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# Modulation of the Reduction Potential of $TiO_{2-x}$ by Fluorination for Efficient and Selective $CH_4$ Generation from $CO_2$ Photoreduction

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#### **Author Contributions**

Mingyang Xing, Yi Zhou and Chunyang Dong contributed equally to this work.

ABSTRACT: Photocatalytic reduction of CO<sub>2</sub> holds great promises for addressing both the environmental and energy issues that are facing the modern society. The major challenge of CO<sub>2</sub> photoreduction into fuels such as methane or methanol is the low yield and poor selectivity. Here, we report an effective strategy to enhance the reduction potential of photo-excited electrons by fluorination of mesoporous single crystals (MSCs) of reduced TiO<sub>2-x</sub>. Density functional theory (DFT) calculations and photoelectricity tests indicate that the Ti<sup>3+</sup> impurity level is upswept by fluorination, owing to the built-in electric field constructed by the substitutional F that replaces surface oxygen vacancies, which leads to the enhanced reduction potential of photo-excited electrons. As a result, the fluorination of the reduced TiO<sub>2-x</sub> dramatically increases the CH<sub>4</sub> production yield by 13 times from 0.125  $\mu$ mol/g·h to 1.63  $\mu$ mol/g·h under solar light illumination, with the CH<sub>4</sub> selectivity being improved from 25.7% to

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2 3	85.8%. Our finding provides a metal-free strategy for the selective CH <sub>4</sub> generation from CO <sub>2</sub>
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Photoreduction of CO<sub>2</sub> into desirable chemicals such as methane or methanol has been widely considered as one of the most promising approaches to reduce the excessive emission of greenhouse gases and produce renewable energy that can replace the traditional fossil feedstocks.<sup>1-5</sup> Currently, much research effort on CO<sub>2</sub> photoreduction has been focused on photocatalysts based on  $TiO_2$ ,<sup>6-13</sup> owing to its high photocatalytic activity and suitable redox potential for CO<sub>2</sub> reduction and H<sub>2</sub>O oxidation.<sup>14</sup> It was found recently that the bandgap of TiO<sub>2</sub> could be narrowed to better utilize the solar energy spectrum by employing reduced TiO<sub>2</sub> (TiO<sub>2</sub>. x) which are self-doped with  $Ti^{3+}$  and oxygen vacancies.<sup>15, 16</sup> Although self-doping of  $Ti^{3+}$ narrows the bandgap of TiO<sub>2</sub>, it also weakens the reduction power of electrons, which greatly slows the kinetics of the reduction reaction from CO<sub>2</sub> to CH<sub>4</sub> which involves eight electrons.<sup>14, 17</sup> It is therefore highly desirable to develop new TiO<sub>2-x</sub> photocatalysts with enhanced reduction potential while maintaining the visible light response. While this represents a significant challenge in the field, there has been some positive progress recently. For example, Zhang et al. demonstrated that the presence of an electron acceptor such as  $Cl_2$  or  $O_2$  on the  $TiO_2$  surface could cause upward band bending due to the formation of Helmholtz layer on the semiconductor surface;<sup>18, 19</sup> and Chen et al. found that the point defects such as F-type color centers in rutile can also induce lattice relaxation and ionic polarization effects,<sup>20</sup> which could induce the upward band bending.<sup>21</sup>

Here, we report that significant improvement of the reduction potential of  $TiO_{2-x}$  mesoporous single crystals (MSCs) could be achieved through a robust fluorination process, while maintaining their visible light response. As indicated by density functional theory (DFT) calculations, fluorination enables doping of F atoms in the lattice interval of  $TiO_{2-x}$  by substituting oxygen vacancies. With its strong electron-withdrawing property, fluorine atoms

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attract electrons from neighboring  $Ti^{3+,18,19}$  regenerating  $Ti^{4+}$  which carries more positive charges. As a result, a built-in electric field is generated between substitutional F and  $Ti^{3+}$ , leading to the upsweep of the  $Ti^{3+}$  impurity level, enhanced reduction potential of the electrons,<sup>20, 21</sup> and consequently significant improvements in the yield and selectivity of CH<sub>4</sub> production in solar-light-driven CO<sub>2</sub> photoreduction.

