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A thermo-photo hybrid process for steam reforming of methane: highly efficient visible light photocatalysis†

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Steam reforming of methane (SRM) is one of the most important industrial processes, which produces 95% of hydrogen used in the USA. However, SRM is an endothermic reaction, which requires a high energy input and a high reaction temperature (> 800 °C) for the current process. Furthermore, its products must be subjected to a water–gas shift (WGS) process. A photocatalytic process is expected to solve the energy issue and to eliminate the necessity of WGS for SRM. However, the hydrogen yield from the current photocatalytic steam reforming of methane (PSRM) is very low (μmol h^{−1} g^{−1} level), which is far below industrial interest. This work demonstrates that a Pt/blackTiO₂ catalyst dispersed on a light-diffuse-reflection-surface is excellent for efficient visible-light PSRM. Under visible light illumination on the catalyst by filtering UV light from AM 1.5G sunlight, CH₄ and H₂O were directly converted into H₂ and CO₂ without WGS, leading to a high H₂ yield of 185 mmol h^{−1} g^{−1} with a quantum efficiency of 60% at 500 °C. The yield is 3 orders of magnitude larger than the reported values, which can be attributed to the synergistic effect between potential and kinetic energies. This opens up a new opportunity for hydrogen production from water and natural gas using solar energy.

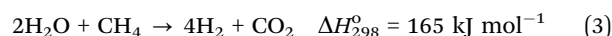
Hydrogen, which possesses the highest specific energy density, is a promising fuel for future transportation, even though developing highly efficient techniques for on-board hydrogen storage and inexpensive fuel cells is still a challenge for the commercialization of fuel cell vehicles. Hydrogen is also an important feed-stock for numerous industrial processes.¹ Currently, 95% of hydrogen used in the United States is produced by steam reforming of methane (SRM):^{2–5}



Since methane is the most stable hydrocarbon, the endothermic SRM requires a high temperature to reach the desired conversion rates of reactants with a large energy input.^{3–5} Furthermore, in commercial hydrogen production,⁵ the CO/H₂ product mixture obtained from SRM is subjected to a subsequent process called water gas shift (WGS, eqn (2)) to enhance the hydrogen yield.



However, this increases the complexity of hydrogen production. Therefore, it is desirable to convert CH₄ and H₂O directly to H₂ and CO₂ as follows:



However, this one-step process (eqn (3)) is unlikely to be obtained with conventional thermocatalytic steam reforming of methane. This happens because the selectivity to produce 4H₂ + CO₂ (eqn (3)) instead of 3H₂ + CO (eqn (1)) thermodynamically prefers a low reaction temperature (Table S1 in the ESI,†). In contrast, a high temperature is kinetically required to activate very stable CH₄ for a desired conversion rate. To solve the conflict over the requirement for operating temperature and the issue of high energy cost in the thermocatalytic process, a photocatalytic approach with solar energy is very necessary.

Fujishima and Honda created a new era in heterogeneous photocatalysis by discovering the photoelectrocatalytic splitting of water in 1972.⁶ As the most important photocatalyst, TiO₂ has been widely investigated. However, it can absorb only ultra-violet (UV) light (about 4% of the total solar energy) due to its relatively large band gap energy (3.0–3.2 eV), leading to a low photo-conversion efficiency.^{7–10} In the past 25 years, numerous pioneering contributions were made to extend the working spectrum of TiO₂ to the visible-light region (which constitutes about 45% of the total solar energy).^{7,11–17} As a breakthrough, Mao and his co-workers demonstrated that black TiO₂ synthesized by hydrogenating TiO₂ can remarkably absorb visible light.⁷ However, the absorbed visible light by the black TiO₂ nanoparticles could not contribute to the photocatalytic process.^{7,10}

