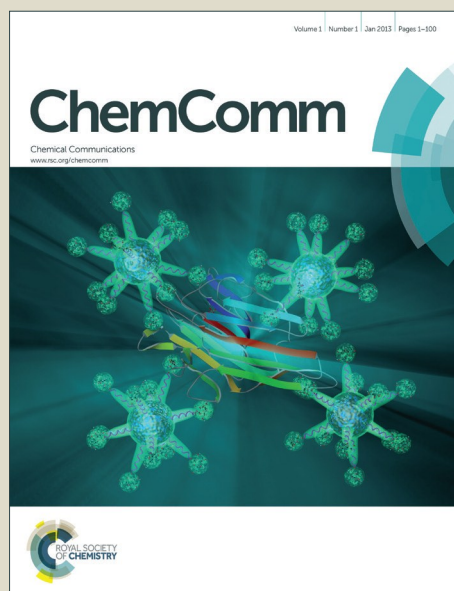


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## COMMUNICATION

# Highly efficient and stable photocatalytic reduction of CO<sub>2</sub> to CH<sub>4</sub> over Ru loaded NaTaO<sub>3</sub>

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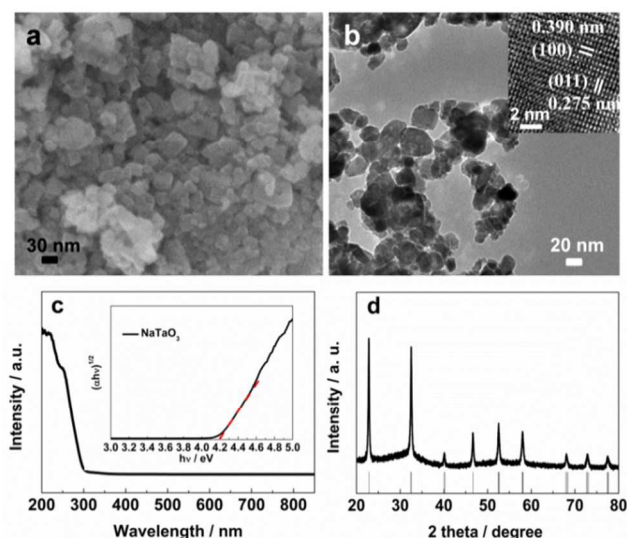
**An efficient and stable photocatalytic activity was obtained over NaTaO<sub>3</sub> by introducing electron donor (H<sub>2</sub>) into the CO<sub>2</sub> reduction process with water. Ru/NaTaO<sub>3</sub> demonstrated the best activity (CH<sub>4</sub> 51.8 μmol h<sup>-1</sup> g<sup>-1</sup>) and product selectivity in converting CO<sub>2</sub> to CH<sub>4</sub>.**

Ever since the profound Honda-Fujishima effect has been discovered by the early 1970s, semiconductor photocatalysis has received much attention as a potential solution to the worldwide energy shortage due to its promising ability in directly converting solar energy into chemical fuels.<sup>1,2</sup> In particular, photoreduction of CO<sub>2</sub> appears to be a highly fascinating process in lessening the requirement of fossil fuels and climate accommodation by atmospheric CO<sub>2</sub> balance. Generally, CO<sub>2</sub> reduction is a chain reaction with the product varying from CO (2e<sup>-</sup>) to CH<sub>4</sub> (8e<sup>-</sup>). Although the reduction potential of CH<sub>4</sub>/CO<sub>2</sub> is about -0.24 V (vs. NHE at pH=7) which seems to be an attainable level to many semiconductors, CO<sub>2</sub> reduction has to go through a tough uphill process and its intermediates' redox potentials are much more negative (E<sup>0</sup>CO<sub>2</sub>/CO = -0.61 V vs. NHE at pH=7).<sup>3</sup> Thus, to date, only a limited number of materials, such as ZnGa<sub>2</sub>O<sub>4</sub>,<sup>4</sup> Zn<sub>2</sub>GeO<sub>4</sub>,<sup>5-7</sup> NaNbO<sub>3</sub>,<sup>8-10</sup> TiO<sub>2</sub>,<sup>11-13</sup> etc., have exhibited photocatalytic activities in CO<sub>2</sub> reduction with various reducing outcomes. In the point view of products, CH<sub>4</sub> is more preferable when considering the high importance as a potential solar fuel.<sup>14</sup> But consequently, it enforces that the semiconductors must possess a negative enough conduction band (CB) to provide enough energy of the photogenerated electrons to overcome the activation barrier and fulfill the 8e<sup>-</sup> reaction during the CO<sub>2</sub> reduction process.<sup>11</sup> NaTaO<sub>3</sub>, which is one of the best pure water splitting photocatalysts reported by Kudo et al.,<sup>15-17</sup> possesses a significantly negative CB and analogous band gap to the above-mentioned semiconductors, likewise, should also bear a gigantic potential in CO<sub>2</sub> reduction, although there are few reports about it.

