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# A refractory selective solar absorber for high performance thermochemical steam reforming

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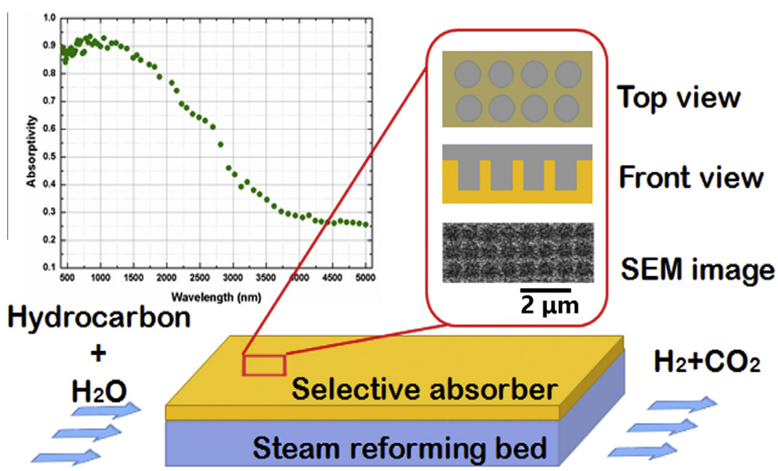
## HIGHLIGHTS

- 2D PhC nano structure is fabricated for achieving solar selective absorption.
- The solar selective absorber shows high surface temperature.
- The steam reformer with selective absorber shows higher fuel conversion rate.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The production of $H_2$ through steam reforming involves intensive energy consumption. Concentrated solar energy could be employed for the endothermic reaction in the steam reformer to produce $H_2$. However, at high operating temperatures, the solar absorber has huge radiation heat loss to the ambient as the radiation energy is proportional to the fourth power of the surface temperature. In order to avoid the large radiation heat loss and obtain higher surface temperature, here we present a 2D photonic crystal (PhC) solar selective absorber. The selective absorber is made from titanium nitride (TiN) thin film. On top of the TiN thin film, nano cavity array structure and $Al_2O_3$ coating are deposited. The absorptivity of the selective absorber is measured at room temperature and the high operating temperature performance is predicted. The fabricated selective absorber is thermal annealed at 800 °C for two hours and proves its thermal stability. By comparing the steam reformers with different absorbers (selective absorber and blackbody absorber), the selective absorber shows superior results including higher surface temperature, higher $C_3H_8$ conversion rate as well as higher $H_2$ production rate. The experimental and simulation results in this study shows that the 2D PhC solar selective absorber is a good candidate in the steam reforming application for $H_2$ production.



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**Nomenclature**

| | |
|---|---|
| $A$ | pre-exponentia constant |
| $c$ | speed of light in vaccum (m/s) |
| $C_p$ | specific capacity of gas phase (J/(kg K)) |
| $d$ | depth of nano cavity (nm) |
| $E$ | activation energy (kJ/mol) |
| $\Delta H_r$ | enthalphy of reaction (J/mol) |
| $k_i$ | reaction rate constant |
| $k_{sr}$ | thermal conductivity of gas in steam reformer (W/(mK)) |
| $n$ | refractive index of dielectric |
| $p$ | period of nano cavity unit (nm) |
| $P_{sr}$ | pressure (Pa) |
| $Q$ | heat source (W/m$^3$) |
| $r$ | radius of nano cavity (nm) |
| $r_i$ | chemical reaction rate (mol/(m$^3$ s)) |
| $T$ | temperature of selective absorber (K) |
| $T_{sr}$ | gas temperature in steam reformer (K) |
| $u$ | speed of gas (m/s) |
| $x'_{mn}$ | $n$th root of Bessel function |
| *Greek symbols* | |
| $\alpha$ | absorptivity |
| $\omega$ | mnp resonance frequency (s$^{-1}$) |
| $\rho$ | density of gas in steam reformer (kg/m$^3$) |
| $\kappa$ | permeability of reformer (m$^2$) |
| $\eta$ | viscosity of gas in steam reformer (Pa s) |
| $\lambda$ | wavelength (nm) |
| *Acronym* | |
| FTIR | Fourier Transform Infrared spectroscopy |

## 1. Introduction

With the large world reservation of element, high heating value and zero greenhouse gas emission from combustion, hydrogen has been regarded as the most promising fuel for the future [1–7]. Various hydrogen based power generation systems are prototyped including fuel cells [8], thermophotovoltaics [9,10] and micro turbines [11]. However, the wide application of the hydrogen fuel is still limited to the high cost during production process. Water electrolysis method is constrained by intensive energy consumption, while the photobiological approach is limited to low production rate [2,12,13]. Steam reforming is now the dominant approach for hydrogen production due to its relatively lower cost and higher production rate compared to other techniques.

