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Highly efficient and stable photocatalytic reduction of CO$_2$ to CH$_4$ over Ru loaded NaTaO$_3$

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An efficient and stable photocatalytic activity was obtained over NaTaO$_3$ by introducing electron donor (H$_2$) into the CO$_2$ reduction process with water. Ru/NaTaO$_3$ demonstrated the best activity (CH$_4$ 51.8 $\mu$mol h$^{-1}$ g$^{-1}$) and product selectivity in converting CO$_2$ to CH$_4$.

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. In particular, photoreduction of CO$_2$ appears to be a highly fascinating process in lessening the requirement of fossil fuels and climate accommodation by atmospheric CO$_2$ balance. Generally, CO$_2$ reduction is a chain reaction with the product varying from CO (2e$^-$) to CH$_4$ (8e$^-$). Although the reduction potential of CH$_4$/CO$_2$ is about -0.24 V (vs. NHE at pH=7) which seems to be an attainable level to many semiconductors, CO$_2$ reduction has to go through a tough uphill process and its intermediates’ redox potentials are much more negative (E$^\circ$CO$_2$/CO = -0.61 V vs. NHE at pH=7). Thus, to date, only a limited number of materials, such as ZnGa$_2$O$_4$$^8$, ZnGeO$_4$$^9$, NaNbO$_3$$^{10}$, TiO$_2$$^{11-13}$ etc., have exhibited photocatalytic activities in CO$_2$ reduction with various reducing outcomes. In the point view of products, CH$_4$ is more preferable when considering the high importance as a potential solar fuel.$^{14}$ 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$^-$ reaction during the CO$_2$ reduction process.$^{15}$ NaTaO$_3$, which is one of the best pure water splitting photocatalysts reported by Kudo et al.$^{16-18}$, possesses a significantly negative CB and analogous band gap to the above-mentioned semiconductors, likewise, should also bear a gigantic potential in CO$_2$ reduction, although there are few reports about it.

In previous researches, water was generally employed in reducing CO$_2$ as an active hydrogen source. However, although it is believed that CO$_2$ could react with H$_2$O to simultaneously produce CH$_4$ and O$_2$ through two respective half reactions with photogenerated electrons and holes in an ideal process,$^3$ O$_2$ could hardly be detected over most of the oxide semiconductors. It is usually accompanied by a decay of reactivity of CO$_2$ reduction reaction, since some peroxide intermediates could form and accumulate at the oxide semiconductor surface during the oxygen photoevolution reaction from water.$^{19}$ 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$_2$. The unstable production rate has significantly limited the development and the practical application of CO$_2$ 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.$^{19-21}$ A recently attempt by Kang et al showed that the photocatalytic activity and stability can be significantly enhanced by replacing water with N$_2$H$_4$·H$_2$O as electron donor.$^{22,23}$ H$_2$ gas has also been confirmed that it can effectively facilitate the CO$_2$ reaction with water.$^{22-23}$ It opens a promising strategy to promote the photocatalytic efficiency and stability by using electron donor.$^{24}$

In this study, an electron donor (H$_2$ 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$_2$ reduction. The effect of different metal cocatalysts for CO$_2$ photoreduction was studied with and without the electron donor, respectively. Among various metal cocatalysts loaded NaTaO$_3$ samples, Ru/NaTaO$_3$ (CH$_4$ 51.8 $\mu$mol h$^{-1}$ g$^{-1}$) and Pt/NaTaO$_3$ (CO 139.1 $\mu$mol h$^{-1}$ g$^{-1}$) exhibited the best products selectivity in the presence of the electron donor. Moreover, Ru/NaTaO$_3$ showed a linear growth of CH$_4$ evolution over 24 hours and demonstrated an efficient and stable photocatalytic activity in converting CO$_2$ to CH$_4$. The key point of the performance over Ru/NaTaO$_3$ is owing to using H$_2$ as electron donor and distributing Ru as co-catalysts.
The NaTaO$_3$ (NTO) samples were synthesized through a furfural alcohol derived polymerization-oxidation (FAPO) process. 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$_3$ prepared through the FAPO route crystallized in a monoclinic system with the space group of $P2_1/m$, 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$_3$ nanoparticles is shown in Fig.1c, with an intense absorption with steep edge in the UV region. The band gap ($E_g$) of NaTaO$_3$ 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 $\alpha$, $h\nu$, $A$, and $E_g$ are the absorption coefficient, light frequency, proportionality constant and band gap, respectively.

The photocatalytic properties of the as-prepared NaTaO$_3$ were estimated by photoreduction of gaseous phase CO$_2$ under the irradiation of a 300 W UV-enhanced Xe lamp. Fig. 2a and Fig. 2b exhibit the results of CO$_2$ reduction over the series of NaTaO$_3$ only using water as the reducing agent. All the samples showed certain abilities, where CH$_4$ 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$_2$ evolution in this reaction condition (CO$_2$+H$_2$O), because H$_2$ evolution is a highly preferred competing reaction. The CO$_2$ reduction reactions exhibited not linear growth of the products evolution. The bent curves indicate an unstable reactivity of CO$_2$ reduction reaction for all the samples. Moreover, O$_2$ could also not be detected as the product of water oxidation. Thus, an obstructive O$_2$ 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. 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, NaTaO$_3$ film was exposed to a 30% H$_2$O$_2$ aqueous solution to position the peak of peroxide intermediates (dot line), the peaks at 834 cm$^{-1}$ and 883 cm$^{-1}$ belong to the peroxide intermediates and H$_2$O$_2$, respectively. During the CO$_2$ 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.