The rutile TiO<sub>2-x</sub> MSCs were prepared by using a hard-template method, according to our previous report.<sup>22</sup> The as-prepared MSCs displayed three-dimensional (3D) connected channels and obvious blue color (Figure 1a and S1), implying the generation of Ti<sup>3+</sup> in MSCs, which was further confirmed by the low temperature EPR results shown in Figure 1b.<sup>23</sup> Interestingly, after fluorination by NH<sub>4</sub>F, the resulting F-MSCs samples showed almost unchanged crystal form (Figure S2 and S3), color appearance (Figure 1a), and visible light absorption (Figure 1c) compared with MSCs. However, the absorption shoulder of F-MSCs showed a significant blue-shift (Figure 1c). And the bandgap of MSCs also has a distinct increase from 3.01 eV to 3.10 eV after the fluorination (inset of Figure 1c), implying that the Ti<sup>3+</sup> impurity level in TiO<sub>2-x</sub> has an upward shift. Meanwhile, the Ti<sup>3+</sup> signals of F-MSCs in the EPR spectra presented an obvious decrease, further confirming the change of Ti<sup>3+</sup> impurity level. The color of F-MSCs remained very stable even upon air exposure for six months (Figure 1a).



**Figure 1.** (a) Photos of various MSCs samples. (b) EPR spectra of the samples on 77 K. (c) UV vis-DRS spectra and transformed Kubelka–Munk function against the photon energy plot (inset) of the samples. (d) FESEM image of F-MSCs. (e) TEM image of F-MSCs. (f) Elemental mapping images of F-MSCs, with red dots denoting element Ti, blue dots element O, and green dots element F.

The TiO<sub>2-x</sub> MSCs were calcined at 500  $^{\circ}$ C in air for 30 min to produce a reference sample (Cal-MSCs), which changed its color to white (Figure 1a). In addition, the EPR signal of Ti<sup>3+</sup> disappeared (Figure 1b), owing to the re-oxidation of Ti<sup>3+</sup> in MSCs. As expected, the bandgap of Cal-MSCs increased to 3.12 eV, which was close to the value of F-MSCs (3.10 eV) but with a white color appearance. We also fluorinated the Cal-MSCs to produce a sample of F-Cal-MSCs,

which however did not display any blue-shift of the light adsorption shoulder (Figure 1c). Its bandgap (3.11 eV) also has no obvious increase compared with that of Cal-MSCs (3.12 eV), indicating that the conduction band (CB) of Cal-MSCs cannot be elevated by fluorination, owing to the absence of Ti<sup>3+</sup> in Cal-MSCs and F-Cal-MSCs.<sup>21</sup> XRD patterns of Cal-MSCs and F-Cal-MSCs are shown in Figure S2a to confirm that the phase of prepared samples remains the same even after calcination. Many reports have demonstrated that doping with Ti<sup>3+</sup> or oxygen vacancy would induce the F-type color centers in a well crystallized TiO<sub>2</sub> surface layer, which could obviously enhance the visible light response.<sup>20, 24-28</sup> The F-MSCs here could maintain the visible light absorption while enhancing the reduction potential of the electrons. On the other hand, the morphological structures of MSCs changed very little after fluorination, as shown in Figure 1d, e. And the elemental mapping results in Figure 1f demonstrate the fluorine atoms have been evenly dispersed in TiO<sub>2-x</sub>.



**Figure 2.** (a) Valence band (VB) XPS spectra of MSCs before and after fluorination; (b) F1s XPS spectra of blue MSCs before and after fluorination; and Mott–Schottky plots of (c) MSCs and (d) F-MSCs.

