Self-doped SrTiO$_{3-x}$ photocatalyst with enhanced activity for artificial photosynthesis under visible light†

Kui Xie,$^{ab}$ Naoto Umezawa,$^{ac}$ Ning Zhang,$^a$ Pakpoom Reunchan,$^a$ Yuanjian Zhang$^{ab}$ and Jinhua Ye$^{ab}$

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Self-doped SrTiO$_{3-x}$ was prepared through a carbon-free one-step combustion method followed by a series of heat treatments in Ar at temperatures ranging from 1200 to 1400 °C. X-Ray Photoelectron Spectroscopy (XPS), Electron Paramagnetic Resonance (EPR) and High-Resolution TEM confirm the presence of Ti$^{3+}$ in samples with oxygen vacancy accommodated in perovskite by forming Ruddlesden–Popper crystallographic shears. The UV-vis spectra and electronic structure calculations show that the oxygen vacancy and Ti$^{3+}$ together induce an in-gap band to enhance the visible light absorption. Pulsed Adsorption of CO$_2$ and Temperature Programmed Desorption (TPD) experiments show that the higher oxygen deficiency tends to improve the chemical adsorption of CO$_2$ on the surface as well as in the bulk of SrTiO$_{3-x}$, especially the accommodation of CO$_2$ molecule in the oxygen vacancy. It is the synergetic effect of visible light absorption and chemical adsorption of CO$_2$ that improves the artificial photosynthesis to generate hydrocarbon fuels from CO$_2$/H$_2$O under visible light irradiation. We also demonstrated that the incorporation of oxygen from CO$_2$/H$_2$O into the oxygen vacancy of SrTiO$_{3-x}$ leads to the absence of oxygen evolution which therefore results in the oxidation of SrTiO$_{3-x}$ (Ti$^{3+}$ → Ti$^{4+}$).

Introduction

There is growing evidence for, and acceptance of, the role of the rising level of anthropogenic emissions of greenhouse gas CO$_2$ into the atmosphere in contributing to potentially dangerous climate change.$^1$ This is mainly the result of our heavy reliance on finite fossil resources that also leads to potential energy crisis. Significant efforts are being devoted to solar cells,$^2$ solid oxide electrolysis cells,$^3,4$ solid oxide fuel cells$^5$ as well as solar fuel conversion,$^6$–$^9$ to carry the renewable energy from where it is available to its point of use. At present, hydrogen has been widely considered as the only renewable energy carrier that can be synthesized efficiently; however, some technical barriers related to its storage and distribution have contributed to the resistance that hydrogen has encountered in becoming practically viable despite a high energy density and zero carbon emission. Synthetic hydrocarbon fuels have therefore been proposed as an alternative form of energy carrier taking into account that they would be compatible with the existing energy infrastructures in addition to

Broader context

Growing concerns over the consequences of global climate change are forcing a major shift in the energy portfolio from the current dominance of fossil fuels towards a rich and diverse mix of energy supply based upon renewable and environmentally benign sources. Emerging technologies such as solar fuel conversion and solar photovoltaics represent recent technical breakthroughs in harnessing renewable solar energy. The progressive move to the clean energy carrier, hydrogen, is seriously impeded by the economic challenge of the unbalanced costs in all aspects of hydrogen production, storage and distribution. In the short and medium terms, synthetic hydrocarbon fuels appear to be the ideal energy carriers for adapting the world to a sustainable energy cycle. Direct visible-light artificial photosynthesis on semiconductor photocatalyst to generate methane, the major component of natural gas, through a photochemical reduction of carbon dioxide in the presence of water is demonstrated in the present work. This new strategy in producing synthetic hydrocarbon fuels can deliver a carbon neutral renewable energy cycle.
their inherent advantages, such as high H/C ratio and the flexibility in hydrocarbon-based power.\cite{19} Through mimicking the natural photosynthesis, some useful hydrocarbons could be directly produced from CO\textsubscript{2}/H\textsubscript{2}O in an artificial photosynthesis process based on semiconductor photocatalyst powders. The recycling of CO\textsubscript{2} would advance us into a carbon-neutral renewable energy cycle. In this process, a semiconductor photocatalyst acts as a microelectrochemical cell which is activated by solar energy. The photo-excited electrons initiate the electrochemical reduction of H\textsubscript{2}O into a hydrogen species that simultaneously reduces CO\textsubscript{2} into useful hydrocarbons.\cite{11,12}

