of NaOH solution can increase the amount of dissolved CO<sub>2</sub> since the caustic NaOH solution dissolves more CO<sub>2</sub> than pure water forming bicarbonate species [8]. The highly concentrated OH<sup>-</sup> ions from NaOH in aqueous solution could also act as strong hole-scavengers, helping to decrease the recombination rate of photo-generated electron-hole pairs [9].

Apart from reaction conditions, the efficiency and selectivity of solar-assisted reactions also strongly depend on the performance of the photocatalyst itself. Titanium dioxide (TiO<sub>2</sub>)-based materials with their low toxicity, good durability, high thermal and chemical stabilities and, most importantly, the capability of generating photoinduced electron-hole pairs allow them to be ideal candidates for CO<sub>2</sub> reduction [10]. Despite intense research on developing efficient TiO<sub>2</sub> materials for producing solar fuels, the effects of the morphology of the photocatalyst on the selectivity and yield in catalytic CO<sub>2</sub> photoreduction are less studied. The efficiency of the photocatalytic reactions is an overall outcome of various steps: light absorption, rate of transport of photo-generated charge carriers to the surface vs. the electron-hole recombination rate, and mass transfer of reagents and scavengers to the catalyst surface. The local structure of the photocatalyst, particularly the particle size and shape, strongly influences the aforementioned parameters [11].

A wide range of TiO<sub>2</sub> architectures, including nanorods, nanosheets, nanowires, nanotubes, and aerogels, have been developed to enhance the photocatalytic activity [12,13]. The improved photocatalytic performance of TiO<sub>2</sub> nanomaterials is a result of several key factors. These include large surface area, enhanced excitation behaviour, high efficiency of light absorption, lower recombination rates etc. [14]. Commonly studied nanoscale TiO<sub>2</sub> materials can be synthesized via a number of different methods, including sol-gel, micellar and solvothermal syntheses, direct oxidation, chemical or physical vapour deposition, electrodeposition, and microwave synthesis. However, some challenges still exist; one of the most important difficulties is associated with controlling the shape and crystallinity of the final product [13,14].

Replication of the natural hierarchical structures has been recently proposed as an avenue for the development of TiO<sub>2</sub>-based photocatalysts with improved light-harvesting function [15]. Bio-inspired systems have emerged as a promising area of research for developing novel materials with a higher standard of environmental compatibility,

recyclability, and energy efficiency [16]. The unique characteristics of green leaf photosystems, which range from the molecular to nanometre to the millimetre scales, make them efficient light-harvesting structures. The main antenna of plant photosystems is the chloroplast. The thylakoid cylindrical stacks (granum) inside the chloroplast are 3-dimensional constructions that are made of interconnected nanolayers, which efficiently harvest light and direct it to chlorophylls as the reactive centres of the plant photochemical machine [17,18].

However, the surface chemical modification of TiO<sub>2</sub> materials is a common approach to redshift the effective wavelength for photocurrent generation in the visible light region. Semiconductors with a narrower bandgap than that of pure titania can be used as sensitizers. The sensitizers include inorganic semiconductors, metals, and organic dyes. Transition metals, such as Cu, Fe, Ru, and Ag, have shown promising results in improving the optical properties of TiO<sub>2</sub> photocatalysts. The well-matched electronic structure of metals and TiO<sub>2</sub> enhances the charge transfer and results in efficient charge separation [19,20].

In this report, TiO<sub>2</sub> architectures with a unique pore network have been synthesized via our improved bio-templating approach. The *Camellia* tree leaves from the Theaceae family, which belongs to C<sub>4</sub> plants that possess the Kranz anatomy, were used as a template. This study focuses on the effect of morphology of bio-templated materials on their photocatalytic performance in photoreduction of CO<sub>2</sub> using water under UV and visible light irradiation. Modification of the new TiO<sub>2</sub> architecture was also achieved by loading ruthenium oxide (RuO<sub>2</sub>) onto the surface to enhance the charge transfer/separation and to redshift the effective wavelength for photocurrent generation in the visible light region. Non-porous commercial titania catalysts, pure anatase, and P25 were used as a benchmark. The advantages of using the new stack-layered TiO<sub>2</sub> nanostructure based on the template of natural leaves to convert CO<sub>2</sub> into methane (CH<sub>4</sub>) using a simple reactor design are demonstrated in this study.

## 2. Materials and methods

### 2.1. Chemicals

All reagents were of analytical grade and were purchased from Sigma-Aldrich. All reagents were used as received. All glassware was oven dried and experiments were performed using the Schlenk line technique to avoid contact with ambient air when required. The high purity CO<sub>2</sub> (≥99.995%) was used to avoid any hydrocarbon contamination.

### 2.2. Synthesis procedure of bio-templated TiO<sub>2</sub> artificial leaves

The synthesis procedure is illustrated in Scheme A1 with full details reported in our earlier study [21]. First, the natural chlorophyll breakdown process was mimicked using an ion-exchange approach. An acid treatment of natural leaves (*Camellia* tree) was conducted until the colour of the leaves became yellow-brown, which indicates the conversion of chlorophyll into pheophorbide [22]. In total, 6.00 g of the pre-washed fresh leaves were cut into small pieces (ca. 5 by 5 mm) and then stirred in a 5 v/v% HCl solution under inert atmosphere (Schlenk line technique) overnight (until the colour of leaves changed). Subsequently, the leaves were treated in 400 mL of 5 v/v% TiCl<sub>3</sub> solution in water (i.e. 5 v/v% of TiCl<sub>3</sub> of ≥12 wt% in HCl by Sigma-Aldrich diluted with 95 v/v% of MilliQ H<sub>2</sub>O) with gentle stirring (250 rpm) at ambient temperature for 24 h. The Ti<sup>3+</sup> exchange was performed under inert atmosphere to protect titanium ions from oxidation and to introduce Ti cations into the nanostructure of thylakoids via ion-exchange with protonated form of the chlorophylls. Next, the treated leaves were coated with TiO<sub>2</sub> using a sol-gel method, which was modified from a reported method in the literature [23]. The Ti<sup>3+</sup>-exchanged leaves were filtered off, washed with MilliQ water and dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub>. Dry leaves were suspended in dry ethanol (250 mL) with

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