In the steam reforming process, the fossil fuels are supplied as sources for hydrogen production [14]. The source fuels pass through a catalytic bed with high temperature (500–1100°) where endothermic chemical reactions take place [15–17]. The endothermic reactions break up the hydrocarbon molecules and generate carbon monoxide as well as hydrogen. The products with steam pass through metal oxides and undergo water–gas shift reaction [18–20]. In this process, more hydrogen can be generated. In the steam reforming technique, a high temperature source is required to serve the endothermic reaction. The performance of the steam reformer relies much on its temperature. Electric heating and gas combustion processes can provide high temperature for the steam reformer, but these processes involve intensive energy consumption. Besides, the byproducts from the combustion process induce contamination into the produced gases. In order to address this problem, concentrated solar energy could be employed as the high temperature source for the steam reforming process [21–23]. The advantages of using concentrated solar energy for steam reforming process include: (i) the calorific value of the methane feed could be upgraded by 22–28% theoretically by using the concentrated solar energy [19,20,24–27], (ii) reduced contamination to the production gas and (iii) pollutants emission to the environment can be avoided. Various concentrated solar steam reforming systems have been developed including trough, tower and dish systems which are capable of obtaining 100, 1000 and 10,000 suns ($I$ = 1 kW/m$^2$) [28]. In these systems, a solar receiver is employed for collecting the concentrated solar energy. The solar receiver is heated to a high temperature for steam reforming process. At the same time, the surface of the solar receiver is losing heat to the environment via convection and radiation heat transfer. The specific heat loss via convection and radiation are plotted in Fig. 1a. The convection heat loss is predicted by Newton's law for cooling and the heat transfer coefficient is estimated by correlation for natural convection [29]. The radiation heat loss is predicted by Stefan-Boltzmann's law for a blackbody [30]. It is found that when the surface temperature is low (below 600 K), the convection heat loss is higher than radiation heat loss. However, with the increase of the surface temperature, the radiation heat loss increases much faster than that of convection. This is because the radiation heat loss is proportional to the fourth power of surface temperature, which is much higher than the convection. Besides, the convection heat loss could be avoided by sealing the solar receiver and steam reforming system in a vacuum chamber. However, the surface of the solar energy receiver could not be covered as it has to face the reflector of the solar concentrator. In order to improve the performance of solar steam reforming system, the radiation heat loss has to be reduced. This could be achieved by a selective absorption surface [31]. It is known that the absorptivity of a surface is the fraction of radiation absorbed at a given wavelength. The selective absorption surface provides a high absorptivity at the solar energy spectrum but very low absorptivity (emissivity) at long wavelength. This facilitates the complete absorption of solar energy and reduces the radiation heat loss. As shown in Fig. 1b, due to the high temperature of the sun (5800 K), the solar energy spectrum is mainly distributed in visible light and near infrared wavelength range. However, the radiation spectrum of the surface of solar energy receiver is in the long wavelength range (greater than 2000 nm) as it has a much lower temperature (blackbody 1000 K). Refer to Wien's displacement law [30], the radiation spectrum will further move to longer wavelength with the decrease of the surface temperature. In this case, with the effect of the selective absorption surface, the radiation heat loss of the solar receiver could be reduced significantly. As a result, a higher surface temperature and better steam reforming performance could be expected.

Various selective solar absorbers have been developed for the past decades including different structures and diverse constituent materials [31–34]. However, these selective absorbers face the problems of easy oxidation or damage at high temperature condition, shortage of world reservation and reduced performance at elevated temperature conditions, etc. [35–37]. Besides, no such selective absorbers have been applied to the steam reforming system to improve the steam reformer performance. Here we demonstrate a titanium nitride (TiN) based 2D photonic crystal (PhC) selective absorber for steam reforming application. The titanium material has a much higher world reservation compared to other selective absorber materials. TiN can be synthesized via chemical vapor deposition (CVD) process. Besides, the TiN shows a melting point of as high as 2930 K, which is stable under the high