Perovskite-type oxide SrTiO\textsubscript{3} has been well known as a wide-gap semiconductor photocatalyst in the field of solar hydrogen.\cite{13,14} Pure SrTiO\textsubscript{3}, however, is not a good photocatalyst candidate, because it is only active under ultraviolet (UV) irradiation. Many studies have tried to introduce various dopants, such as Fe, C, N and Cr, to extend the light absorption to the visible region.\cite{15–18} In contrast, the self-doping of oxygen vacancy is of essence since the oxygen vacancy is the fundamental and intrinsic defect in perovskite oxide and hence gives the critical impacts on their optical properties. In addition, the higher oxygen deficiency tends to bring on linear vacancy ordering with defect–defect interaction in the perovskite and therefore induces a new in-gap band that might enhance visible light absorption according to some theoretical calculations.\cite{19,20} On the other hand, it is believed that reduced SrTiO\textsubscript{3} has the ability to chemically adsorb and activate CO\textsubscript{2}, especially to incorporate molecular CO\textsubscript{2} in the oxygen vacancy in the form of carbonate ion to act as active site for heterogeneous CO\textsubscript{2} reduction;\cite{21,22} however, to the best of our knowledge, improvement of chemical absorption of CO\textsubscript{2} has not been reported to facilitate the photoreduction of CO\textsubscript{2} on semiconductor photocatalysts.

In this work, we report self-doped SrTiO\textsubscript{3–d} photocatalysts with enhanced visible light activity for artificial photosynthesis from CO\textsubscript{2}/H\textsubscript{2}O to produce useful hydrocarbon fuels. The oxygen deficiency of SrTiO\textsubscript{3–d} photocatalysts was continuously tuned to improve the visible light absorption as well as the chemical adsorption of CO\textsubscript{2}. A systematic theoretical calculation was also performed to understand the electronic structure and the origin of visible light absorption of SrTiO\textsubscript{3–d} photocatalyst. After that, the artificial photosynthesis with CO\textsubscript{2}/H\textsubscript{2}O was evaluated under visible light and the oxidized species was also identified when the reduced product was produced.

**Experimental**

The self-doped SrTiO\textsubscript{3–d} powders were first prepared by a carbon-free combustion method from TiN and Sr(NO\textsubscript{3})\textsubscript{2} in air.\cite{23} In this process, 0.05 mol TiN and 0.05 mol Sr(NO\textsubscript{3})\textsubscript{2} were dissolved in 30% H\textsubscript{2}O\textsubscript{2} (pH = 1) and heated at 90 °C under magnetic stirring. Finally, the obtained green powders were fired at 1200 °C for 20 h in air to get the final yellow powder sample. In this process H\textsubscript{2}O is used to oxidize the majority of Ti\textsuperscript{3+} into Ti\textsuperscript{4+}, whereas the Ti\textsuperscript{2+} residual in the precursors is used to introduce oxygen deficiency in SrTiO\textsubscript{3–d}. XRD for phase detection was performed with a RIGAKU Rint-2000 X-ray diffractometer equipped with graphite monochromatized Cu K\textsubscript{α} radiation (0.5° per min, λ = 1.54178 Å). XRD data for Rietveld refinement were recorded on a Stoe Stadi-P diffractometer with Cu K\textsubscript{α1} radiation (Stoe & CieGmbH, Germany) and analyzed using GSAS software. The N residual was analyzed with an ICP Mass Spectrometer LECO Co. TC-436AR and Pulsed furnace-Infrared rays detector with Si\textsubscript{2}N\textsubscript{4} (JCRM, R003, N = 39.0%) as the standard reference heated at 110 °C for 120 min. The Electron Paramagnetic Resonance (EPR) of the samples was recorded at 120 K to confirm the presence of high spin Ti\textsuperscript{3+} as well as oxygen deficiency on a JES-FA200 Electron Spin Resonance Spectrometer. X-Ray Photoelectron Spectroscopy (XPS) was performed on a Thermo ESCALAB 250 using monochromatized Al K\textsubscript{α} at hν = 1486.6 eV to analyze the surface of the sample powder. The binding energies were calibrated to the C 1s peak at 284.6 eV. To further investigate the stability of oxygen deficient SrTiO\textsubscript{3–d}, the yellow sample powder was treated in pure oxygen at 1200 °C for 48 h and illuminated under UV + vis irradiation for 360 h, respectively. After that, the crystal structure and optical properties were examined in an ambient environment.

