Efficient visible-light driven photo-thermal conversion of CO$_2$ to methane by nickel nanoparticles supported on barium titanate

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Abstract

Solar-driven methanation represents a potentially cost-efficient and environmentally friendly route for the direct hydrogenation of CO$_2$. Recently, photo-thermal catalysis, which involves the combination of both photochemical and thermochemical pathways, has emerged as a promising strategy for the production of solar fuels. For a photo-thermal catalyst to efficiently convert CO$_2$ under illumination, in the absence of external heating, effective light harvesting, an excellent photo-thermal conversion and efficient active sites are required. Here, we report a new composite catalyst consisting of Ni nanoparticles supported on barium titanate (BTO) that, under optimal reaction conditions, is able to hydrogenate CO$_2$ to CH$_4$ at nearly 100% selectivity with production rates as high as 103.7 mmol g$^{-1}$ h$^{-1}$ under both UV-visible and visible irradiation (production rate: 40.3 mmol g$^{-1}$ h$^{-1}$). Mechanistic studies suggest that reaction mostly proceeds through a non-thermal hot-electron-driven pathway, with a smaller thermal contribution.

1. Introduction
Global energy demand has increased over the last few decades and recent forecasts estimate increases of up to 30% by 2040.\textsuperscript{[1]} The massive consumption of fossil fuels in order to meet this energy demand has led to an alarming level of atmospheric carbon dioxide (CO\textsubscript{2}), the main responsible for global warming. In this spirit, the recycling of CO\textsubscript{2} in the production of renewable fuels by solar energy offers a very attractive mitigation pathway. A possible approach for the solar fuel production from CO\textsubscript{2} requires an active photocatalyst that can enable the photoexcitation of electrons to high-energy states. Traditionally, these photocatalysts are based on wide band gap inorganic semiconductors.\textsuperscript{[2]} However, the efficiency of photocatalytic CO\textsubscript{2} conversion using H\textsubscript{2}O or H\textsubscript{2} remains very low (in the range of µmol g\textsuperscript{-1} h\textsuperscript{-1}) due mainly to the fast charge-carrier recombination, the limited ability to activate CO\textsubscript{2} molecules and the low absorption and utilization of the solar spectrum of traditional semiconductors.\textsuperscript{[3]}

Recently, photo-thermal catalysis, which involves the combination of both photochemical and thermochemical pathways, has emerged as a promising strategy for the production of solar fuels and chemicals.\textsuperscript{[4]} Upon light irradiation of metal nanoparticles (NPs), the photo-thermal effect can trigger a series of processes including the generation of so-called “hot electrons” (electrons with energy above the Fermi level) and/or the local temperature rise of the NPs due to electron-lattice collisions. These processes can eventually activate adsorbed species and lead to an outstanding enhancement of the catalytic activity.\textsuperscript{[5]} An additional advantage of the photo-thermal strategy is its effective harvesting of the solar spectrum, including the absorption of visible and infrared light that would be insufficient to promote pure photochemical reactions. In 2014, Ye and collaborators demonstrated the application of this photo-thermal effect for the efficient conversion of CO\textsubscript{2} to CH\textsubscript{4} using Group VIII metals. \textsuperscript{[6]} More recently, Ozin et al. reported the use of RuO\textsubscript{2} and Pd NPs supported on silicon and Nb\textsubscript{2}O\textsubscript{5} semiconductors, respectively, for the photo-thermal CO\textsubscript{2} reduction achieving production rates in the order of mmol g\textsubscript{metal}^{-1} h\textsuperscript{-1}.\textsuperscript{[7]} Following this approach, and for the sake of sustainability, it would be interesting to develop new efficient photo-thermal systems based on abundant, non-critical
first-row transition metals. In this regard, Ni would be an obvious candidate given its availability, low-cost and high methanation activity.\[^8\]

In the last years, the use of perovskite oxides in photocatalytic CO\(_2\) reduction has demonstrated a great potential but in most of the cases the production rates are still too low for practical solar-to-fuel applications.\[^3d,9\] Barium titanate (BTO) is one of the archetypical titanate perovskite oxides with cubic structure (ABO\(_3\)) and it has attracted extensive attention due to its ability to split water into H\(_2\) and O\(_2\).\[^10\] However, as far as we know, up to now there is no precedent in the literature using BTO-based photocatalytic systems to promote CO\(_2\) conversion, particularly photo-thermal CO\(_2\) reduction with H\(_2\).