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Very recently, we found that the inefficiency of absorbed visible light for the photocatalytic H_2 production from water over black TiO_2 at room temperature was due to the kinetic limitation.¹⁸ Furthermore, we demonstrated that this kinetic issue can be addressed using an elevated temperature,¹⁸ leading to a high visible light conversion efficiency for the CO_2 reduction with methane and the hydrogen production from water splitting.^{18,19} So far, however, research on the photocatalytic conversion of methane with water to chemicals and hydrogen fuel is in its infancy. For the direct synthesis of methanol from methane and liquid water under illumination, several metal oxides, such as TiO_2 and WO_3 , have been explored as photocatalysts.^{20,21} For hydrogen production from photocatalytic steam reforming of methane (PSRM), large-band-gap semiconductors (TiO_2 , NaTaO_3/La , CaTiO_3 , Ga_2O_3 , and $\text{K}_2\text{Ti}_6\text{O}_{13}$) with a noble metal (Pt and Rh) have been employed as photocatalysts, which exploited only UV light (about 4% of the total solar energy), leading to a very low H_2 yield (at the level of $\mu\text{mol h}^{-1} \text{g}^{-1}$).^{22,23} It is a long-time goal for photocatalytic processes to efficiently utilize visible light, since they account for $\sim 45\%$ of solar energy. In this work, we demonstrated that our invented catalyst system of the Pt/black TiO_2 catalyst on a light-diffuse-reflection surface is highly efficient for visible light photocatalytic steam reforming of methane (PSRM). Furthermore, the novel PSRM process can provide a very high hydrogen yield ($199 \text{ mmol h}^{-1} \text{g}^{-1}$ for 1.5G sunlight and $185 \text{ mmol h}^{-1} \text{g}^{-1}$ for visible light) at 500°C , which is 1000 times larger than the reported values at room temperature.

It is well-known that an efficient visible light photocatalyst must meet three requirements: an ability to absorb visible light, a suitable band structure of the catalyst to match the redox potentials of a reaction, and high efficiency for light absorption. To meet those requirements, the Pt/black TiO_2 catalyst on a light-diffuse-reflection-surface is considered to be a promising catalyst system for PSRM. First, this catalyst system can efficiently absorb light, since light absorption could be increased 100 times upon dispersing photocatalyst particles on the light-diffuse surface of a SiO_2 substrate.¹⁸ Second, different from pristine TiO_2 with a wide bandgap of about 3.2 eV (absorbing only UV light), black TiO_2 exhibits a narrow bandgap of about 1.0 eV, which is small enough to absorb visible light and even near-IR.⁷ Furthermore, we recently found that the absorbed visible light by black TiO_2 can contribute to photocatalysis at a temperature above 200°C .^{18,19} Therefore, the Pt/black TiO_2 catalyst is efficient for visible light absorption. Third, the band structure of black TiO_2 was evaluated (see band potential measurements in the ESI,†) and are shown in Fig. 1a. One can see that (a) $\text{H}_2\text{O}/\text{H}_2$ reduction potential is more positive than the TiO_2 conduction band (CB) edge and (b) the oxidation potential of CO_2/CH_4 and CO/CH_4 is more negative than the energy level of Ti^{3+} , which accounts for visible light absorption. This indicates that those energies meet the thermodynamic requirement for visible light PSRM over black TiO_2 . To confirm the feasibility of this catalyst system for PSRM, the Pt/black TiO_2 catalyst (15 mg) was prepared and dispersed on the light-diffuse-reflection-surface of a 4 cm^2 SiO_2 substrate. The obtained catalyst/substrate was loaded into a

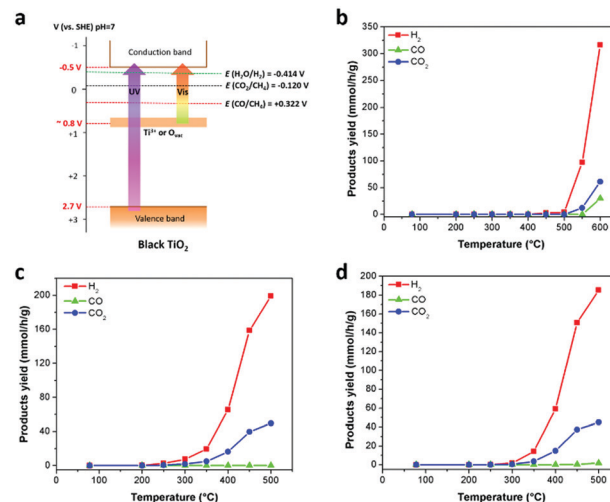


Fig. 1 Part I. Relationship between the band structure of black TiO_2 and redox potentials of methane steam reforming: (a) the absorption of UV generates the excitation of electrons from the valence band of TiO_2 to its conduction band, whereas the absorption of visible light is associated with excitation of electrons from the Ti^{3+} donor level to the TiO_2 conduction band. Part II. Product yields from steam reforming of methane ($\text{H}_2\text{O}/\text{CH}_4$ molar ratio 1:1 and GHSV = $80\,000 \text{ ml h}^{-1} \text{g}^{-1}$) over the Pt/Black TiO_2 catalyst dispersed on the light-diffuse-reflection-surface of a SiO_2 substrate: (b) without light irradiation; (c) under 1.5G sun light irradiation; and (d) under $\lambda > 420 \text{ nm}$ visible light irradiation.