To induce more oxygen deficiency and Ti\textsuperscript{3+} in SrTiO\textsubscript{3–d}, the powders prepared in air were divided into 5 batches and treated in Ar at 1200, 1250, 1300, 1350 and 1400 °C, for 20 hours, respectively. XRD, EPR and XPS (under the same conditions) were also performed to further characterize the samples after treatments. Scanning Electron Microscopy (SEM) images were recorded to observe the morphology with scanning electron microscope (JEOL 6700F field emission scanning electron microscope). Brunauer–Emmett–Teller (BET) measurements were carried out to analyze the surface areas on a BELSORP II Surface Area Analyzer. Transmission Electron Microscopy (TEM) was performed to observe the defects in the bulk of a 1400 °C sample with a JEOL 2100F field emission transmission electron microscope operated at 200 kV. UV-visible diffuse reflectance spectra of the powder samples were recorded with a Shimadzu UV-2500 Spectrophotometer at room temperature in air. The Pulsed Adsorption of CO\textsubscript{2} and Temperature Programmed Desorption (TPD) of CO\textsubscript{2} were recorded with a Micromeritics 2000. Here the powder samples were pre-treated in air at 400 °C for 1 h to eliminate absorbed species and then treated at 200 °C in Ar for 1 h before Pulsed Adsorption of CO\textsubscript{2}. The Temperature Programmed Desorption of CO\textsubscript{2} was tested from room temperature to 800 °C at 10 °C min\textsuperscript{-1} with He gas carrier. The details of measurement parameters and program are shown in the ESI.\textsuperscript{†}

To confirm the C element in hydrocarbon products indeed from the photoreduction of CO\textsubscript{2} in the presence of H\textsubscript{2}O\textsubscript{2}, a series of control experiments were carefully conducted with different gas precursors, such as Ar, CO\textsubscript{2}, H\textsubscript{2}O, and H\textsubscript{2}O/CO\textsubscript{2}, under visible light irradiation or in the dark. In this process, 1200 °C SrTiO\textsubscript{3–d} photocatalyst powder (0.3 g) loaded with 0.3% Pt cocatalyst (weight ratio) was utilized for the control experiments. All the experiments were carried out for 3 h and the sampling was carried out one time per hour. The light source was a 300 W Xe lamp equipped with a 420 nm filter (ca. 53.1 mW cm\textsuperscript{-2}). In the first control experiment under irradiation, the gas precursor was only pure Ar to check the gas leakage and adsorbed organic chemicals. In this experiment, no gas leakage and adsorbed organic were detected. In the second control experiment, only pure CO\textsubscript{2} was utilized for photo-reduction under irradiation; however, no CO and O\textsubscript{2} were detected, indicating that CO\textsubscript{2} cannot be directly photo-split. In the third control experiment
under irradiation, 2% H₂O + 98% Ar were utilized as gas precursors; however, no hydrogen was detected which shows the gaseous H₂O cannot be directly split under irradiation. In the fourth experiment, 2% H₂O + 98% CO₂ were utilized as gas precursors but the experiment was carried out under dark. Here no organic chemical, hydrogen and CO were detected because artificial photosynthesis was not achieved under dark. On the other hand, all these results also demonstrate the absence of carbon residual because any carbon residual would lead to the generation of H₂ or CO. Actually, any carbon residual was removed after the treatment of the sample at 1200 °C in air for 20 h.

After that, the 5 photocatalysts (0.3 g) loaded with 0.3% Pt (weight ratio) were utilized for the artificial photosynthesis with 2% H₂O + 98% CO₂ under visible irradiation. The product was analyzed with Gas Chromatography. (The organic chemicals were analyzed using a GC GC-14B, Shimadzu Corp., Japan and the oxygen was detected with a GC Shimadzu GC-8A equipped with a thermal detector TCD.) To check the influence of Pt co-catalyst, the 1400 °C SrTiO₃ sample without Pt loading was utilized to perform artificial photosynthesis under the same conditions. The apparent quantum yield at a wavelength of 600 ± 15 nm was measured under the light intensity of 56.1 μW cm⁻². The apparent quantum yield was calculated according to the equation: A.Q.Y. = [N(CH₄) × 8]/[N(photon) × 100%], where N(CH₄) and N(photon) signify the molecular number of CH₄ generated in unit time and the number of incident photons in unit time, respectively. (One CH₄ molecule consumes 8 electrons as shown: CO₂ + 8e⁻ + 8H⁺ → CH₄ + 2H₂O.)