In the present work, we demonstrate that composite materials consisting of Ni nanoparticles supported on BTO are highly efficient photocatalysts to promote the complete photo-thermal methanation of CO\(_2\) without any external heating. Catalytic data indicate an excellent photo-thermal performance under visible-IR radiation and suggest a reaction mechanism dominated by a non-thermal hot-electron-driven process.

2. Results and Discussion

Ni-BTO samples were prepared by wet impregnation of commercial BTO with different amounts of Ni(NO\(_3\))\(_6\)-6H\(_2\)O, followed by calcination in air at 300 °C and a final reduction step under H\(_2)/Ar\) flow at 500 °C (see the Experimental Section for further details). The X-ray diffraction patterns (XRD) of the as-prepared Ni(5)-BTO sample (Figure 1a) show the characteristic diffraction peaks and confirmed the presence of Ni metal and BTO. As shown in Figure 1b, the Ni-BTO sample displays an excellent light absorption over a broad range that covers the UV, visible and near infrared regions of the spectrum. This intense absorption suggests an efficient light harvesting and it is a characteristic feature of nanoparticles of group VIII metals.\[^11\]
Figure 1. A) XRD patterns of Ni metal (blue line), BTO (black line) and Ni(5)-BTO photocatalyst (red line). B) UV-visible spectra of BTO (black line) and Ni(5)-BTO (red line).

The presence of Ni nanoparticles was observed by scanning transmission electron microscopy (STEM). Images acquired in high-angle annular dark-field (HAADF) STEM and the corresponding elemental mapping obtained from energy dispersive X-ray (EDX) analysis confirmed that the larger particles (30-70 nm) are mainly composed of Ba and Ti, corresponding to BTO, while the smaller NPs (9.5 ± 3.8 nm, see Figure S1 for particle size distribution) correspond to metallic Ni (Figure 2). The analysis of the full scanned X-ray Photoelectron Spectroscopy (XPS) spectrum for the photocatalyst revealed the presence of Ni, Ba, Ti and O (Figure S2, Supporting Information). As shown in Figure S2c, the Ni 2p spectrum presented two main peaks centered at 855.6 and 873.0 eV, together with one satellite peak located at 861.2 eV, all attributable to Ni(OH)$_2$. The spin-energy separation of 17.6 eV between the two main peaks is also characteristic of the Ni(OH)$_2$ phase. Furthermore, the Ni 2p$_{3/2}$ also showed a minor contribution of metallic Ni located at 852.1 eV. Therefore, in addition to metallic Ni as the predominant phase characterized by XRD, XPS showed the presence of Ni(OH)$_2$. To conciliate both observations, it should be mentioned that while XRD probes the whole sample, XPS only provides information of the outermost nanometers of the metal nanoparticle that are more susceptible to undergo spontaneous oxidation upon exposure to the ambient. Additional
STEM images with elemental mapping confirmed the presence of this thin layer of oxygen covering Ni NPs corresponding to the Ni(OH)$_2$ phase observed in XPS (Figure S3, Supporting Information).

Figure 2. A) HAADF-STEM image of Ni(5)-BTO photocatalyst acquired in dark field. B) Elemental analysis for the individual elements of Ni(5)-BTO photocatalyst by EDS.