quartz tube reactor located in an electrical furnace (Fig. S3 in the ESI,†). A water/ CH_4 mixture gas (GHSV = $80\,000 \text{ ml h}^{-1} \text{g}^{-1}$) flow was introduced into the reactor and heated to a selected temperature. All products were analyzed by Gas Chromatography (GC) and Mass Spectrometry (MS). The yields of products over the Pt/black TiO_2 catalyst without illumination are shown in Fig. 1b. The reaction hardly took place at 500°C or below. When the reaction temperature was increased to 550°C , the yield ($97 \text{ mmol h}^{-1} \text{g}^{-1}$) of H_2 (with CO and CO_2 formation) was obtained. This is a typical thermocatalytic SRM, which needs a high operating temperature. To avoid the thermocatalytic process, we select temperatures $\leq 500^\circ\text{C}$ for photocatalytic SRM. When the Pt/black TiO_2 catalyst was irradiated with simulated AM 1.5G sunlight, the reaction started at 200°C , which is 300°C lower than that without illumination. The H_2 yield increased with increasing temperature, leading to a high H_2 yield of $199 \text{ mmol h}^{-1} \text{g}^{-1}$ at 500°C . This impressive yield is about three orders of magnitude larger than the reported results at room temperature.²³ Furthermore, the product of CH_4 oxidation is CO_2 with negligible CO , leading to a molar ratio of 4 for H_2/CO_2 (Fig. 1c and d), which indicates the direct conversion of CH_4 and $2\text{H}_2\text{O}$ to 4H_2 and CO_2 (eqn (3)). This can be explained as follows: in the photocatalytic SRM, the potential driving force to overcome the barrier of methane oxidation is the difference between the oxidation potential level of methane and the potential level of Ti^{3+} . As shown in Fig. 1a, one can see that the driving forces are about 0.478 and 0.920 eV for CH_4 oxidation to CO and CO_2 , respectively. This suggests that the high selectivity for CO_2 formation with negligible CO is due to a larger driving force for CH_4 oxidation to CO_2 than to CO .

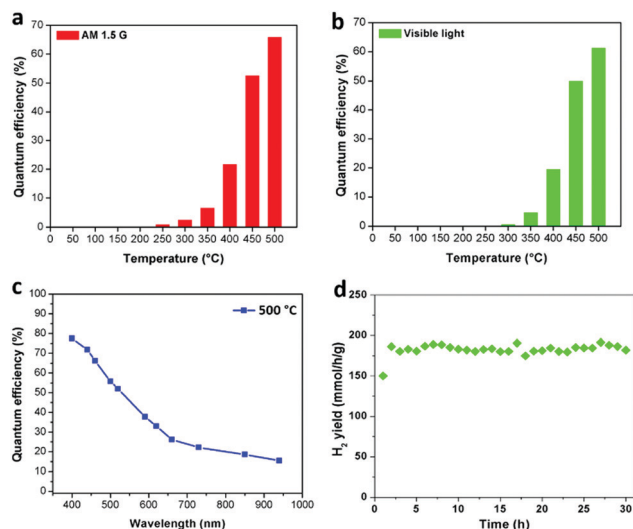


Fig. 2 Photocatalytic steam reforming of methane ($\text{H}_2\text{O}/\text{CH}_4$ molar ratio 1:1 and GHSV = $80\,000\text{ ml h}^{-1}\text{ g}^{-1}$) over the Pt/BlackTiO₂ catalyst dispersed on the light-diffuse-reflection-surface of a SiO₂ substrate: (a) quantum efficiency vs. reaction temperature under AM 1.5G illumination, (b) quantum efficiency vs. reaction temperature under $\lambda > 420\text{ nm}$ visible light illumination, (c) quantum efficiencies vs. wavelengths at 500 °C, and the (d) H₂ yield vs. reaction time under visible light ($\lambda > 420\text{ nm}$) illumination at 500 °C.

