

# Broadband Plasmonic Photocatalysis Enhanced by Photothermal Light Absorbers

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## ABSTRACT

Plasmonic photocatalysis is an emerging research field that holds promise for sustainable energy applications, particularly in solar energy conversion. In this study, we focus on the enhancement of broadband light absorption capabilities for plasmonic photocatalyst under white light illumination. By replacing parts of the catalyst with solar absorber, we can significantly improve the total reaction rate under mild heating conditions with less catalyst. Through careful comparison of reaction conditions and systematic optimization of the contributions from photothermal and non-thermal effects, we demonstrate a substantial enhancement in broadband light absorption capacity and overall light effectiveness, paving the way for advanced plasmonic photocatalysts with greater efficiency and practical applicability using solar light as the energy source.

## INTRODUCTION

With the rapid depletion of fossil fuels and the projected doubling of global energy demand by the mid-century, there is an urgent need for alternative energy sources.<sup>1</sup> In recent years, solar radiation has emerged as a promising and sustainable solution, offering a reliable substitute to traditional fossil fuels. Solar energy harnesses the vast and clean power of the sun, providing a renewable and environmentally friendly source of electricity generation.<sup>2</sup> The efficiency of converting solar radiation into usable heat critically depends on the absorptivity of a solar thermal collector, thus emphasizing the pivotal role of the solar absorber in the solar thermal systems. Since approximately 95% of solar radiation falls within the wavelength range of 0.3 to 2.0  $\mu\text{m}$ , spanning from UV to NIR, it becomes imperative for the material surface to exhibit optimal optical absorption in the visible and near-infrared (IR) spectral range. Some common used light absorbers are plasmonic nanoparticles ( $\text{Au}^{3-6}$ ,  $\text{Ag}^{7-9}$ ,  $\text{Pd}^{10, 11}$ ), semiconductors ( $\text{Cu}_{2-x}\text{S}^{12, 13}$ ,  $\text{Ti}_2\text{O}_3^{14, 15}$ ,  $\text{Fe}_3\text{O}_4^{16}$ ), carbon based materials<sup>17, 18</sup> and polymers<sup>19, 20</sup>. While these solar absorbers have found effective in water desalination and evaporation<sup>21-24</sup> and water splitting<sup>25, 26</sup>, their utilization in gas phase reactions, such as photocatalytic  $\text{CO}_2$  reduction, which is crucial for solar-to-fuel conversion and energy storage, remains less explored.<sup>27, 28</sup>

For traditional photocatalytic reaction, semiconductor such as  $\text{TiO}_2$  has shown to be a good support for gaseous reactions.<sup>29-31</sup> Limited by the poor absorption of photons under visible light and fast recombination rate between generated electron-hole pairs, semiconductors could overcome these disadvantages by adding the metal nanoparticles (NPs) as co-catalysts to improve the catalytic performance.<sup>32</sup> Plasmonic metal nanoparticles exhibit localized surface plasmon resonance (LSPR), generating high-energy electrons or holes upon resonance wavelength excitation. The chemical reactions of adsorbates, triggered by high-energy electrons or holes generated from the decay of LSPR, either through electron or vibrational excitation, represent widely accepted mechanisms in plasmon-induced photochemistry.<sup>33</sup> Experimental evidence has shown that hot

carriers (HC) can effectively lower activation barriers and facilitate molecular rearrangement.<sup>34, 35</sup> Given that the bandgap of TiO<sub>2</sub> is approximately 3.2 eV, requiring ultraviolet (UV) radiation with wavelengths shorter than 385 nm, photocatalysis with TiO<sub>2</sub> utilizes only less than 5% of the energy available in sunlight. By introducing plasmonic NPs, like Au<sup>32, 36</sup>, Ag<sup>37, 38</sup>, Cu<sup>39, 40</sup>, Al<sup>41, 42</sup>, and Rh NPs<sup>43, 44</sup> enhanced productivity, selectivity and absorption in the UV to visible range can be achieved. Rh/TiO<sub>2</sub> was used as plasmonic photocatalyst since it showed great production rate and high selectivity towards CH<sub>4</sub> under mild thermal conditions in CO<sub>2</sub> reduction reaction.<sup>43, 45, 46</sup>

Despite its promise, the research field of plasmonic catalysis remains encumbered by several challenges and ongoing debates.<sup>47</sup> One such ongoing debate build around the relative significance between photothermal and non-thermal effects. Distinguishing between these two effects in plasmonic catalysis is crucial for deciphering the underlying reaction mechanisms. Previous studies have indicated that certain reactions are primarily driven by photothermal effects<sup>48</sup>, while others depend more on non-thermal effects.<sup>49, 50</sup> However, only a handful of investigations have sought to exploit the synergistic relationship between these thermal and non-thermal influences.<sup>32, 51</sup> From a practical application perspective, the ultimate enhanced production rate and effective utilization of light are desired. However in current plasmonic photocatalysis, researchers are trying hard in quantitatively separate the thermal and non-thermal effects and trying to study the effects and mechanisms separately.<sup>34, 52, 53</sup> By studying the synergetic effects from photothermal and non-thermal contributions, a better way of light utilization can be achieved.<sup>30, 43, 44, 54</sup> Therefore, it is important to study how we could enhance the photothermal contribution to the reaction and the most effective way of combining them.