The solar-driven methanation activity of the Ni-BTO samples was evaluated under UV-visible irradiation from a Xe lamp (5 bar, H$_2$/CO$_2$ = 4/1) without any external heating and the temperature and pressure inside the photoreactor were monitored (Figure 3). The corresponding CO$_2$ conversion values and photocatalytic rates are summarized in Table 1. Both temperature and pressure variation showed a similar trend when increasing the amount of Ni: temperature increased as a result of radiative heating, the photo-thermal effect of Ni NPs and the exothermicity of the reaction, while pressure decreased due to the consumption of reactants ($\delta = -2$). As expected, the rise in the number of catalytic sites and nano-heater centers created upon increasing the Ni loading led to a remarkably enhanced photocatalytic rate. Besides the CH$_4$ detected in the gas phase, small droplets of water condensed in the reactor body when the light was off and temperature decreased. The presence of water gives further evidence of the methanation reaction. Since the Ni(5)-BTO sample represented a good balance between
photocatalytic activity and Ni loading, subsequent experiments were preferentially performed with this sample unless otherwise indicated.

Figure 3. Temperature (black lines) and pressure (red lines) profile of Ni(1)-BTO (squares), Ni(5)-BTO (circles), Ni(10)-BTO (triangles) and Ni(20)-BTO (diamonds) under photo-thermal CO$_2$ conversion. Reaction conditions: 50 mg photocatalyst, 5 bar (H$_2$/CO$_2$ = 4) and 293 mW cm$^{-2}$ light intensity.

A control experiment under dark conditions and 250 °C resulted in a 75 % CO$_2$ conversion after 20 min of reaction, compared to the complete conversion (>95 %) achieved under light irradiation. In agreement with previous reports, these results confirmed a higher efficiency under illumination than under conventional heating. This improvement is explained by the effective utilization of light to both photochemically and thermally stimulate the catalytic active sites.$^{[7a]}$ Additional blank experiments under dark conditions at temperatures in the range between 100-160 °C displayed lower conversion values and slower reaction kinetics than under illumination (Figure S4, Supporting Information). In order to extract the possible light contribution to the temperature increase of the system, a blank experiment monitoring the temperature of irradiated BTO, where reaction does not take place, was carried out (Figure S5,
As it can be observed, light radiation caused an increase of the temperature up to 216 °C, which was almost 160 °C lower than in the presence of Ni(10)-BTO. Besides, in order to prove the photo-thermal effect derived from Ni NPs an additional control experiment using Ni(10)-BTO under He atmosphere was performed (Figure S5, Supporting Information). This experiment showed an increment of the temperature of the catalyst bed up to 270 °C upon irradiation, thus demonstrating the efficient light-to-heat conversion of Ni NPs. Overall, these results evidenced that the temperature increase was not only related to light radiation, but also to the contribution of both the photo-thermal effect displayed by supported Ni NPs and the exothermicity of the reaction.

Traditional photocatalytic systems for CO\textsubscript{2} conversion based on wide band gap semiconductors with appropriate band energy levels are strongly dependent on UV irradiation.\textsuperscript{[2a-c]} In contrast to these systems, the photo-thermal CO\textsubscript{2} conversion over Ni-BTO could operate under visible and infrared irradiation given its broad absorption of light in these regions. Thus, in the absence of UV light, complete photo-thermal CO\textsubscript{2} conversion was still observed within 20 min of reaction (Figure S6, Supporting Information). Compared to UV-visible-IR irradiation, in which a value of 103.7 mmol g\textsuperscript{-1} h\textsuperscript{-1} was obtained, CH\textsubscript{4} production rate under visible-infrared radiation was as high as 40.3 mmol g\textsuperscript{-1} h\textsuperscript{-1}, confirming the large potential of the here presented Ni-BTO catalysts in solar-induced CO\textsubscript{2} conversion. Of great importance from the reaction mechanism point of view, this wavelength dependence on the photocatalytic reaction rate also suggests an electron-driven reaction pathway. Under UV radiation, electron-hole pair generation takes place in the BTO semiconductor, thus leading to the enhancement of the photocatalytic activity thanks to the effective charge separation at the Ni-BTO interface, as discussed below.