The XPS characterization and the Mott-Schottky plots were used to investigate the change of valence band (VB) and CB in F-MSCs (Figure 2), respectively. It is found that the fluorination does not contribute to the additional valence band-edge states of the Ti<sup>3+</sup> doped MSCs, and the VB of catalyst is fixed at 2.38 eV (Figure 2a). Mott-Schottky plots give an answer for the broadened bandgap of F-MSCs, that is, the CB of MSCs has elevated from -0.63 eV to -0.71 eV (Figure 2c,d), which implies the strengthened reduction potential of TiO<sub>2-x</sub> by fluorination. F 1s XPS results indicate there is a new peak appearing at 684.6 eV after the fluorination (Figure 2b). The peak at 683.7 eV is ascribed to the surface Ti-F.<sup>8, 29</sup> The new peak at a higher binding energy is assigned to the substitutional F that replaces oxygen vacancy (as confirmed by the following DFT calculations), which is caused by NH<sub>4</sub>F-fluorination. A weak peak at 400.0 eV in the N 1s XPS suggest a very low possibility of nitrogen doping in the TiO<sub>2-x</sub> (Figure S4).<sup>29-31</sup> In our previous work,<sup>29</sup> the generation of Ti<sup>3+</sup> and the doping of F occurred at the same time by the onestep vacuum activation method. As a result, there is a strong F1s XPS peak at 689.8 eV, which is ascribed to the doped F in the lattice of TiO<sub>2</sub>. There is no XPS peak observed between the surface  $\equiv$ Ti–F species and doped F. More importantly, there is no blue-shift in light absorption after the modification of TiO<sub>2</sub> in the previous work. But in this case, the Ti<sup>3+</sup> was introduced into TiO<sub>2</sub> firstly, and then the fluorination was carried out over the Ti<sup>3+</sup> doped TiO<sub>2</sub>. A new F 1s XPS peak appearing at 684.6 eV was observed after the fluorination, which is located between the peaks of surface  $\equiv$ Ti–F and doped F. Interestingly, the fluorination induces an obvious blue-shift

of light absorption. Hence, we can conclude that the fluorination over  $Ti^{3+}$ - $TiO_2$  reported here is very different from the conventional fluorination modification of  $TiO_2$ , which could cause changes in the band structure of  $Ti^{3+}$ - $TiO_2$ . On the other hand, when the  $Ti^{3+}$  was eliminated by calcination (Cal-MSCs), the subsequent fluorination treatment (F-Cal-MSCs) would result in no change of importance in the CB and VB locations (Figure S5). In fact, the tests of UV-DRS and Mott–Schottky analysis were repeated for several times using samples of different batches to eliminate the measurement error (Figure S6). These results indicate the presence of interaction between  $Ti^{3+}$  and substitutional F in F-MSCs, which plays a key role in the elevation of CB.



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**Figure 3.** (a) Calculated structures for rutile  $TiO_{2-x}$  (110) before (left) and after (right) fluorination. For the construction of structure model, the concentration of  $Ti^{3+}$  before and after fluorination was fixed at 3.7% and 2.7% respectively, according to the EPR and XPS results. And the substitution fluorine concentration was fixed at 4.1% based on the XPS results. (b-d) Calculated DOS of clean rutile  $TiO_2$ ,  $TiO_{2-x}$ , and  $F-TiO_{2-x}$ , and (e-g) the corresponding amplification DOS (the magnetizations of  $TiO_2$ ,  $TiO_{2-x}$ , and  $F-TiO_{2-x}$  are 0, 4.0 and 3.0 respectively).

In order to investigate the interaction between substitutional F and  $Ti^{3+}$ , we employed the DFT calculations to study the effect of fluorination on the energy band structure of TiO<sub>2-x</sub>. Some previous DFT calculations have shown that fluorine doping could reduce the VB location of TiO<sub>2</sub>,<sup>32, 33</sup> which is very different from our results, probably because most of these studies ignored the impact of the defects such as the oxygen vacancies in TiO<sub>2-x</sub>. In our case, we considered the oxygen vacancies (surface and bulk) while building the rutile (110) structure, as shown in Figure 3a. The concentration of Ti<sup>3+</sup> and F in the model was consistent with the actual quantity obtained from the XPS and EPR results. Interestingly, when the fluorine atoms occupy the position of surface oxygen vacancies, the corresponding results of DFT calculation are very consistent with the experimental results. Compared with clean TiO<sub>2</sub>, the DOS of TiO<sub>2-x</sub> shows an obvious impurity level under the CB location (Figure 3e, f), which is induced by the introduction of Ti<sup>3+</sup>. After the fluorination, the impurity level of F-TiO<sub>2-x</sub> has a distinct upper-shift, as shown in Figure 3f, g. Meanwhile, the magnetization of TiO<sub>2-x</sub> decreases from 4.0 to 3.0 after the fluorination, suggesting the decreased spin electrons and reduced Ti<sup>3+</sup> concentration. After the substitution of F for oxygen vacancy, an internal electric field was established between the