Furthermore, we have previously introduced a new index named as overall light effectiveness (OLE) to evaluate the combined photothermal and non-thermal effects. We reported that, using Rh/TiO<sub>2</sub> in CO<sub>2</sub> reduction, the highest OLE was achieved at 325 °C under 0.67 W·cm<sup>-2</sup> UV light (365 nm) irradiation. These results indicated that the highest light effectiveness can only be achieved by combing both photothermal and non-thermal effects. Therefore, in order to enhance the absorptivity of the catalyst under solar light and increase the contribution of photothermal effects towards higher OLE, here we propose an innovative method by mixing the plasmonic photocatalyst with the broad bandgap solar absorber to enhance the catalytic performance under milder heating conditions with white light illumination. One of the solar absorbers we studied is titanium nitride (TiN). TiN has previously shown to play a significant role in enhancing the solar absorptivity efficiency, and been used in multiple dielectric solar absorbers for solar energy harvesting.<sup>55-57</sup> The main conclusion is that by mixing the solar absorber with plasmonic photocatalysis, the total production rate and OLE increased under milder heating environment with an extended absorption spectrum under white light illumination compared to UV light. Consequently, it is possible to design plasmonic catalysts that can utilize the energy from the full spectrum of sunlight for efficient enhancement of important chemical reactions, overcoming the limitation of traditional photocatalysis.

## METHODS

**Material synthesis.** The catalyst synthesis process can be found in our previous publication.<sup>43</sup> In general, rhodium nanoparticles are prepared by a modified polyol method. Polyvinylpyrrolidone

(100 mg, PVP,  $M_w = 55,000$ , Aldrich) was dissolved in ethylene glycol (22.4 mL, EG, Fisher) in a 100 mL round bottom flask, and stirred in an oil bath with constant heating at 160 °C for 30 min. Rhodium (III) chloride hydrate (48 mg,  $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ , 40% Rh, Pressure Chemical) was first dissolved in 1.6 mL EG in a separate vial and quickly injected into the hot solution. The reaction mixture was kept stirring for another 30 min, and then cooled to room temperature. The brownish solution of Rh nanospheres was washed with 20 mL acetone three times to remove the spectator ions. The residue was mixed with 3 mL of deionized water and 30 mL ethanol under sonication till fully dissolved. The oxide support, titanium dioxide ( $\sim 380$  mg,  $\text{TiO}_2$ , Degussa, P25, specific surface area  $35\text{-}65 \text{ m}^2 \cdot \text{g}^{-1}$ ), was activated in air at 500 °C for 5 h before impregnation. The pre-heated  $\text{TiO}_2$  was added to nanoparticle solution and stirred vigorously overnight. The mixture was then dried on the hotplate till all the solvent evaporated. The remained solid was ground into a fine powder and calcined in air at 400 °C for 2h. The collected powder was stored in oven at 70 °C for further measurement.

Titanium nitride (TiN, 99.5%, metal basis, Thermo scientific) was used as received and mixed with Rh/ $\text{TiO}_2$  to reach 4:1 ratio by mass. The mixture was grounded in a mortar and pestle set for 30 minutes to get an even mixing. The powder was then collected and stored for measurements.

**CO<sub>2</sub> reduction and product analysis.** All data shown in this work is obtained using a system consisting of a gas delivery system, a fixed-bed reactor equipped with a quartz window, LED/laser light sources ((Prizmatix, UHP-F, 365 nm), an online mass spectrometer, and a multi-thermocouple setup with a programmable temperature controller. The catalysts are placed inside the Harrick reactor, and thermocouples (TCs) are used for temperature measurements. There is a total of 3 TCs that have been placed inside the reactor, and any one of the TC can be selected to maintain the set temperature and monitored by a PID temperature controller kit (Harrick, ATK-024-3). The surface TC (TC1) is the one that being placed nearest to the top surface of the catalyst layer. The collected temperature is expected to be the real surface temperature. The bottom TC (TC2) measures the temperature at the lower part of the catalyst. The heater TC (TC3) is placed right above the heating cable and is supposed to record the temperature from the cable heater. T3 is selected as the reference TC for controlling the PID output of the external heating, since it is buried deep inside the reactor and will endure the least amount of influences from light. Therefore, the external heating should be constant under the same set temperature. The other two TCs are connected with a handheld temperature data logger (Omega, RDXL6SD-USB) and used to record the real-time temperatures from two positions in the reaction chamber.

For each experiment, approximately 20 mg of the prepared Rh/ $\text{TiO}_2$  catalyst and 5 mg TiN was loaded in the reactor to fill a 6-mm diameter, 3-mm height catalyst cup (stainless steel, 500 mesh, 0.0010”) to ensure the complete absorption of light for the catalytic measurement. The Rh/ $\text{TiO}_2$ :TiN photocatalysts were first reduced under 60 standard cubic centimeters per minute (sccm)  $\text{H}_2$  and 40 sccm Ar at 350 °C for 2 h to remove any Rh oxidation, and then the gas flow was switched to a mixture of  $\text{CO}_2$ ,  $\text{H}_2$ , and Ar with the desired ratio and a total flow rate of 60 sccm. The gaseous product was monitored by an inline quadrupole mass spectrometer (Hiden, HPR-20) equipped with a Faraday cup and secondary electron multiplier (SEM) detector at  $m/z = 2$  ( $\text{H}_2$ ), 15 ( $\text{CH}_4$ ), 18 ( $\text{H}_2\text{O}$ ), 28 ( $\text{CO}$ ), 40 (Ar) and 44 ( $\text{CO}_2$ ) in real time with filament settings of

70 V and 250  $\mu$ A. The detection limit of the mass spectrometer was  $\sim 0.001\%$  conversion of  $\text{CO}_2$ . For each temperature and light intensity condition, at least 30 min elapsed before ten sequential measurements were made to ascertain the steady-state concentration of each gas and the associated reaction rates and uncertainties. All reactions were operated under atmospheric pressure. Mass spectrometer signals were calibrated using calibration gases (Gasco, Inc., 1 vol%  $\text{CH}_4/\text{Ar}$ ) over a range of flow rates and with argon gas as an internal standard. For example, the  $\text{CH}_4$  production rate was calculated according to Eq. (1).