In order to elucidate the role of the different catalyst components, additional control experiments on bare BTO (no Ni present) and Ni supported on other substrates, both semiconductors (TiO\textsubscript{2}) and insulators (Al\textsubscript{2}O\textsubscript{3}) were performed. Results are summarized in Table 1. While the bare BTO did not result in any CO\textsubscript{2} conversion, Ni supported in TiO\textsubscript{2} and
Al₂O₃ catalysts showed a much lower activity than that found when combining Ni and BTO (see Table 1 and Figure S7). These results demonstrate the synergy between the BTO support and Ni nanoparticles.

In order to gain insight into the photo-thermal performance and to distinguish between photochemical and thermal contributions, Ozin and collaborators recently defined a temperature-dependent dimensionless photo-thermal figure of merit, PTF (Equation 1):

$$PTF(T) = \eta_{CT}(T^* \alpha \frac{\kappa_{int}(T^*) T^*}{\kappa_{cat}(T^*) T})$$  \hspace{1cm} (1)

where $\alpha$ is the solar absorptance, $\eta_{CT}(T^*)$ is the photochemical charge transfer efficiency at temperature $T^*$, $\kappa_{int}$ is the thermal conductivity of the nanoheater, $\kappa_{cat}$ is the thermal conductivity of the substrate, $T^*$ is the local temperature, and $T$ is the measured temperature of the photocatalyst.\(^{14}\)

Both TiO₂ and BTO showed a similar solar absorptance, however, TiO₂ presented a higher thermal conductivity (8.5 W m⁻¹ K⁻¹) than BTO (1.3-6.0 W m⁻¹ K⁻¹) and this could justify the higher efficiency of BTO as a support for the photo-thermal CO₂ reduction reaction.\(^{15}\)

Furthermore, regarding the photochemical charge transfer efficiency of both supports ($\eta_{CT}$), band gap and XPS valence band measurements of both semiconductors (see Figure S8 and Table S1 in Supporting Information) showed that BTO presented a 0.52 eV more reductive conduction band than TiO₂, as previously reported.\(^{16}\) This higher-energy conduction band would be responsible of a better $\eta_{CT}$ in BTO, thus explaining the improved photo-thermal performance of this support compared to TiO₂. Recent reports in the literature have already suggested that differences in photocatalytic activity among semiconductors are mainly attributed to their conduction band levels.\(^{3e,17}\) Our results are very much in line with the work of Ye and co-workers in which they observed a remarkable enhancement of CO₂ photo-thermal
conversion with Ni NPs supported on TiO$_2$ compared with a homologous photocatalyst based on Al$_2$O$_3$.\[^{[6]}\] We hypothesize that both low solar absorptance and photochemical charge transfer efficiency of Al$_2$O$_3$ together with its high thermal conductivity (30.0 W m$^{-1}$ K$^{-1}$) could justify the poor catalytic activity of Ni-Al$_2$O$_3$ under reaction conditions.\[^{[18]}\]

Overall, the enhanced CH$_4$ production observed for Ni-BTO photocatalysts with respect to Ni-TiO$_2$ and Ni-Al$_2$O$_3$ could be explained by a combination of factors including the low thermal conductivity of BTO that maximizes the formation of hot spots at the Ni active sites, the photoactive semiconducting properties of BTO and TiO$_2$ and the higher $\eta_{CT}$ of BTO with respect to TiO$_2$.

Studying the influence of light intensity on the photocatalytic rate can be a powerful analytic tool to understand reaction mechanisms in photo-thermally driven processes. If a reaction is considered to be catalyzed by a photo-thermal process, it will have an exponential relationship between the reaction rate and light intensity.\[^{[17]}\] On the contrary, a linear relationship is considered a characteristic feature of a non-thermal hot-electron-driven process.\[^{[18]}\] In order to assess which of the pathways is predominant in our system, the intensity of light was varied in the range from 193 mW cm$^{-2}$ to 293 mW cm$^{-2}$ and the CH$_4$ production rate together with CO$_2$ conversion were monitored. As depicted in Figure S9, there was a positive linear relationship between light intensity and the photocatalytic rate. Ni nanoparticles supported on BTO displayed a maximum CH$_4$ production rate of 93.9 mmol g$^{-1}$ h$^{-1}$ and 38 % CO$_2$ conversion after 10 min of irradiation at 293 mW cm$^{-2}$. Under light intensity of 235 and 193 mW cm$^{-2}$ the CH$_4$ production rate decreased to 46.3 and 7.6 mmol g$^{-1}$ h$^{-1}$, respectively. Mechanistically, these results demonstrate the existence of a non-thermal hot-electron-driven CO$_2$ reduction pathway.