Electronic structure calculations

To understand the electronic structure of self-doped SrTiO₃₋₅, we performed density functional calculations based on the local density approximation (LDA) + U approach. Projector-augmented wave pseudopotentials were employed as implemented in the VASP code. The valence configurations of the pseudo-potentials were 4s²4p⁵5s² for Sr, 3p³4d⁴s² for Ti and 2s²2p⁴ for O. The energy cutoff for the plane-wave basis set expansion was set at 500 eV. The Monkhorst–Pack k-point sets of 6 × 6 × 6 and 2 × 2 × 2 were used for a 5 atom unit cell and a 80 atom supercell of cubic SrTiO₃, respectively. We applied U to Ti d and O p (U(Ti d) = 9.14 eV and U(O p) = 5.32 eV) which were determined so as to reproduce the experimental band gap (3.2 eV). The importance of applying U to O p as well as Ti d states was discussed elsewhere. The 5 atom unit cell was fully relaxed for atomic positions and cell volume. The optimized lattice constant (3.92 Å) is in good agreement with an experimental value (3.905 Å). The 80 atom supercell was generated by extending the unit cell for 2 × 4 × 2. Four oxygen atoms were removed from the supercell to create model structures of SrTiO₂₋₅, which generally correspond to the composition ratio of the 1400 °C sample.

To set up a realistic model for the reduced SrTiO₃, we constructed four different model structures (model A–D) with different configurations of lined oxygen vacancies as shown in Fig. 1(a)–(d), respectively. In the figure, the 80 atom supercell was extended along the x and z direction twice for visualization. Sr and O atoms are not shown in the figure. These model structures are relaxed not only for atomic positions but also for the cell volume (lattice constants). We found that all the models give the same trend in terms of the change in lattice constants: a and b decrease while c increases with respect to those of the perfect crystal, in consistent with our experimental observation (Table 1). The small difference might be attributed to the overestimation of oxygen deficiency according to EPR and XRD results. The total energies of models A, B, and C are higher than that of model D by 0.15 eV, 0.01 eV, and 0.39 eV, respectively. Thus, model D was adopted for the discussions below. Fig. 2(a)–(d) show the partial charge densities corresponding to the four occupied gap states at gamma point associated with oxygen vacancies in model D. It is clearly shown that the defect levels mainly consist of the Ti d–Ti d bonding states across the vacancy sites.

Results and discussions

The SrTiO₃₋₅ photocatalyst prepared at 1200 °C in air is yellow in colour showing the sample would be visible light active. As
shown in Fig. 3(a), the XRD of the as prepared sample only shows the strong peaks corresponding to SrTiO$_3$ with space group $P4/nmm$. Fig. 3(b) shows the XRD Rietveld refinement which discloses the nominal chemical formula SrTiO$_{2.91}$ as well as the oxygen deficiency $\delta = 0.09$. The yellow colour of the sample also demonstrates the high-temperature stability of the photocatalyst. In order to check if there is N element residual in the sample, ICP Mass Spectroscopy was conducted with the Si$_3$N$_4$ reference. As shown in Table S1*,†, the residual of N is already beyond the detection limit of $0.01\%$, which shows the complete exchange between N and O after heat treatment in air at such a high temperature. This result is also consistent with other reports where N doped solid oxide materials tend to completely release N at around 500–900 $^\circ$C in air. To further investigate the stability of oxygen deficient SrTiO$_{3-\delta}$, two samples were treated in pure oxygen at 1200 $^\circ$C for 48 h and illuminated under UV + vis irradiation for 360 h, respectively. As shown in Fig. 4(a) and (b), the optical property and crystal structure of SrTiO$_{3-\delta}$ are remarkably stable without any change or degradation after UV + vis irradiation in air for 360 h. In addition, the SrTiO$_{3-\delta}$ is high-temperature stable. The crystal structure of SrTiO$_3$-$\delta$ is highly stable and there is no degradation of optical property, even after treatment in pure oxygen at 1200 $^\circ$C for 48 h.