$$R_{\text{CH}_4}(\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}) = \frac{\left(\text{flow} \frac{\text{CH}_4}{\text{Ar}} \text{ratio}\right) (f_{\text{Ar}}, \text{sccm})(10^6, \mu\text{mol} \cdot \text{mol}^{-1})}{(60, \text{s} \cdot \text{min}^{-1})(22,400, \text{mL} \cdot \text{mol}^{-1})(m_{\text{catalyst}}, \text{g})} \quad (1)$$

**Characterization.** Transmission electron microscopy (TEM) images were collected by an FEI Tecnai G2 Twin operating at 200 kV. The TEM samples were prepared by dispersing the Rh nanospheres and Rh photocatalysts in ethanol with sonication, then depositing on a copper grid coated with a carbon film (Ted Pella, 01813). Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) images were collected by a ThermoFisher Scientific Apreo 2 SEM. Diffuse reflectance UV–vis extinction spectra were obtained on an Agilent Cary 5000 equipped with an external diffuse reflectance accessory (DRA-2500). The composition of the photocatalysts was measured by a Kratos Analytical Axis Ultra X-ray photoelectron spectrometer (XPS).

## RESULTS AND DISCUSSION

The TEM characterizations of both Rh/TiO<sub>2</sub> and Rh/TiO<sub>2</sub>:TiN (4:1) is shown in Figure 1. As can be seen, after grinding TiN and Rh/TiO<sub>2</sub> for 30 min, they achieved an even mixture where large TiN particles are surrounded by Rh/TiO<sub>2</sub> (Figure 1b). The UV-Vis spectra of the studied materials show the enhanced absorption for Rh/TiO<sub>2</sub>:TiN within the visible light region compared to Rh/TiO<sub>2</sub> (Figure 1c). For TiO<sub>2</sub>, it shows the highest absorption peak under UV region, which is related to the band gap energy in the TiO<sub>2</sub> structure. Enhance absorption in the region of 400 – 800 nm, compared with pure P25 TiO<sub>2</sub> particles was observed with sample with Rh NP deposition. Rh NPs show a general size distribution around 5-6 nm (Figure S1, Supporting Information). Even though Rh NPs only generate LSPR effect under UV region, adding Rh NPs can still enhance the absorption under visible light (Figure S2a).<sup>58</sup> The inclusion of TiN further amplified the enhancement. Moreover, for comparison study, Rh/TiO<sub>2</sub>:TiO<sub>2</sub> (4:1) was prepared through the same method. The UV-Vis spectrum shows no enhancement with the addition of TiO<sub>2</sub> onto Rh/TiO<sub>2</sub> (Figure S2b). XPS was employed to confirm the mix of Rh/TiO<sub>2</sub> and TiN as well. Due to the small portion of TiN, the N 1s peak (397 eV) is too weak to be shown in the survey XPS spectra of Rh/TiO<sub>2</sub>:TiN (4:1) (Figure 1d). However, the Ti 2p XPS spectra indicate the existence of TiN (Figure 1e). There are two typical peaks at 456.0 and 457.7 eV, which represent the Ti-N bonds and the Ti-O bonds on the surface, respectively. Moreover, the XPS results showed that the Ti 2p remained unchanged and Rh 3d oxidize state reduced under H<sub>2</sub> reduction at 400 °C for 2 hours, indicating the primary role for H<sub>2</sub> reduction before experiment in removing the potential oxidized species on Rh NPs (Figure S3).

We then performed the catalytic studies using Rh/TiO<sub>2</sub> and Rh/TiO<sub>2</sub>:solar absorber for CO<sub>2</sub> reduction reaction. The reaction studied here was  $\text{CO}_2 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ . The selectivity towards CH<sub>4</sub> under 400 °C heating and 1.4 W·cm<sup>-2</sup> UV light illumination was nearly 100% with trace amount of CO signal increment detected under higher thermal condition (Figure S4).<sup>43</sup> In general, 5 mg of TiO<sub>2</sub> was put under 20 mg of catalyst to support the catalyst and maintain the same surface level (Figure 2a). The addition of TiO<sub>2</sub> played a crucial role in maintaining the same distance between light source and catalyst surface to control the light effects. Several thermal couples were placed inside the reactor to record and control the temperature profile (Figure S5). The total production rate of methane was studied, and we conducted a screening of potential solar absorber combinations, like TiN, Ti<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, CoWO<sub>4</sub>, (Figure 2b) and with different ratios (1:1, 3:2, 4:1) (Figure 2c). The results showed that the addition of TiN as solar absorber in 4:1 ratio by mass can greatly enhance the photocatalytic performance of Rh/TiO<sub>2</sub> under 100 °C external heating with white light illumination.