Hot electrons may transfer out of the metallic NPs and occupy unpopulated orbitals of adsorbed species like CO$_2$ or H$_2$, thus leading to the breaking of molecular bonds and to CO$_2$ reduction on the nanoparticle surface.\[^{[19]}\] García and Corma suggested recently a similar reaction mechanism involving hydrogen activation via the formation of Ni-H species for the CO$_2$
photocatalytic reduction using commercial Ni/SiO₂-Al₂O₃. In spite of this, the co-existence of a photo-thermal contribution to the reaction mechanism in our system cannot be completely dismissed, as electron-lattice collisions can eventually produce heat in the metal nanoparticle and influence the catalytic activity in a similar way to the conventional thermal catalysis. This thermal contribution is not trivial and would partially justify the better catalytic performance of BTO as a support of Ni NPs compared to TiO₂ or Al₂O₃, according to the difference in their thermal conductivities.

In order to provide further evidence of the generation of photoinduced charge transfer and to find out the role of Ni NPs at Ni-BTO interface, we performed femtosecond transient absorption (fs-TA) spectroscopy (see Supporting Information for the details of the experimental setup) and compared the charge carrier recombination dynamics of BTO with and without Ni in acetonitrile (ACN). Before digging in depth into the charge transfer dynamics, it is important to explore the ground state properties of the NPs. As shown in Figure S10a, the normalized steady-state absorption spectra of BTO and Ni-BTO indicated that Ni NPs elevated the light absorption of the BTO by absorbing the light in entire visible region. The fs-TA spectra in response to 350-nm optical excitation of BTO and Ni-BTO in ACN are depicted in Figures S9b and , respectively. The fs-TA spectra of Ni-BTO showed a broad negative absorption (ground state bleach, GSB) in 450 to 700 nm spectral region, which is consistent with the steady-state spectrum. On the other hand, BTO showed a broad positive absorption (photoinduced absorption, PIA) due to the excited state absorption of the photoexcited electrons. The charge-recombination dynamics at 550 nm are compared between BTO and Ni-BTO in Figure S10d. It is important to note that owing to strong PIA of BTO, the ground state blech was not prominent, however, a narrow bleach band at early time delay below 525 nm was observed (Figure S11). Interestingly, the charge recombination dynamics is much slower for Ni-BTO ($t_1 = 156\pm10$ ps, 75%; $t_2 > 5$ ns, 25%) compared with bare BTO ($t_1 = 117\pm8$ ps, 52%; $t_2 = 3.1\pm0.1$ ns, 48%). These results provide another piece of evidence for an efficient charge
separation at the Ni-BTO interface, which implies the enhancement of the photocatalytic activity.

Altogether, the experimental data here presented suggest that the CO$_2$ photo-methanation by Ni-BTO is driven predominantly by a non-thermal hot-electron reaction pathway, with an additional minor thermal contribution. If the thermal contribution ruled the reaction mechanism, then it would be easy to explain the considerable differences of catalytic performance between Al$_2$O$_3$ and the other semiconductors, according to its high thermal conductivity that minimizes hot spots in Ni active sites. However, in this case it would be difficult to rationalize the disparity in the observed photocatalytic activities of TiO$_2$ and BTO, as their thermal conductivities do not enoughly differ to explain some orders of magnitude difference between the catalytic performance of both semiconductors. On the contrary, a non-thermal hot-electron-driven mechanism with smaller thermal contribution would better reconcile these findings.