In previous researches, water was generally employed in reducing CO<sub>2</sub> as an active hydrogen source. However, although it is believed that CO<sub>2</sub> could react with H<sub>2</sub>O to simultaneously produce CH<sub>4</sub> and O<sub>2</sub>

through two respective half reactions with photogenerated electrons and holes in an ideal process,<sup>5</sup> O<sub>2</sub> could hardly be detected over most of the oxide semiconductors. It is usually accompanied by a decay of reactivity of CO<sub>2</sub> reduction reaction, since some peroxide intermediates could form and accumulate at the oxide semiconductor surface during the oxygen photoevolution reaction from water.<sup>18</sup> These peroxides would hinder the holes to oxidize the water and increase the recombination of the photogenerated electrons and holes, and consequently suppress the release of O<sub>2</sub>. The unstable production rate has significantly limited the development and the practical application of CO<sub>2</sub> photoreduction. On the other hand, in the point view of reduction reaction, metal cocatalysts are commonly considered effective and broadly used in facilitating photocatalytic activities of semiconductors by (i) promoting the charge separation, (ii) improving the photostability, and (iii) lowering the activation energy of the catalytic reaction.<sup>19,20</sup> A recently attempt by Kang et al showed that the photocatalytic activity and stability can be significantly enhanced by replacing water with N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O as electron donor.<sup>21</sup> H<sub>2</sub> gas has also been confirmed that it can effectively facilitate the CO<sub>2</sub> reaction with water.<sup>22-23</sup> It opens a promising strategy to promote the photocatalytic efficiency and stability by using electron donor<sup>21</sup>.

In this study, an electron donor (H<sub>2</sub> gas) was introduced to the reaction system to verify the peroxide intermediates mechanism during the water oxidation reaction and to enhance the activity as well as the stability of the CO<sub>2</sub> reduction. The effect of different metal cocatalysts for CO<sub>2</sub> photoreduction was studied with and without the electron donor, respectively. Among various metal cocatalysts loaded NaTaO<sub>3</sub> samples, Ru/NaTaO<sub>3</sub> (CH<sub>4</sub> 51.8 μmol h<sup>-1</sup> g<sup>-1</sup>) and Pt/NaTaO<sub>3</sub> (CO 139.1 μmol h<sup>-1</sup> g<sup>-1</sup>) exhibited the best products selectivity in the presence of the electron donor. Moreover, Ru/NaTaO<sub>3</sub> showed a linear growth of CH<sub>4</sub> evolution over 24 hours and demonstrated an efficient and stable photocatalytic activity in converting CO<sub>2</sub> to CH<sub>4</sub>. The key point of the performance over Ru/NaTaO<sub>3</sub> is owing to using H<sub>2</sub> as electron donor and distributing Ru as co-catalysts.

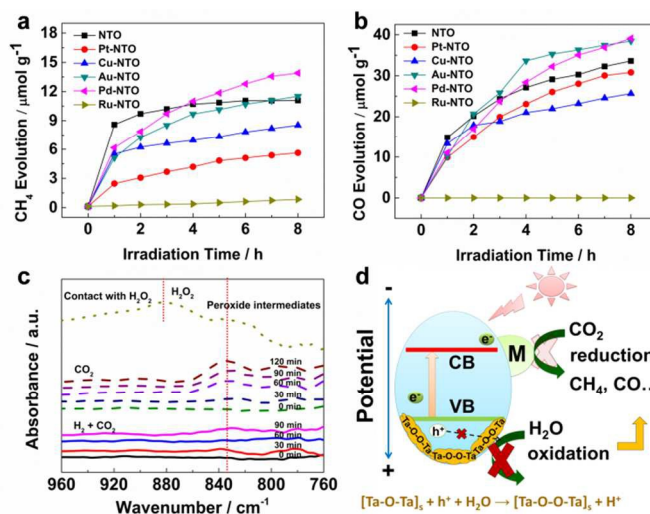


**Fig. 1** (a) SEM image of NaTaO<sub>3</sub> sample; (b) TEM image of NaTaO<sub>3</sub> sample, the insert shows HRTEM image; (c) UV-vis absorption spectrum of NaTaO<sub>3</sub> sample and the inset is the corresponding  $(\alpha h\nu)^{1/2}$ – $h\nu$  curve; (d) XRD pattern of NaTaO<sub>3</sub> sample.