Since Rh NP can only be LSPR excited under UV light, the catalyst would not generate non-thermal effect under white light.<sup>58</sup> Contrary to the addition of TiO<sub>2</sub>, which can absorb UV light, replacing 20 % amount of Rh/TiO<sub>2</sub> into TiN would not decrease the production rate under light illumination, but increase the production rate by a factor of 1.26 due to the enhanced visible light absorption and increased photothermal contribution (Figure 3a). The result showed that the measured surface temperature by TC1 increased from 196 to 216 °C with addition of TiN under 100 °C heating and 1.9 W·cm<sup>-2</sup> white light illumination (Figure 3b). Similar increment in production rate was observed when the external heating increased to 325 °C under low light intensities (Figure 3c). As the light intensity increased from 0.7 to 1.9 W·cm<sup>-2</sup>, the increment in total production rate dropped from 10% to nearly zero. With 0 W·cm<sup>-2</sup> light intensity, there was no light effect, and all the catalyst would undergo dark thermal heating mechanism. The results showed that both Rh/TiO<sub>2</sub>:TiN (4:1) and Rh/TiO<sub>2</sub>:TiO<sub>2</sub> (4:1), both containing 16 mg of catalyst, generated about 80% amount of product compared to 20 mg pure catalyst under dark condition. However, with the increase in light intensity, the photothermal effect from TiN leads to the increased production rates from 0.5 – 1.5 W·cm<sup>-2</sup> compared to the pure catalyst. These three catalysts ultimately reached to a similar production rate beyond 1.5 W·cm<sup>-2</sup>, where the photothermal contribution approached to a limit, and the total production rates would not increase further with the changes in light intensity and surface temperature (Figure 3d). This trend indicated that as the external heating increased from 100 to 325 °C and light intensity from 0 to 1.9 W·cm<sup>-2</sup>, the photothermal effect from the top of catalyst layer would contribute less to the total production rate, while the external thermal effect from the bottom dark catalyst contributed more. To eliminate the interference from solar absorbers towards the catalytic performance of the catalyst mixture, we performed the studies with TiN only. The results showed that TiN exhibits minimum photocatalytic and thermocatalytic performances under white light compared to Rh/TiO<sub>2</sub> (Figure S6a). Therefore, we were able to show that by replacing part of the catalyst as solar absorber, fewer amount of catalyst were used to achieve a better production rate due to the extra generated photothermal effects from the addition of solar absorbers.

After showing the enhancement in total production rate in a simpler system with only photothermal effect, we then performed the study to see how the extra photothermal effect could influence the plasmonic photocatalysis when performing the same reaction under UV light. The wavelength dependence study on TiN showed little difference between white light and UV under 325 °C (Figure S6b). Moreover, the studies on the catalytic performance of TiO<sub>2</sub> showed that under dark condition, TiO<sub>2</sub> as a porous material can help the methane production. The introduction of UV light did not influence the behavior, indicating the poor TiO<sub>2</sub> photocatalytic performance (Figure S7). Therefore, the catalytic effects from TiN and TiO<sub>2</sub> in Rh/TiO<sub>2</sub>:TiN (4:1) could still be ignored.

Based on the performances of Rh/TiO<sub>2</sub>, which is a well-studied UV-active plasmonic catalyst<sup>43</sup>, the methane production was higher under UV than white with similar light intensities due to the existence of non-thermal effects generated from LSPR of Rh NP for 100 °C (Figure 4a). Additionally, the same reaction performed using Rh/TiO<sub>2</sub>:TiN (4:1) showed a reverse trend, where the production rate was higher under white light (0.59  $\mu\text{mol}\cdot\text{s}^{-1}$ ) than UV (0.35  $\mu\text{mol}\cdot\text{s}^{-1}$ ) for 70 % with 100 °C heating and 1.4  $\text{W}\cdot\text{cm}^{-2}$  light illumination, where the photothermal effect from TiN was dominant. We could then cross compared the catalytic behaviors between these two catalysts under same wavelength. Under 1.4  $\text{W}\cdot\text{cm}^{-2}$  UV light, the production rate was 0.31  $\mu\text{mol}\cdot\text{s}^{-1}$  for Rh/TiO<sub>2</sub> and 0.34  $\mu\text{mol}\cdot\text{s}^{-1}$  for Rh/TiO<sub>2</sub>:TiN (4:1). Under 1.5  $\text{W}\cdot\text{cm}^{-2}$  white light, the production rate was 0.31  $\mu\text{mol}\cdot\text{s}^{-1}$  for Rh/TiO<sub>2</sub> and 0.59  $\mu\text{mol}\cdot\text{s}^{-1}$  for Rh/TiO<sub>2</sub>:TiN (4:1). The increases in production rate were 11% under UV light and 92% under white light with relatively similar light intensity, where the increases in surface temperature were the same after adding the solar absorber (Figure 4b). Similar trend could be seen from Rh/TiO<sub>2</sub> under 325 °C with an enhancement on production rate between UV and white between 0.5 – 1  $\text{W}\cdot\text{cm}^{-2}$  due to the non-thermal effect (Figure 4c). However, the rate enhancement due to replacement was lower and nearly indistinguishable between UV and white light, when we increased the external heating to 325 °C, regardless the similar surface temperature increment by solar absorber (Figure 4d).

Under a mild heating condition, like 100 °C, the replacement of catalyst to TiN would increase of photothermal effects but sacrificing the surface non-thermal contribution from Rh/TiO<sub>2</sub> under UV light. Clearly, the results illustrated that replacing the surface catalyst with solar absorber would bring more positive effects to the total production rate and showed the importance of heat effects in a photocatalytic reaction. As we keep increasing the external heating to 325 °C, the reaction would ultimately reach to a steady stage, where thermal heating outcompetes the effects of photothermal heating, and the non-thermal effect was also suppressed due to the elevated temperature. The temperature dependence studies on plasmonic NPs for their absorption efficiency showed that as temperature increases from 100 to 700 K, the corresponding absorption efficiency and electric field enhancement decrease.<sup>59</sup> Since the absorption efficiency is directly related to the polarizability of NPs, the enhanced thermal oscillation can degrade polarizability. Moreover, the increased light intensity would linearly increase the generation of hot electron and the interaction between electron to substrate. But it would quadratically increase the rate of electron hole pair recombination. As a result, the reaction rate would increase linearly as light intensity in the low-intensity region, but it would reach a plateau under high light intensity, since the recombination rate is faster than electron transferring within NP or towards the substrate.<sup>60-62</sup> To eliminate the

mass-transfer limit hypothesis, we performed the calculation for reaction quotient. The equilibrium constant of CO<sub>2</sub> methanation decreases when increasing the temperature and is around 1808 (mol/L)<sup>-2</sup> at 400°C.<sup>63</sup> The highest reaction quotient observed for our system increased with temperature increase and reached its maximum value of 361 (mol/L)<sup>-2</sup> at 400°C under 1.41 W·cm<sup>-2</sup> (Figure S8a), which is much lower than the literature value. Thus, the reaction is far away from equilibrium under our reaction conditions discussed. Figure S7b shows the conversion of CO<sub>2</sub> and H<sub>2</sub>, the H<sub>2</sub> is the limiting agent.