It is worth commenting that the Ni(5)-BTO photocatalyst reported a maximum CH$_4$ production rate of 103.7 mmol g$^{-1}$ h$^{-1}$ referred to the total photocatalyst mass and a complete CO$_2$ conversion after 15 min of reaction under 293 mW cm$^{-2}$ light intensity. A previous work by Ye and collaborators observed that Ni-Al$_2$O$_3$ (4.9 wt%) achieved a photo-thermal CO$_2$ methanation rate of 25.0 mmol g$^{-1}$ h$^{-1}$ after 10 min of irradiation.[6] Furthermore, García and co-workers reported complete photocatalytic reduction of CO$_2$ to CH$_4$ with 65 % loading of Ni supported on high surface silica-alumina (Ni/SiO$_2$-Al$_2$O$_3$) at a rate of 56.2 mmol g$^{-1}$ h$^{-1}$ after 15 min of reaction. [20a] Compared with our results, it seems that BTO is a more efficient support for Ni nanoparticles in the photo-thermal reduction of CO$_2$, probably due to its higher photochemical charge transfer efficiency and low thermal conductivity. As far as we know, the presented Ni-BTO photocatalyst appears to be among the most active materials described so far for the photo-thermal CO$_2$ conversion (Table S2, Supporting Information).

The stability and reusability of the Ni-BTO photocatalyst were evaluated by performing a series of consecutive experiments with the same Ni-BTO sample. The results in terms of CO$_2$
conversion are shown in Figure S12. As it can be seen, the photocatalyst underwent a progressive deactivation upon reuses and after the second use, its activity decreased to 47 and 23 % of CO₂ conversion in the third and fourth use, respectively. At this point, the photocatalyst was *ex-situ* re-activated under H₂/Ar flow for 2 h at 500 °C and this treatment re-established the photocatalytic activity for at least three more consecutive catalytic cycles. In order to completely integrate light into the process, we also explored a different approach to restore the photocatalytic activity of the catalyst. Thus, instead of a thermal re-activation at 500 °C conducted in an external furnace, a photo-thermal re-activation of the catalyst with H₂ and light was performed after each catalytic cycle in the same reactor used for the photocatalytic studies (see the Experimental Section for further details). As shown in Figure 4, this treatment allowed completing five consecutive photo-thermal cycles of CO₂ reduction without any apparent deactivation.

**Figure 4.** CO₂ conversion (black lines) and pressure (red lines) profile of Ni(5)-BTO photocatalyst upon consecutive catalytic cycles. After each catalytic cycle, photocatalyst was
activated photo-thermally with H₂ for 2 h. Reaction conditions: 50 mg photocatalyst, 5 bar (H₂/CO₂ = 4) and 293 mW cm⁻² light intensity.

The gradual deactivation observed after several catalytic cycles does not seem to be related to an increase in the particle size of Ni NPs, as demonstrated by HRTEM analysis of the spent (after four reaction cycles) catalyst (Figure S13), but it is more likely due to surface oxidation of Ni. In order to demonstrate this hypothesis, the XPS analysis of the used Ni-BTO sample was performed (Figure S14 in Supporting Information). Compared with the fresh sample, the two main peaks in Ni 2p spectrum centered at 855.5 and 873.0 eV that belong to Ni(OH)₂ are more intense. Furthermore, in the O 1s spectrum of the used sample the component at 531 eV related to Ni(OH)₂ was also identified. This partial oxidation of the Ni active sites could be related to the presence of water in the reaction environment as a byproduct of the CO₂ methanation. Ultimately, water could adsorb on the active sites and inhibit further methanation reaction as it has been previously reported. ⁷a, 21 In view of these results, the active species for CO₂ photothermal methanation should be metallic Ni. However, in order to have a better understanding of the active phase in our photocatalyst, we also performed near-ambient pressure (NAP) XPS measurements under reaction conditions (H₂/CO₂ = 4, 250 °C) (Figure S15). As it can be seen, the Ni metal peak is considerably higher under reaction conditions compared to the fresh and spent sample, suggesting that metallic Ni is the active phase towards CO₂ methanation and that the oxidation state is a key factor that determines the catalytic performance of Ni NPs. Indeed, a control experiment using Ni(10)-BTO catalyst omitting the H₂/Ar reduction step led to a negligible catalytic activity (less than 2% conversion) after 20 min of reaction.