In order to further confirm the presence of Ti$^{3+}$ in the sample, Electron Paramagnetic Resonance (EPR) was performed at 120 K to determine the presence of unpaired electron in the sample. As shown in Fig. 5(a), the sample shows a strong EPR signal at $g = 1.975$, which is characteristic of paramagnetic Ti$^{3+}$ ion, confirming the presence of Ti$^{3+}$ as well as oxygen deficiency in SrTiO$_{3-\delta}$. The signal $g = 1.995$ is generated by the cavity. The signal of $g = 2.002$ is produced by the adsorption of atmospheric oxygen accommodated in the surface oxygen vacancy to generate superoxide ion O$_2^-$. The adsorption of molecular oxygen is expected to lead to the oxidation of surface Ti$^{3+}$ to Ti$^{4+}$, which is also confirmed by XPS results shown in Fig. 5(c), where no Ti$^{3+}$ signal was detected. As shown in Fig. 5(d), the presence of superoxide ion was also detected by XPS, which further confirms the adsorption of oxygen molecule in the oxygen vacancy on the photocatalyst surface. Fig. 5(b) shows the absence of the XPS signal of N$1s$ which is consistent with the result of ICP mass spectroscopy. It is reasonable to conclude that the Ti$^{3+}$ only exists in the bulk of self-doped SrTiO$_{3-\delta}$ because surface Ti$^{3+}$ seems to be oxidized. The as prepared powders were then further treated at 1200, 1250, 1300, 1350 and 1400 $^\circ$C in Ar for 20 hours to introduce more Ti$^{3+}$ as well as oxygen vacancies in different samples, respectively.

After the above treatments in Ar, the 5 samples were analyzed using XRD, EPR, XPS, SEM and BET. The XRD as shown in Fig. 6(a) confirms the pure phase ($P4/nmm$) of the corresponding 5 samples after heat treatments in Ar at temperatures ranging from 1200 to 1400 $^\circ$C. However, the right shift of 2$\theta$ versus treatment temperature was also observed as shown in Fig. 6(b), which demonstrates the gradual decrease of cell volume with more oxygen loss at higher temperatures. As shown in Table 2, the cell volumes decrease versus treatment temperatures because
the higher temperatures tend to result in more loss of oxygen in solid oxide materials in Ar atmosphere. It should be also noted that the cell parameter $c$ is increasing versus oxygen deficiency; however, $a$ and $b$ change in a reverse trend, which may be attributed to the formation of Ruddlesden–Popper defects as the capability of SrTiO$_3$ is rather limited to accommodate oxygen defects, as reported by Irvine and his co-workers.

In our work, crystallographic shears were also observed as shown in TEM (Fig. S1*(a)†), which is caused by the shifting of $1/2$ $h$ $001$ as shown in Fig. S1*(b)†. This kind of defects results in two neighboring SrO layers with a larger facet distance along the $h001$ direction as reported by Zhu and her co-workers, which is the reason why $c$ increases versus oxygen deficiency. Furthermore, XPS and EPR (Fig. S2*–S6*†) results together demonstrate the existence of Ti$^{3+}$ in the bulk and superoxide ion on the surface of photocatalysts. The nominal formulae are estimated to be SrTiO$_2.90$, SrTiO$_2.87$, SrTiO$_2.83$, SrTiO$_2.80$ and SrTiO$_2.76$ from EPR and XRD results, respectively. The specific surface areas of the 5 samples decrease from 2.4 to 1.8, 1.2, 1.1 and 0.8 m$^2$ g$^{-1}$ with treatment temperature (Table S2*†), which is attributed to the particle growth at higher temperatures as confirmed by the morphology change in SEM photos as shown in Fig. 7.

Table 2  Cell parameters of samples treated at different temperatures in Ar

<table>
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<tr>
<th>Sample $/ ^{\circ}$C</th>
<th>$V$/Å$^3$</th>
<th>$a$/Å</th>
<th>$b$/Å</th>
<th>$c$/Å</th>
<th>$\alpha^\circ$</th>
<th>$\beta^\circ$</th>
<th>$\gamma^\circ$</th>
<th>Space group</th>
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<td>1250 $/ ^{\circ}$C</td>
<td>59.5107</td>
<td>3.9072</td>
<td>3.9072</td>
<td>3.8982</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>P4/mmm</td>
</tr>
<tr>
<td>1300 $/ ^{\circ}$C</td>
<td>59.4877</td>
<td>3.8990</td>
<td>3.8990</td>
<td>3.9131</td>
<td>90</td>
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<td>90</td>
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</tr>
<tr>
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<td>3.9141</td>
<td>90</td>
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<td>3.9161</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>P4/mmm</td>
</tr>
</tbody>
</table>

Fig. 7 SEM of SrTiO$_{3-x}$ : (a) 1200 $/ ^{\circ}$C prepared in air and the samples treated in Ar at (b) 1200 (c) 1250 (d) 1300 (e)1350 and (f) 1400 $/ ^{\circ}$C.