The NaTaO<sub>3</sub> (NTO) samples were synthesized through a furfural alcohol derived polymerization–oxidation (FAPO) process.<sup>8,9</sup> The detailed characteristics were examined by X-ray diffraction (XRD), ultraviolet-visible (UV-vis) spectroscopy, scanning electron microscope (SEM) and transmission electron microscopy (TEM). The XRD pattern (Fig. 1d) and its corresponding HRTEM (insert in Fig. 1b) show that the NaTaO<sub>3</sub> prepared through the FAPO route crystallized in a monoclinic system with the space group of *P2<sub>1</sub>/m*, which could be well indexed to the JCPDS database card (JCPDS-01-074-2477). According to the SEM and TEM images (Fig. 1a and 1b), the sample mainly contains particles about 20 ~ 30 nm. UV-visible absorption spectrum of the NaTaO<sub>3</sub> nanoparticles is shown in Fig. 1c, with an intense absorption with steep edge in the UV region. The band gap ( $E_g$ ) of NaTaO<sub>3</sub> was determined to be 4.2 eV according to the following equation  $(\alpha h\nu)^{1/2} = A(h\nu - E_g)$  and shown in the inset of Fig. 1c, in which  $\alpha$ ,  $\nu$ ,  $A$ , and  $E_g$  are the absorption coefficient, light frequency, proportionality constant and band gap, respectively.

The photocatalytic properties of the as-prepared NaTaO<sub>3</sub> were estimated by photoreduction of gaseous phase CO<sub>2</sub> under the irradiation of a 300 W UV-enhanced Xe lamp. Fig. 2a and Fig. 2b exhibit the results of CO<sub>2</sub> reduction over the series of NaTaO<sub>3</sub> only using water as the reducing agent. All the samples showed certain abilities, where CH<sub>4</sub> and CO presented to be the two main carbon products as well as some trace amount of other hydrocarbon compounds (Fig. S11) with CO appears more dominant. The total productivities were listed in Table S2. Metal cocatalysts mainly benefited H<sub>2</sub> evolution in this reaction condition (CO<sub>2</sub>+H<sub>2</sub>O), because H<sub>2</sub> evolution is a highly preferred competing reaction. The CO<sub>2</sub> reduction reactions exhibited not linear growth of the products evolution. The bent curves indicate an unstable reactivity of CO<sub>2</sub> reduction reaction for all the samples. Moreover, O<sub>2</sub> could also not be detected as the product of water oxidation. Thus, an obstructive O<sub>2</sub> release process should be the main reason for the above phenomena. It has been reported that some peroxide intermediates would be

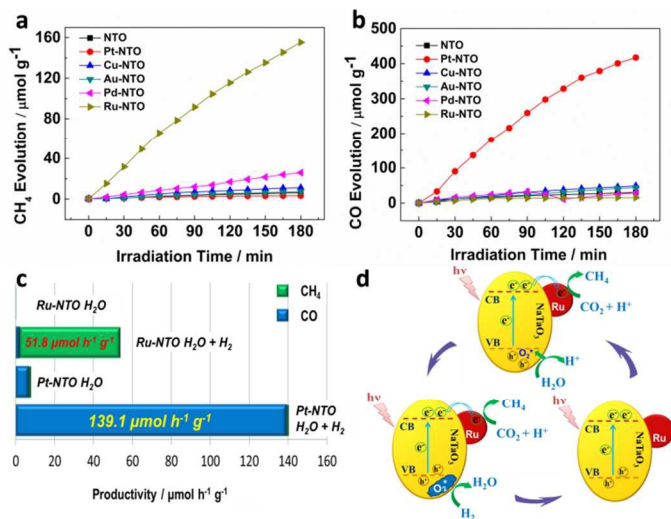
formed at the oxide semiconductor surface during the oxygen photoevolution reaction from water.<sup>18</sup> As shown in Fig. 2c, the intermediates are proved to be generated by the in situ FTIR spectra. By referring the method reported in the literature,<sup>18</sup> NaTaO<sub>3</sub> film was exposed to a 30% H<sub>2</sub>O<sub>2</sub> aqueous solution to position the peak of peroxide intermediates (dot line), the peaks at 834 cm<sup>-1</sup> and 883 cm<sup>-1</sup> belong to the peroxide intermediates and H<sub>2</sub>O<sub>2</sub>, respectively. During the CO<sub>2</sub> reduction process, the peroxide intermediates formed and accumulated with the time when only using water as the reducing agent (dash line). As the schematic model shown in Fig. 2d, the peroxide intermediates hindered the photogenerated holes to oxidize water. Consequently, the recombination of electrons and holes increased, and so that reflects on a decreased photocatalytic activity.