Therefore, an additional reactor for WGS may not be needed for the photocatalytic SRM process. In addition, as shown in Fig. 2a, one can see that the apparent quantum efficiency (QE) for the entire AM 1.5G sunlight increased with increasing temperature, achieving the maximum value of 65% at 500 °C.

It is important to ensure that the light-enhanced H₂ yield over Pt/blackTiO₂ is only due to a photocatalytic process instead of a light-caused temperature increase. A high performance thermal imager was employed to obtain thermal images of t/black TiO₂ dispersed on the SiO₂ substrate. As shown in Fig. S4 (ESI[†]), one can see that the temperature of the catalyst bed without light illumination is uniform with 0.7–5.9 °C difference between maximum and minimum temperatures at various furnace-setting-temperatures. Under AM 1.5G light illumination, the average temperature of the catalyst increased by only 4.7–8.1 °C. Furthermore, the catalyst temperature under light irradiation is also uniform just with 0.6–3.7 °C difference between maximum and minimum temperatures. This clearly demonstrated that the AM 1.5G light illumination did not create hot spots on the catalyst. Furthermore, although the increase in the catalyst temperature caused by AM 1.5G illumination was small (8.1 °C or less), the increased temperature was eliminated by reducing the electrical furnace heating. There was no difference in the H₂ yield with and without light illumination over Pt/Al₂O₃ that is not a photocatalyst due to the large band gap energy of Al₂O₃ (> 8 eV) (Fig. S5 in the ESI[†]). This clearly confirms that the light-enhanced H₂ yield over Pt/blackTiO₂ originates only from a photocatalytic process.

To evaluate the efficiency of visible light for the PSRM over the Pt/blackTiO₂ catalyst dispersed on the light-diffuse-reflection-surface of a SiO₂ substrate, UV light ($\lambda < 420\text{ nm}$) was completely

filtered from simulated AM 1.5G sunlight. Under visible light illumination, H₂ and CO₂ could be detected at a temperature as low as 250 °C (Fig. 1d). Furthermore, the H₂ yield increased with increasing temperature, reaching $185\text{ mmol h}^{-1}\text{ g}^{-1}$ at 500 °C. Impressive apparent QEs (49% at 450 °C and 60% at 500 °C) were obtained for the entire visible light range (Fig. 2b). The photocatalytic activity under visible light illumination was further confirmed by the relationship between QE and wavelength (Fig. 2c). Namely, the QE decreased monotonously with increasing wavelength for the entire visible light range (from 400 to 940 nm). The catalyst stability for the visible light PSRM was also evaluated. As shown in Fig. 2d, one can see that the hydrogen yield remained almost unchanged at 500 °C for 30 hours, indicating the excellent stability of the catalyst (Fig. 2d).

As discussed above, the remarkable effect of temperature on QE was observed for photocatalytic SRM, namely, QE increases with the increasing reaction temperature (Fig. 2a and b). It is well-known that increasing the temperature can shorten the lifetime of excited electrons due to a faster recombination between excited electrons and holes, which decreases QE. However, the increased temperature enhances kinetic energy of reactants, which can accelerate their oxidation to donate electrons to the holes of the photocatalyst and their reduction to accept excited electrons from the photocatalyst, leading to the increase in QE.¹⁸ In other words, the enhanced QE with increasing temperature indicates that the temperature effect is greater on redox reactions of reactants than on the electron-hole recombination in the photocatalytic SRM. This would be considered as a synergistic effect between potential energy and kinetic energy. The activation of a reactant must overcome an energy barrier. In the photocatalytic SRM, the potential driving force to overcome the barrier for activation of methane and water can be attributed to the differences between the redox potential levels of reactants (methane and water) and the potential levels of the photocatalyst. However, kinetic energy (associated with temperature) is also a driving force to activate reactants, which was widely demonstrated in thermocatalytic processes. Because most of the photocatalytic processes were carried out at ambient temperature, the effect of kinetic energy on the photocatalytic process may be ignored. When the photocatalytic SRM was performed at an elevated temperature, the kinetic energy became large enough to play a role in the activation of methane and water. Therefore, at an elevated temperature, there is a synergistic contribution of potential energy and kinetic energy to the photocatalytic SRM, leading to an excellent photocatalytic performance.