After studying the performance of replacing Rh/TiO<sub>2</sub> to TiN to achieve a higher surface temperature and better production rate under UV and white light. We then want to qualitatively compare the enhanced light effects and their light effectiveness. We previously propose a new index named as overall light effectiveness (OLE), defined as the amount of additional products produced under direct illumination (compare to dark conditions) per second per unit power of light, regardless of catalyst mass (Eq. 2).

$$\text{Overall light effectiveness } (\mu\text{mol}\cdot\text{s}^{-1}/\text{W}\cdot\text{cm}^{-2}) = \frac{\text{Total production rate enhanced by light } (\mu\text{mol}\cdot\text{s}^{-1})}{\text{Light intensity } (\text{W}\cdot\text{cm}^{-2})} \quad (2)$$

OLE is different from apparent quantum efficiency (AQE), where AQE only consider the amount of product generated over the number of photon being absorbed under specific wavelength. However, AQE itself is not sufficient to describe the overall enhancement from light in such a complicated process where both photothermal and non-thermal effects exist and it is difficult to show the photothermal effect using quantum efficiency. Based on the calculations, there are an increased light effectiveness under both UV and white light under 100 °C, and the highest OLE enhancement exist around 1.5 W·cm<sup>-2</sup>, and become smaller as light intensity increases (Figure 5a). As we increased the external heating effects to 325°C, 20 mg Rh/TiO<sub>2</sub> achieved an OLE around 0.83 μmol·s<sup>-1</sup>/W·cm<sup>-2</sup> under UV light at 0.67 W·cm<sup>-2</sup> (Figure 5b). The result is consistence with our previous study. However, Rh/TiO<sub>2</sub>:TiN (4:1) shows a better performance under both UV and white light, since there are only 80% of catalyst and generate less product under dark thermal conditions. These results indicate the enhanced photothermal contribution and the importance of the non-thermal effect since the highest OLE is obtained under UV light. Moreover, the enhanced OLE illustrates a more efficient way of catalyst design in combing the photothermal and non-thermal effects together to achieve a better light utilization as well as product generation.

For the broadband solar absorber TiN, it would undergo single light to heat mechanism. When the energy of the incident light is larger than the band gap of the semiconductor, the electrons in the valence band (VB) of the semiconductor are excited to the conduction band (CB) by photons, and the corresponding holes are generated in the VB. The generated electron would eventually return to the lower energy states and release energy in the form of radiative relaxation, emitting photons, or non-radiative relaxation in the form of phonons (heat) by transferring energy to surroundings. When energy is released in the form of phonons, it causes localized heating of the lattice, establishing a temperature distribution that depends on the optical absorption and volume/surface recombination characteristics. The photothermal effect is a consequence of this temperature distribution resulting from the diffusion of optically excited carriers throughout the material and their recombination.<sup>64</sup> Even though, some reports indicate that TiN exhibits a

plasmonic effect under visible light range.<sup>56, 65-67</sup> The TiN we used has an averaged particle size of 200-400 nm. As the NP size increases, the plasmon-coupled peak undergoes red-shift and peak broadening, leading to a weaker LSPR effect.<sup>68-70</sup> The control experiments show little enhancement for our TiN under white light for photocatalysis. (Fig. S3b). By the same time, the plasmonic photocatalyst Rh/TiO<sub>2</sub> undergo photothermal, hot-electron or non-thermal and external heating effects. Our previous studies quantitatively separate the non-thermal and photothermal effects through different methods.<sup>43</sup> For plasmonic nanoparticles, it will undergo LSPR and lead to the generation of hot electrons. The coherent oscillation can be damped by coupling to phonons, resulting in highly efficient photothermal heating at the nanoparticle surface and in its direct surroundings. The environment will subsequently be heated up due to the photoinduced temperature gradient.<sup>71</sup> When Rh/TiO<sub>2</sub> and TiN mixed together, the photothermal effect from TiN would assist and heat up the surrounding even further to achieve a better light absorptivity and overall light enhancement.

## CONCLUSION

Overall, this work proposes a new idea in catalysis preparation, by mixing plasmonic photocatalyst with broadband solar absorbers. Our results showed that under milder heating conditions and light illumination, replacing part of the catalyst with solar absorber would not decrease the total production rate, but instead enhance the performance as well as the overall light effectiveness. Thus, highest OLE could always be achieved when we consider enhancing the light absorptivity of catalyst and utilize both photothermal and non-thermal effects. Further research should try other nanocomposites when designing the catalyst and study the performance under solar light illumination where more light can be absorbed.

## ASSOCIATED CONTENT

### Supporting Information Description

The supporting information includes size distribution and TEM image of Rh NPs; UV-vis spectra of Rh NP, TiO<sub>2</sub>, Rh/TiO<sub>2</sub>, Rh/TiO<sub>2</sub>:TiO<sub>2</sub> (4:1), and emission spectra of UV and White light; XPS studies; selectivity study; reactor setup illustration; thermocatalysis and photocatalysis study for Rh/TiO<sub>2</sub>, TiO<sub>2</sub> and TiN; equilibrium study.