**Fig. 2** Gaseous product generation over 0.5 wt% co-catalysts loaded NaTaO<sub>3</sub> in H<sub>2</sub>O and CO<sub>2</sub> atmosphere: (a) CH<sub>4</sub>, (b) CO; (c) In situ FTIR spectra of NaTaO<sub>3</sub> during the CO<sub>2</sub> reduction process; (d) Schematic model of the formation and accumulation of peroxides at the surface of NaTaO<sub>3</sub>.

In order to eliminate the hamper of peroxide intermediates and realize a stable reduction of CO<sub>2</sub>, an electron donor (H<sub>2</sub> gas) was introduced to the reaction system to release the peroxides. Fig. 3a and 3b show the results of CO<sub>2</sub> reduction over the series of NaTaO<sub>3</sub> in the presence of H<sub>2</sub>O, CO<sub>2</sub> and H<sub>2</sub>. All the samples exhibit promotions of the catalytic activity compared with the counterparts only using H<sub>2</sub>O and CO<sub>2</sub> as shown in Table S2. Almost linear curves indicate that enhanced stabilities and activities of the CO<sub>2</sub> reduction are obtained over the catalysts, especially for Ru/ NaTaO<sub>3</sub> (Fig. S4a). As the solid lines in Fig. 2c shown, there is almost no accumulation of the peroxides in the presence of electron donor H<sub>2</sub>. It can be concluded that the peroxide intermediates are effectively reduced by H<sub>2</sub> and so that a stable reduction of CO<sub>2</sub> are observed. An isotope experiment within a D<sub>2</sub>O, CO<sub>2</sub> and H<sub>2</sub> atmosphere was carried out to distinguish the hydrogen source between water (D<sub>2</sub>O) and H<sub>2</sub> of the produced methane. Initially, CD<sub>4</sub> is the dominant methane products (Fig. S2a), which illustrates clearly that the hydrogen in methane comes from water (D<sub>2</sub>O). With the reaction proceeded after several hours, some CD<sub>3</sub>H and CD<sub>2</sub>H<sub>2</sub> can be observed among the methane products (Fig. S2b). It is deduced that the protium atoms should mainly derive from the normal water (H<sub>2</sub>O) reduced from peroxides at NaTaO<sub>3</sub> surface by

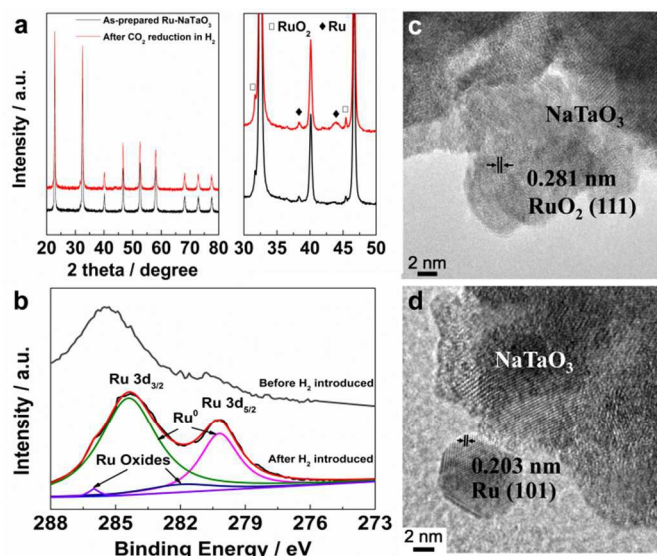
H<sub>2</sub>. Thus, it is confirmed that the direct hydrogen source of the CO<sub>2</sub> reduction is still water, but not the H<sub>2</sub> gas introduced as the electron donor. H<sub>2</sub> promotes the CO<sub>2</sub> reduction reaction by a successful conversion of peroxide intermediates (O<sub>2</sub><sup>•</sup>) into water rather than directly reduces CO<sub>2</sub> to CH<sub>4</sub> as the schematic model shows in Fig. 3d. This is because that the requisite active hydrogen to react with CO<sub>2</sub> in a photocatalytic process should be atomic hydrogen rather than molecular hydrogen. The hydrogenation reaction between molecular hydrogen and CO<sub>2</sub> must climb over an energy barrier to push forward,<sup>25,26</sup> where the requirement could not be met in this work. The atomic hydrogen is activated from other hydrogen sources (water in this work), although there are hydrogen molecules in the system.<sup>21</sup>