Although there is still no consensus regarding the mechanism of CO₂ methanation, the formation of CO as intermediate and its subsequent hydrogenation have been proposed as the most plausible rate-determining step. ²² Figure S16a shows the CO and CH₄ selectivities as a function of CO₂ conversion using Ni-BTO as photocatalyst. As per this figure, at low CO₂
conversions, the selectivity towards CO was almost 30 %. However, as the CO$_2$ conversion increased, the CO selectivity dropped below 1 %. These results suggest that the rate-determining step for CH$_4$ formation is the reverse water gas shift reaction in which CO$_2$ is converted to CO. It should be mentioned, however, that another key factor that determines the exact reaction pathway and product selectivity is the nature of support. Therefore, we compared product selectivities for the photo-thermal methanation of CO$_2$ using Ni NPs supported on different substrates (Figure S16b). Interestingly, we found that both TiO$_2$ and Al$_2$O$_3$ supports led to a product distribution dominated by CO. However, when Ni NPs were supported on BTO, the main product was CH$_4$ even under comparable CO$_2$ conversion values. Altogether, these results clearly indicate that the interface between Ni NPs and the substrate plays a crucial role not only in terms of catalytic activity, but also in terms of product distribution and reaction mechanism.

3. Conclusions

In summary, we have prepared a highly efficient photocatalyst for the complete photo-thermal conversion of CO$_2$ based on Ni NPs supported on barium titanate perovskite. The remarkable catalytic activity derives from a combination of factors that include an effective utilization of light and an excellent photo-thermal performance due to the optical, electronic and thermal properties of the photocatalyst. Mechanistic studies indicate that a non-thermal hot-electron-driven pathway dominates reactivity in co-existence with a minor thermal contribution to the photo-thermal process. Future work should focus on exploring new cost-efficient photo-thermal catalysts that could promote the conversion of CO$_2$ into other useful chemicals. Furthermore, we believe photo-thermal catalysis should be explored under continuous flow conditions in order to further explore the application potential of this exciting field of research.
Acknowledgements

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Conflict of interest

Authors declare no conflict of interest.

References


[22] W. Wei, G. Jinlong, Frontiers of Chemical Science and Engineering 2011, 5, 2-10
Table 1. Ni content, CO$_2$ conversion and photocatalytic rate of the different photocatalysts.\textsuperscript{a)}

<table>
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<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Ni loading [wt%]</th>
<th>CO$_2$ conversion [%]</th>
<th>CH$_4$ production [mmol g$^{-1}$ h$^{-1}$]</th>
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\textsuperscript{a)} Reaction conditions: no external heating, 5 bar, H$_2$/CO$_2$ = 4, photocatalyst mass: 50 mg, irradiation time: 10 min, 300 W Xe lamp at 293 mW cm$^{-2}$. \textsuperscript{b)} Blank experiment, bare BaTiO$_3$ under above conditions. \textsuperscript{c)} Reaction conditions: no external heating, 5 bar, H$_2$/CO$_2$ = 4, photocatalyst mass: 50 mg, irradiation time: 20 min, 300 W Xe lamp at 293 mW cm$^{-2}$. Note that in these experiments, CO was the main product.
The present manuscript reports the complete photo-thermal CO₂ conversion to methane using a new composite catalyst based on Ni nanoparticles supported on barium titanate (BTO). Under optimal conditions, the photocatalyst displays an outstanding CH₄ production rate of 103.7 mmol g⁻¹ h⁻¹ derived from its excellent photo-thermal performance and light harvesting properties.

**Photo-thermal catalysis**

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![Diagram of photo-thermal catalysis](ToC figure)