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### **Notes**

The authors declare no competing financial interest.

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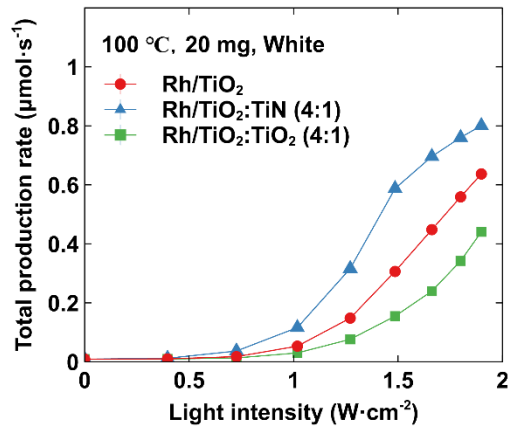
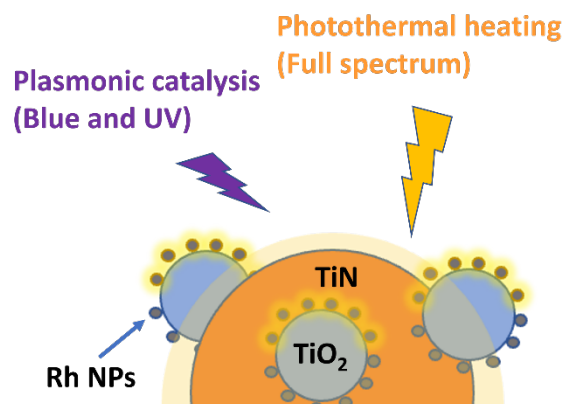
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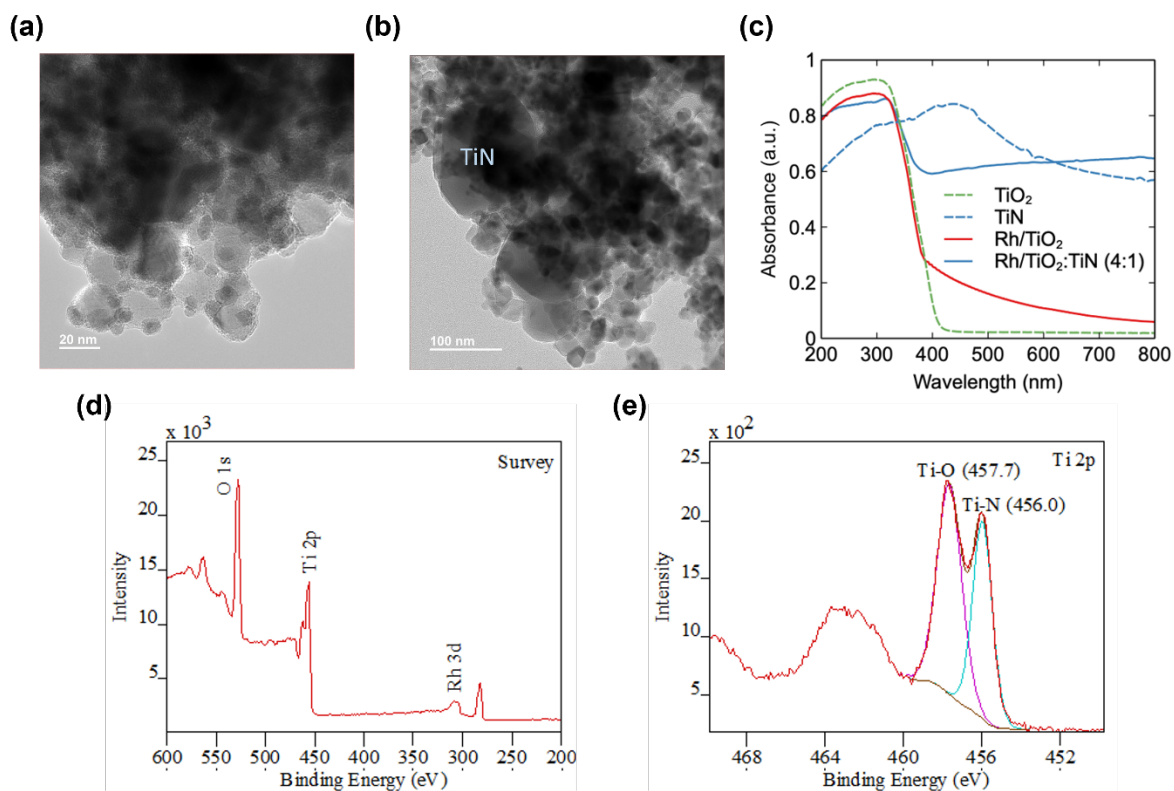
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## TOC Graphic