**Fig. 3** Gaseous product generation over 0.5 wt% co-catalysts loaded NaTaO<sub>3</sub> in CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub> atmosphere: (a) CH<sub>4</sub>, (b) CO; (c) Productivity with and without H<sub>2</sub> over Ru-NaTaO<sub>3</sub> and Pt-NaTaO<sub>3</sub>; (d) Schematic model of a proposed reaction process of Ru-NaTaO<sub>3</sub> in CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub> atmosphere.

In the point view of cocatalyst, except for Ru and Pt, other cocatalysts did not exhibit a pronounced activity enhancement and selectivities of CO<sub>2</sub> reduction due to their natural properties as shown in Table S2. Ru/NaTaO<sub>3</sub> (CH<sub>4</sub> 51.8 μmol h<sup>-1</sup> g<sup>-1</sup>) and Pt/NaTaO<sub>3</sub> (CO 139.1 μmol h<sup>-1</sup> g<sup>-1</sup>) exhibited the best activities and products selectivity over the series (Fig. 3a and Fig. 3b). The CH<sub>4</sub> or CO versus total carbon products (CH<sub>4</sub> + CO) ratio is about 0.96 for Ru/NaTaO<sub>3</sub> and 0.99 for Pt/NaTaO<sub>3</sub> (Fig. 3c). These results accord well with the results in the literatures.<sup>26–28</sup> It is mainly attributed to the excellent abilities of Ru and Pt in hydrogen activation, stabilization and utilization, since these two metals are commonly used materials for hydrogen storage<sup>29,30</sup> and fuel cells.<sup>31,32</sup> Since converting CO<sub>2</sub> to CH<sub>4</sub> is a multiple-step and multiple-electron reaction (Fig. S3), there must be an inexhaustible supply of active hydrogen (H<sup>•</sup>) to CO<sub>2</sub>. CO molecules possess dominant adsorption ability than H<sub>2</sub>O at Pt surface.<sup>33</sup> After CO<sub>2</sub> molecules have been reduced to CO, the supply of active hydrogen decrease gradually until the Pt surface was fully occupied by CO and finally poisoned by them.<sup>33,34</sup> Thus, the CO<sub>2</sub> reduction over Pt predominantly carries out a 2e<sup>-</sup> reaction and CO become the main product. Conversely, water molecules are more adsorptive at Ru surface,<sup>33</sup> and Ru has a relative high overpotential in H<sub>2</sub> evolution<sup>35</sup> to depress the H<sup>•</sup> recombining to H<sub>2</sub>. Thus, active hydrogens could be

constantly provided to CO<sub>2</sub> to carry out 8e<sup>-</sup> reaction. In addition, the state of Ru is also very important to the activity. Different from other noble metals, Ru is very easy to be oxidized during the drying process. Moreover, this oxidation might be even enhanced when only using water as the reductant due to the formation of Ru(OH)<sub>ads</sub>.<sup>32,33</sup> Thus, the real state of the cocatalysts should be a mixture of Ru and RuO<sub>2</sub> or RuO<sub>x</sub> (Fig. 4a). The partially oxidized RuO<sub>x</sub> not only hinder the electron transfer from NaTaO<sub>3</sub> to Ru, but also weaken the hydrogen activation on metal Ru. So that it lead to a very poor activity (Fig. 1). However, after introducing the electron donor H<sub>2</sub>, RuO<sub>x</sub> could be reduced and transformed to metal Ru again (Fig. 4). As the XPS spectra shown in Fig. 4b, Ru oxides in the as-prepared Ru-NaTaO<sub>3</sub> were reduced to metal Ru. The corresponding TEM image (Fig. 4c and 4d) also indicates the successful transformation to metal Ru. Thus, a stable CO<sub>2</sub> reduction can be ensured over Ru/NaTaO<sub>3</sub>.