Fig. 8 UV-vis spectra of commercial SrTiO$_3$ and as prepared SrTiO$_{3-x}$ samples reduced in Ar at different temperatures.

Fig. 8 shows the UV-vis spectra of commercial SrTiO$_3$ and the 5 treated samples where commercial SrTiO$_3$ is only active under UV irradiation while the photoresponse of self-doped SrTiO$_{3-x}$ is effectively extended into the visible and near infrared region. It was also observed that the visible light absorption is positively related to oxygen deficiency. To understand the origin of the visible light absorption, we performed electronic structure calculations based on the density-functional theory (DFT) + $U$ approach. To create a model structure that can reproduce the variation of the lattice constants upon oxygen reduction of SrTiO$_3$ observed in our experiments, we introduced line defects associated with oxygen vacancies along (100) and (001) directions (Fig. 9(a)) as discussed before (model D in Fig. 1). The composition ratio of our model SrTiO$_{2.75}$ nearly corresponds to that of the sample annealed in Ar at 1400 $/ ^{\circ}$C. The formation of such line defects in SrTiO$_3$ with $d$ larger than 0.01 was also reported elsewhere. From the total and local density of states (DOS) for the model structure, it is understood that such a line defect creates a new band in the band gap as shown in Fig. 9(c) compared to the DOS plot for a perfect crystal (Fig. 9(b)). From the local density of states and partial charge densities corresponding to the defect-related states, we understood that the newly formed band is mainly composed of Ti d–Ti d bonding states across the vacancy sites (Fig. 2). Thus, the introduction of oxygen vacancies should promote the formation of Ti–Ti bonds, giving rise to bonding states in the band gap. Importantly, the defect-related band is occupied with electrons, and thus photoexcitations are allowed from the defect band to the conduction band within the range of visible light. We suggest that this is a possible origin of the visible light absorption enhanced in the
self-doped SrTiO$_3$–d. It should be also noted that the conduction band edge is not lowered upon the defect formation, which thus maintains the reduction power of photoexcited electrons.

It is popularly believed that reduced solid oxide materials have the ability to chemically adsorb and activate CO$_2$, especially to incorporate CO$_2$ molecules in the oxygen vacancy in the form of carbonate ion to act as active site for heterogeneous CO$_2$ reduction.$^{21,22}$ To investigate the adsorption of CO$_2$ on self-doped SrTiO$_{3-d}$ powder photocatalysts, Pulsed Adsorption of CO$_2$ and Temperature Programmed Desorption were performed to study the physical and chemical adsorptions of CO$_2$ on powder samples. Fig. 10(a) and (b) show the CO$_2$ adsorption and desorption on the 1200 °C sample, where the total adsorption of CO$_2$ was around 0.01 ml m$^{-2}$cata which was mainly dominated by physical adsorption. The chemical desorptions as shown in Fig. 10(b) at ~130 to 150 °C and ~450 °C are related to the basic sites and basic property of the SrTiO$_{3-d}$ surface as expected.$^{37,38}$ On the other hand, the dipole–dipole coupling between CO$_2$ molecules and particle surface may promote chemical adsorption that results in chemical desorption in a similar temperature region of ~130 to 150 °C.$^{39}$ It should be also noted that CO$_2$ desorption (TPD signal) still occurs at ~750 °C which is attributed to the release of CO$_2$ incorporated in the oxygen vacancy in the samples.$^{21,22}$ The Pulsed Adsorption of CO$_2$ and Temperature Programmed Desorption of 1250, 1300 and 1350 °C samples are shown in Fig. S7*–S9*. As shown in Fig. 10(c) and (d), the 1400 °C sample shows ~0.04 ml m$^{-2}$cata where great enhancement of chemical adsorption of CO$_2$ was observed and the chemical adsorption dominates the total adsorption. The higher oxygen deficiency leads to enhanced chemical adsorption of CO$_2$, which therefore facilitates the activation of CO$_2$ for photosynthesis. On the other hand, the oxygen vacancy also has the ability to accommodate and chemically activate H$_2$O molecule for artificial photosynthesis.$^{40}$