In order to eliminate the hamper of peroxide intermediates and realize a stable reduction of CO$_2$, an electron donor (H$_2$ gas) was introduced to the reaction system to release the peroxides. Fig. 3a and 3b show the results of CO$_2$ reduction over the series of NaTaO$_3$ in the presence of H$_2$, CO$_2$, and H$_2$. All the samples exhibit promotions of the catalytic activity compared with the counterparts only using H$_2$O and CO$_2$ as shown in Table S2. Almost linear curves indicate that enhanced abilities and activities of the CO$_2$ reduction are obtained over the catalysts, especially for Ru/NaTaO$_3$ (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$_2$. It can be concluded that the peroxide intermediates are effectively reduced by H$_2$, so that a stable reduction of CO$_2$ is observed. An isotope experiment within a D$_2$O, CO$_2$, and H$_2$ atmosphere was carried out to distinguish the hydrogen source between water (D$_2$O) and H$_2$ of the produced methane. Initially, CD$_4$ is the dominant methane products (Fig. S2a), which illustrates clearly that the hydrogen in methane comes from water (D$_2$O). With the reaction proceeded after several hours, some CD$_3$H and CD$_2$H$_2$ can be observed among the methane products (Fig. S2b). It is deduced that the protium atoms should mainly derive from the normal water (H$_2$O) reduced from peroxides at NaTaO$_3$ surface by
H2O
dominant adsorption ability than H2, conversely, water molecules are more adsorptive at Ru than H2 over Ru-NaTaOx cocatalysts did not exhibit a pronounced activity enhancement and selectivities of CO2 reduction due to their natural properties as shown in Table S2. Ru-NaTaOx (CH4, 11.8 μmol h−1 g−1) and Pt/NaTaOx (CO 139.1 μmol h−1 g−1) exhibited the best activities and products selectivity over the series (Fig. 3a and Fig. 3b). The CH4 or CO versus total carbon products (CH4 + CO) ratio is about 0.96 for Ru/NaTaOx and 0.99 for Pt/NaTaOx (Fig. 3c). These results accord well with the results in the literatures. 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 and Pt in hydrogen activation, since these two metals are commonly used materials for hydrogen storage (Fig. 4). Both Ru/NaTaOx and Pt/NaTaOx 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 CO2 was photocatalytically reduced over Ru/NaTaOx and Pt/NaTaOx, as NaTaOx is a wide band-gap semiconductor (4.2 eV). An isotope experiment was carried out over Ru/NaTaOx for further investigation using 13CO2. The GC-MS spectrum exactly confirmed that the organic product 13CH4 was reduced from 13CO2 (Fig. S6). In addition, Ru loaded SrTiO3 and TiO2 also exhibit stable photocatalytic activities of converting CO2 to CH4 in the presence of long-playing experiments were carried out to examine the stabilities of these two samples, respectively (Fig. S4). Ru/NaTaOx keeps a linear growth of CH4 evolution even overnight, whereas Pt/NaTaOx exhibits a decay of CO evolution after several hours due to the poisoning of Pt by the produced CO. Further experiments were also carried out to confirm the light dependent photocatalytic activity (Fig. S5). Both Ru/NaTaOx and Pt/NaTaOx 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 CO2 was photocatalytically reduced over Ru/NaTaOx and Pt/NaTaOx, as NaTaOx is a wide band-gap semiconductor (4.2 eV). An isotope experiment was carried out over Ru/NaTaOx for further investigation using 13CO2. The GC-MS spectrum exactly confirmed that the organic product 13CH4 was reduced from 13CO2 (Fig. S6). In addition, Ru loaded SrTiO3 and TiO2 also exhibit stable photocatalytic activities of converting CO2 to CH4 in the presence of long-playing experiments were carried out to examine the stabilities of these two samples, respectively (Fig. S4). Ru/NaTaOx keeps a linear growth of CH4 evolution even overnight, whereas Pt/NaTaOx exhibits a decay of CO evolution after several hours due to the poisoning of Pt by the produced CO. Further experiments were also carried out to confirm the light dependent photocatalytic activity (Fig. S5).
electron donor $H_2$ (Fig. S7a). The activity differences among NaTaO$_2$, SrTiO$_2$, and 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 CO$_2$. Some other electron donor will be studied to substitute H$_2$ in the following work.

In conclusion, this study demonstrated that the photocatalytic activities of NaTaO$_2$ are greatly affected by reducing agents and cocatalysts. By introducing electron donor H$_2$ into the system, a stable reactivity has been obtained over the series of NaTaO$_2$ due to an effective release of the peroxides intermediates of water oxidation. Ru/NaTaO$_2$ (CH$_3$$_2$$_8$H$_5$+ $\cdot$ $g^+\cdot$ $g^-$) and Pt/NaTaO$_2$ (CO $\cdot$ $g^+$ $\cdot$ $g^-$) exhibited the best products selectivity in the presence of the electron donor. Besides, Ru demonstrated an efficient and stable photocatalytic activity in converting CO$_2$ to 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 CO$_2$ to CH$_4$.

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