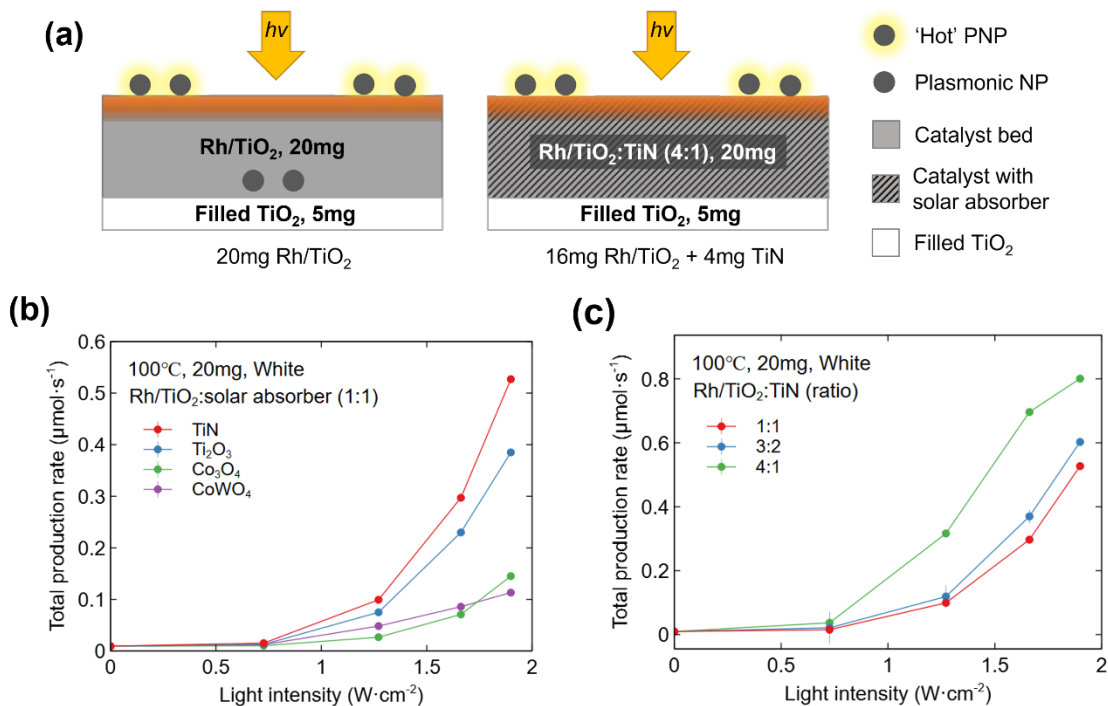


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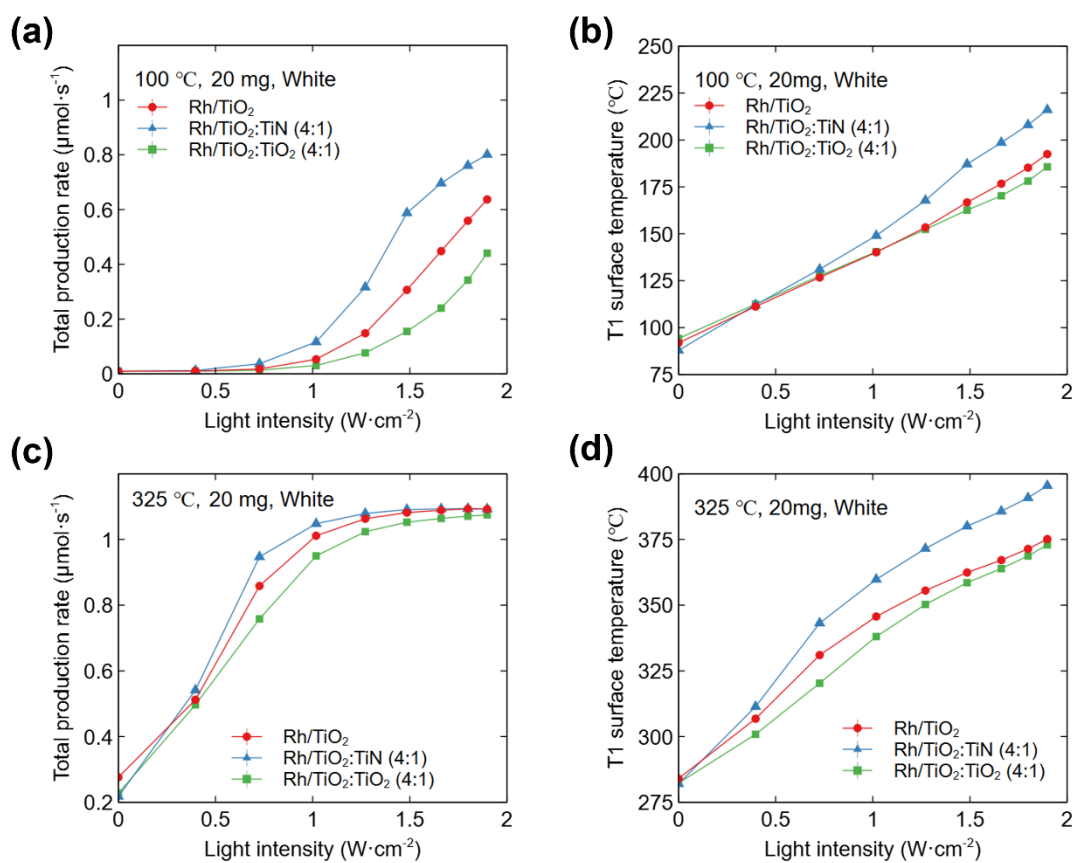


**Figure 1.** TEM characterization of (a) Rh/TiO<sub>2</sub>, scale bar at 20 nm and (b) Rh/TiO<sub>2</sub>:TiN (4:1), scale bar at 100nm. (c) UV-vis absorption spectra for TiO<sub>2</sub> (green dash line), TiN (blue dash line), Rh/TiO<sub>2</sub> (red solid line), and Rh/TiO<sub>2</sub>:TiN (4:1) (blue solid line). XPS spectra of Rh/TiO<sub>2</sub>:TiN (4:1). (d) Survey spectra; (e) high-resolution Ti 2p spectra.