As shown in Table 3, a blank experiment with Ar precursor gas confirmed that there is no adventitious hydrocarbon in our system. On the other hand, there is no carbon residual in the sample because the carbon residual would lead to the evolution of CO or H$_2$ with CO$_2$ or H$_2$O precursor. In addition, there is no adsorption of organic chemicals on the sample as confirmed by the control experiment with H$_2$O/CO$_2$ under dark. It was also observed that only H$_2$O or CO$_2$ cannot be directly photo-split in the gaseous condition. However, the artificial photosynthesis from CO$_2$/H$_2$O was successfully achieved under visible light irradiation, which implies that CO$_2$ was photoreduced in the presence of H$_2$O. The hydrocarbons from CO$_2$/H$_2$O might be related to the electrochemical reaction of hydrogen species with activated carbon dioxide on self-doped SrTiO$_{3-d}$. Fig. 11 shows the artificial photosynthesis performance using different self-doped SrTiO$_{3-d}$ samples with gaseous CO$_2$/H$_2$O under visible light irradiations. In this process, only 2% H$_2$O was utilized to offer hydrogen species for CO$_2$ reduction because lower H$_2$O content may be favorable for CO$_2$ adsorption. Methane is the main product whose rate is enhanced from ~0.05 μmol m$^{-2}$cata h$^{-1}$ for the 1200 °C sample to ~0.25 μmol m$^{-2}$cata h$^{-1}$ for the 1300 °C sample under the synergetic effect of visible light.

![Image](55x559 to 277x725)

Fig. 9 (a) Relaxed geometry of the model structure used for our electronic structure calculations. Here, green, blue, and red particles denote Sr, Ti, and O atoms, respectively. The striped circles indicate the positions of oxygen vacancies. Ti–Ti bonds across the vacancy sites are shown as solid bars. The total density of states (gray) and the local density of states (red) for Ti d are also shown for (b) pristine SrTiO$_3$ and (c) the defected system. Here, the sphere of Ti radius was set to 1.323 Å. The zero energy is at the valence-band maximum of the perfect crystal of SrTiO$_3$. In Fig. 2(c), the origin is calibrated for aligning p states of several Ti atoms located far away from the defects with respect to that of pristine SrTiO$_3$. The vertical broken line denotes the highest occupied state in each system.

![Image](311x521 to 547x725)

Fig. 10 Pulsed Adsorption of CO$_2$ (TCD signal) and Temperature Programmed Desorption (TPD signal) on 1 m$^2$ (surface area) 1200 °C and 1400 °C SrTiO$_{3-d}$ photocatalyst.

### Table 3 Control experiments using the 1200 °C sample with different gas precursors under irradiation or dark

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<th>H$_2$</th>
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<td>No</td>
<td>No</td>
<td>No</td>
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</tr>
<tr>
<td>2$^{nd}$</td>
<td>CO$_2$</td>
<td>No</td>
<td>No</td>
<td>No</td>
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<tr>
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<td>H$_2$O</td>
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</tr>
<tr>
<td>4$^{th}$</td>
<td>CO$_2$ + H$_2$O</td>
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<td>Dark</td>
</tr>
<tr>
<td>5$^{th}$</td>
<td>CO$_2$ + H$_2$O</td>
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</tbody>
</table>
absorption and chemical adsorption of CO₂. However, the methane rate drastically decreased for 1350 and 1400 °C samples though the visible light absorption and chemical adsorption of CO₂ were continuously enhanced. At this stage, the recombination of electron and hole might be the limitations that lead to the degradation of photosynthesis. Additionally, we also conducted the experiment under irradiation with 600 nm wavelength (~2.07 eV) and confirmed that the artificial photosynthesis proceeded as well, which further proves the reasonability of calculation results of the in-gap band. The quantum efficiency at 600 nm was measured and calculated to be 0.21% for the 1300 °C sample. For comparison, the 1400 °C sample without Pt shows lower performance than that of the Pt-loaded one as shown in Fig. 11(e). In our experiment, Pt works as a co-catalyst to facilitate the separation of electron and hole. The collection of electron on Pt would enable the multi-electron reduction of CO₂. This may be the reason why Pt loaded samples show better performances. In this work, the turnover number was also calculated to evaluate the photocatalytic reactions. We estimate the turnover number in terms of Ti³⁺ ions in the sample and the photons consumed for methane generation. We consider that the outer atomic layer with a thickness of 10 Å initiates the artificial photosynthesis on the sample surface. (For the 1300 °C sample, SrTiO₂.83, ~4.8 g cm⁻³, ~0.34 mol Ti³⁺ per mol SrTiO₂.83.) The amount of Ti³⁺ ions of 1 m² SrTiO₂.83 can be calculated from Nsurf(Ti³⁺) = 1/5 × m/M × 0.34, where m and M signify the mass and molar mass of SrTiO₂.83 on the surface. Here the Nsurf(Ti³⁺) is calculated to be 1.7 μmol for 1 m² SrTiO₂.83. The methane evolution under visible-light irradiation in 4 h in the reaction consumes 7.2 μmol photons. The turnover number for 4 h is therefore 7.2/1.7 = 4.2. Actually, the bulk Ti³⁺ might be also involved in reaction for the consumption of oxygen species.