The structures of the Pt/BlackTiO₂ catalyst before and after photocatalytic SRM were characterized by various techniques. The electron paramagnetic resonance (EPR) measurements show a peak with a *g* value of 1.97–1.98 (Fig. S8a, ESI[†]), which is attributed to Ti³⁺ species.^{24,25} Furthermore, the EPR peak intensity increased after photocatalytic SRM, indicating that the Ti³⁺ species were not oxidized, which could contribute to the excellent stability of the catalyst (Fig. S8d, ESI[†]). XPS, which is a surface characterization technique, shows only Ti⁴⁺ peaks (without Ti³⁺) regardless of the reaction (Fig. S8b, ESI[†]), indicating no Ti³⁺ species in the surface layer. Therefore, the Ti³⁺ species are

located inside the catalyst, which would be protected by the Ti^{4+} surface layer. This could explain why Ti^{3+} is stable in the photocatalytic SRM even at 500 °C. The visible light absorption by Ti^{3+} species generated photo-electrons, which can diffuse from the inside to the surface of the catalyst to reduce reactants. The high stability of the catalyst was further supported by XRD, which shows an unchanged diffraction pattern of the catalyst after the reaction (Fig. S8c, ESI†). High resolution TEM was employed to evaluate the microstructure of the catalyst. As shown in Fig. S8d and e (ESI†), one can see that the TiO_2 particle sizes, which originally ranged from 25 to 50 nm, slightly increased after the reaction. The average crystal particle sizes of TiO_2 (calculated from XRD patterns), which are almost the same (28.6 and 27.5 nm, respectively) before and after the reaction, demonstrated the stable crystal structure of TiO_2 . The apparent particles (with sizes of about 25–50 nm) observed from TEM images would comprise 1–2 primary crystal particles (about 28 nm). The Pt particle sizes are about 2–5 nm regardless of the reaction, indicating its excellent stability. Furthermore, the high resolution TEM image revealed that the exposed surface of the single crystal Pt particle is a cubic (111) plane (Fig. S8f, ESI†). EPR, XPS, XRD, and TEM evaluations strongly support the excellent photocatalytic performance for SRM.

Temperature-dependence of the TiO_2 band gap was evaluated using a high temperature UV-Visible spectrometer. It was found that the band gap between the valence band (VB) and the conduction band (CB) slightly and linearly decreased with increasing temperature (Fig. S7 in the ESI†). Namely, when the temperature was changed by 345 °C (from 25 to 370 °C), only 0.109 eV decrease in the VB–CB energy gap (from 3.046 to 2.937 eV) was observed. Based on the obtained linear relationship between the band gap and temperature, the band gap of 2.908 eV was observed at 500 °C. This indicates that only 0.138 eV in the band gap was decreased by increasing the temperature from 25 to 500 °C. This small decrease in the VB–CB gap of TiO_2 was further supported by high temperature XRD measurements, in which the XRD pattern of TiO_2 remained unchanged with increasing temperature from room temperature to 500 °C. This indicates that interatomic spaces in TiO_2 remained almost unchanged with increasing temperature. It is well-known that the VB–CB bandgap of semiconductors tends to decrease with increasing temperature as interatomic spacing increases. Therefore, with increasing temperature from 25 to 500 °C, the unchanged interatomic spaces support a very little change of the band gap for TiO_2 .

In summary, a highly efficient visible-light photocatalytic steam reforming of methane (PSRM) was demonstrated with a Pt/black- TiO_2 catalyst dispersed on a light-diffuse-reflection-surface. Under visible light illumination by filtering UV light from AM 1.5G sunlight, the H_2 yield can reach 185 mmol h^{-1} g^{-1} , with a quantum efficiency of 60% at 500 °C (Fig. 2). The impressive yield is 3 orders of magnitude larger than the reported values.

Furthermore, the unique catalyst system can allow PSRM to achieve the direct conversion of CH_4 and $2\text{H}_2\text{O}$ to 4H_2 and CO_2 without an additional water-gas shift reaction. This indicates a bright future for hydrogen production from water and natural gas using solar energy.

Y. H. H. designed the process. B. H. synthesized catalysts and materials, tested their photocatalytic performance, and carried out some characterization. W. W. conducted the stability test. M. L. recorded UV-Visible spectra at elevated temperatures. K. S. carried out TEM and XPS characterization. All authors contributed to manuscript preparation. Y. H. H. wrote the manuscript.

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Conflicts of interest

There are no conflicts to declare.

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