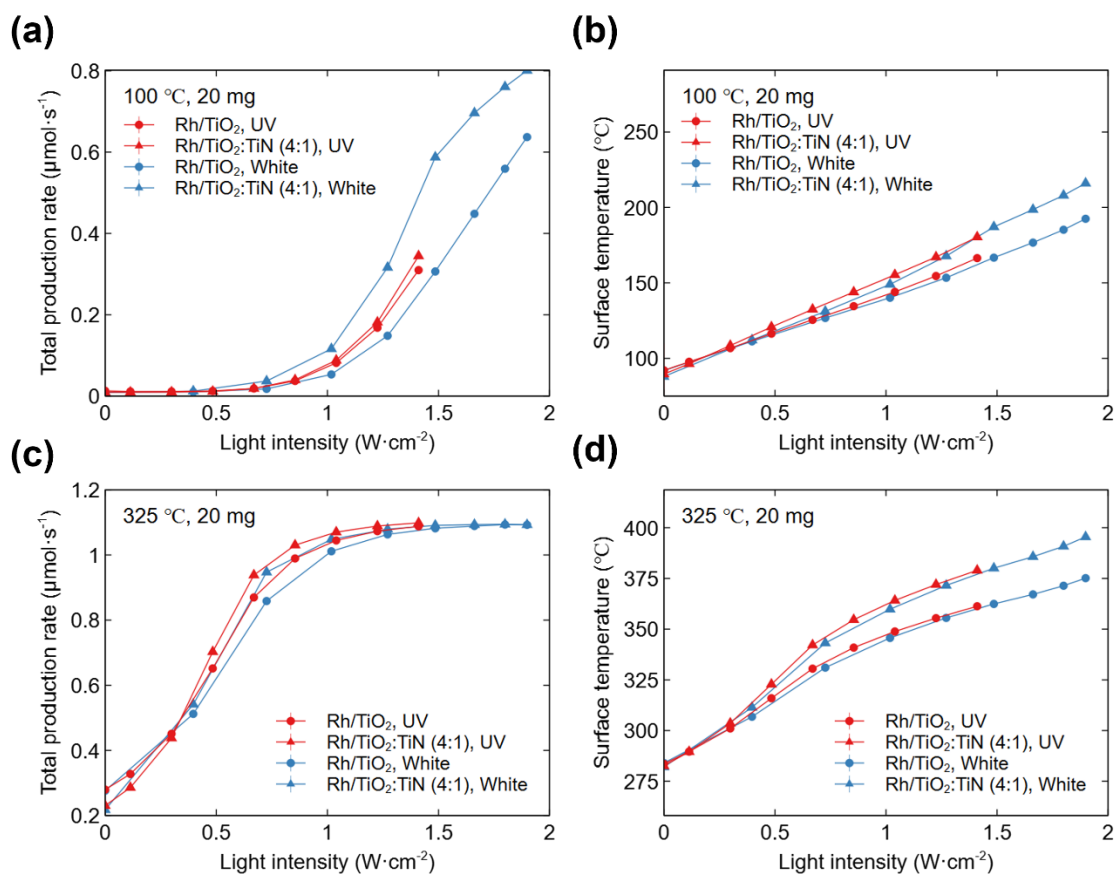




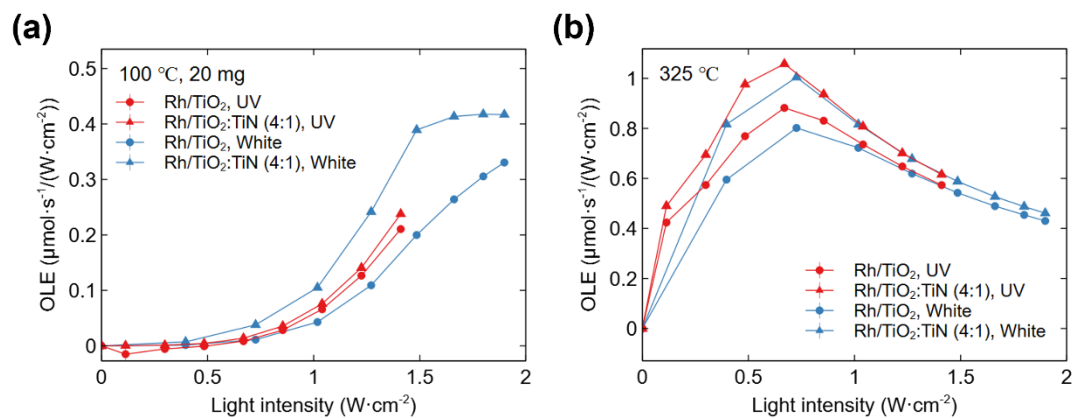
**Figure 2.** (a) Catalyst bed setup illustrations for both 20 mg Rh/TiO<sub>2</sub> and Rh/TiO<sub>2</sub>:TiN (4:1) with filled 5 mg TiO<sub>2</sub> at the bottom. Study the catalytic performance of catalyst mixed with (b) different solar absorbers with 1:1 ratio by mass; (c) TiN at different ratio by mass under 100 °C heating with white light.



**Figure 3.** The total production rate and measured surface temperature as a relationship with light intensity for 20 mg of Rh/TiO<sub>2</sub> (red circle), Rh/TiO<sub>2</sub>:TiN (4:1, blue triangle), and Rh/TiO<sub>2</sub>:TiO<sub>2</sub> (4:1, green square) at (a, b) 100 °C, and (c, d) 325 °C under white light illumination.



**Figure 4.** The total production rate, and measured surface temperature as a relationship with light intensity for 20 mg of Rh/TiO<sub>2</sub> (circle), Rh/TiO<sub>2</sub>:TiN (4:1, triangle) at (a, b) 100 °C, and (c, d) 325 °C as a comparison between UV (red) and white light (blue).



**Figure 5.** Calculated overall light effectiveness as a relationship with light intensity for 20 mg of Rh/TiO<sub>2</sub> (circle), Rh/TiO<sub>2</sub>:TiN (4:1, triangle) at (a) 100 °C, and (b) 325 °C as a comparison between UV (red) and white light (blue).