It should be noted that no oxygen evolution was detected in all of the above artificial photosynthesis processes, which demonstrates that the CO₂/H₂O was not sufficiently photo-oxidized to reach the oxygen evolution though the reduced products proceed to generate accompanied by the consumption of excited electrons. The oxygen from CO₂/H₂O seems to be incorporated into the SrTiO₃₋₅ powder, ¹⁴, ⁴² which is expected to simultaneously result in the consumption of holes as well as the oxidation of self-doped SrTiO₃₋₅ (Ti³⁺ → Ti⁴⁺). In order to further confirm the above speculation, we conducted an EPR test of the 1200 °C sample before and after photosynthesis experiments (7-day experiment). As shown in Fig. 12, the EPR signal at g = 1.975 (the characteristics of paramagnetic Ti³⁺) of the 1200 °C sample after experiment is obviously lower than that of the sample before the experiment, confirming the decrease of Ti³⁺ content as well as the oxygen deficiency in SrTiO₃₋₅. In order to further support this evidence, we also conducted XRD tests for the 1200 °C sample before and after the experiment. The incorporation of oxygen is expected to lead to the change of cell volume of the sample. As shown in Fig. 13, a slight left shift of 2θ was observed for the sample after irradiation for 3 days which is caused by the incorporation of oxygen into the sample leading to the increase of cell volume. It is therefore reasonable to conclude that the oxygen vacancy and high-spin Ti³⁺ not only contribute to the enhancement of visible light activity and adsorption of CO₂ but also serve as a specific sacrificial agent to achieve the
generation of reduced products in photosynthesis. However, the continuous consumption of Ti$^{3+}$ in SrTiO$_3$ may result in the degradation of photosynthesis performance. Actually, in our experiments, the photosynthesis significantly declined in the initial 10 hours though it still proceeded even after a 3-day continuous test. But it may be possible that the performance could be recovered again by treating SrTiO$_3$ in Ar to introduce Ti$^{3+}$ as well as the oxygen vacancy. As shown in Fig. 14, the cycled performance of the 1200 °C sample greatly decreased in contrast to the fresh sample, which might be attributed to the consumption of Ti$^{3+}$. However, reasonable recovery of artificial photosynthesis performance was also achieved by again treating the cycled sample in Ar at 1200 °C to introduce more Ti$^{3+}$ in the sample.

Conclusions

In summary, we reported self-doped SrTiO$_3$-d photocatalysts with enhanced visible light activity for photosynthesis from CO$_2$/H$_2$O. Experimental results and theoretical calculations together confirm that it is the oxygen vacancy and Ti$^{3+}$ that induce an in-gap band to enhance the visible light absorption. It was demonstrated that the oxygen deficiency related defects tend to promote chemical adsorption of CO$_2$. The synergetic effect of light absorption and chemical adsorption of CO$_2$ together enhance the artificial photosynthesis under visible light. The incorporation of oxygen from CO$_2$/H$_2$O into SrTiO$_3$-d photocatalysts leads to the absence of oxygen evolution as well as the oxidation of Ti$^{3+}$ to Ti$^{4+}$ in SrTiO$_3$-d. We also demonstrated the recovery of artificial photosynthesis performance by again treating the sample in Ar to introduce Ti$^{3+}$ as well as the oxygen vacancy. Improvements of the performance could be further implemented by developing nano-size or mesoporous photocatalysts with high surface areas.

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