**Fig. 4** (a) XRD patterns of Ru/NaTaO<sub>3</sub> samples. Black line: as-prepared Ru/NaTaO<sub>3</sub>, Red line: Ru/NaTaO<sub>3</sub> after a CO<sub>2</sub> reduction under H<sub>2</sub> atmosphere. □ RuO<sub>2</sub>, ◆ Ru. 10 wt% Ru/NaTaO<sub>3</sub> was adopted for better observation of the responds of RuO<sub>2</sub> and Ru. (b) XPS spectra of Ru/NaTaO<sub>3</sub> before and after CO<sub>2</sub> reduction in H<sub>2</sub> atmosphere. TEM image of (c) as-prepared Ru/NaTaO<sub>3</sub>; (d) Ru/NaTaO<sub>3</sub> after CO<sub>2</sub> reduction in H<sub>2</sub> atmosphere.

Long-playing experiments were carried out to examine the stabilities of these two samples, respectively (Fig. S4). Ru/NaTaO<sub>3</sub> keeps a linear growth of CH<sub>4</sub> evolution even overnight, whereas Pt/NaTaO<sub>3</sub> exhibits a decay of CO evolution after several hours due to the poisoning of Pt by the produced CO.<sup>33,34</sup> Further experiments were also carried out to confirm the light dependent photocatalytic activity (Fig. S5). Both Ru/NaTaO<sub>3</sub> and Pt/NaTaO<sub>3</sub> expressed obviously feedbacks, i.e., the reactions exhibit very poor activities under visible light irradiation and there were hardly increases of the products until the L42 filter was removed. Thus, it could be definitely concluded that CO<sub>2</sub> was photocatalytically reduced over Ru/NaTaO<sub>3</sub> and Pt/NaTaO<sub>3</sub>, as NaTaO<sub>3</sub> is a wide band-gap semiconductor (4.2 eV). An isotope experiment was carried out over Ru/NaTaO<sub>3</sub> for further investigation using <sup>13</sup>CO<sub>2</sub>. The GC-MS spectrum exactly confirmed that the organic product <sup>13</sup>CH<sub>4</sub> was reduced from <sup>13</sup>CO<sub>2</sub> (Fig. S6).

In addition, Ru loaded SrTiO<sub>3</sub> and TiO<sub>2</sub> also exhibit stable photocatalytic activities of converting CO<sub>2</sub> to CH<sub>4</sub> in the presence of



electron donor  $\text{H}_2$  (Fig. S7a). The activity differences among  $\text{NaTaO}_3$ ,  $\text{SrTiO}_3$  and  $\text{TiO}_2$  are mainly attributed to their different CB levels (Fig. S7 and Fig. S8). Moreover, these results demonstrate that electron donor could also be extended to other semiconductors to realize a stable photoreduction of  $\text{CO}_2$ . Some other electron donor will be studied to substitute  $\text{H}_2$  in the following work.

In conclusion, this study demonstrated that the photocatalytic activities of  $\text{NaTaO}_3$  are greatly affected by reducing agents and cocatalysts. By introducing electron donor  $\text{H}_2$  into the system, a stable reactivity has been obtained over the series of  $\text{NaTaO}_3$  due to an effective release of the peroxides intermediates of water oxidation.  $\text{Ru}/\text{NaTaO}_3$  ( $\text{CH}_4$  51.8  $\mu\text{mol h}^{-1} \text{g}^{-1}$ ) and  $\text{Pt}/\text{NaTaO}_3$  ( $\text{CO}$  139.1  $\mu\text{mol h}^{-1} \text{g}^{-1}$ ) exhibited the best products selectivity in the presence of the electron donor. Besides, Ru demonstrated an efficient and stable photocatalytic activity in converting  $\text{CO}_2$  to  $\text{CH}_4$  beyond 24 hours. These results and discussion reveal that as co-catalysts, Ru possesses an efficient ability to promote the photogenerated charge separation as well as the hydrogen activation, stabilization and utilization in the presence of electron donor in photoreducing  $\text{CO}_2$  to  $\text{CH}_4$ .

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## Notes and references

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