neighboring  $Ti^{3^+}$  and substitutional F. The electron on  $Ti^{3^+}$  would transfer to F to generate the  $Ti^{4^+}$  owing to the strong electronegativity of F atoms, which is responsible for the decrease of  $Ti^{3^+}$  concentration after the fluorination. In addition, we also have considered the effect of bulk F (on the subsurface of  $TiO_2$ , below 5 nm depth) for the construction of DFT model. As shown in Figure S7, after the fluorination, the impurity level of F- $TiO_{2-x}$  still exhibits a distinct upper-shift. The result indicates that the bulk F plays an ignorable role for the upper-shift of  $Ti^{3^+}$  levels in F-MSCs. Hence, the DFT calculation results suggest that the F atoms for the substitution of oxygen vacancies in the  $TiO_{2-x}$  can induce the elevation of impurity levels and the decrease of  $Ti^{3^+}$ , which is very consistent with the Mott–Schottky plots and EPR results in Figure 2c, d and 1b.

Theoretically, there are two possibilities for the elevation of impurity levels in F-MSCs: one is the overall upward mobility and the other the upsweep. The impedance, photocurrent and photoluminescence (PL) emission spectra were measured to eliminate the possibility of overall upward mobility of impurity levels, as seen in Figure S8. Otherwise, the conductivity, PL intensity and photocurrent intensity should display an obvious reduction, due to the widening of bandgap of TiO<sub>2-x</sub>. In our case, the impedance and conductivity of F-MSCs showed no sign of waning (Figure S8a), indicating efficient electron transfer in the single crystal. Interestingly, the photocurrent intensity of F-MSCs was higher than that of MSCs (Figure S8c). Theoretically, there are two possibilities for the enhancement of photocurrent intensity over F-MSCs: one is the improvement of separation efficiency of photo-generated carriers, and the other is the increase of the kinetic over-potential ( $\Delta$ E) of electrons. However, the unchanged PL intensity of F-MSCs indicated that this enhanced photocurrent intensity was not induced by the improvement of electron-hole separation efficiency (Figure S8b). Hence, we can infer that the enhanced photocurrent intensity of F-MSCs is induced by the increase in  $\Delta$ E, which further allows us to

conclude that the Ti<sup>3+</sup> impurity level in F-MSCs is upswept by the fluorination. The enhanced photocurrent intensity of F-MSCs indicated that the F-TiO<sub>2-x</sub> has much more electrons escaping from the impurity levels than the TiO<sub>2-x</sub>, owing to the presence of polarization effect. However, once we added a 10 mV bias voltage during the photocurrent measurement, the photocurrent intensity of TiO<sub>2-x</sub> changed to close to that of F-TiO<sub>2-x</sub> (Figure S8d). Under the same external voltage, the bending band of MSCs turned to be more flat than that of F-MSCs, owing to the stronger band bending degree of F-MSCs than TiO<sub>2-x</sub>. Hence, there were many electrons escaping from the bending band over TiO<sub>2-x</sub> under an external voltage, whose current intensity equaled to the intensity of F-TiO<sub>2-x</sub>. This result further confirmed the existence of strong bending band in F-MSCs. Additionally, the very similar photocurrent between Cal-MSCs and F-Cal-MSCs suggested that the establishment of internal electric field was caused by the interaction between Ti<sup>3+</sup> and substitution fluorine (Figure S9). Doping of F in TiO<sub>2</sub> induced a certain degree of lattice distortion, which reduced the symmetry of the lattice. Meanwhile, the Ti<sup>3+</sup> could interact with the neighboring F to build an internal electric filed, owing to the strong electronegativity of fluorine.<sup>21</sup>



**Figure 4.** (a) Time course evolution of CH<sub>4</sub> production over different samples under the solar light irradiation for 4 h (300 W Xenon lamp with an AM 1.5 filter,  $CO_2 + H_2O$ ). (b) Selectivity of photocatalytic reduction of  $CO_2$  and  $H_2O$  vapor over MSCs and F-MSCs (Selectivity of CH<sub>4</sub> =  $[8n(CH_4)]/[2n(CO) +8n(CH_4) + 2n(H_2)] \times 100\%$ , Selectivity of CO =  $[2n(CO)]/[2n(CO) +8n(CH_4) + 2n(H_2)] \times 100\%$ ).<sup>34, 35.</sup> (c) Time course evolution of CH<sub>4</sub> production over F-MSCs under continuous illumination for 16 h (300 W Xenon lamp with an AM 1.5 filter,  $CO_2 + H_2O$ ). (d) F 1s XPS spectra of F-MSCs before and after CO<sub>2</sub> photoreduction (continuous illumination for 16 h). (e) Scheme illustration of the difference of Ti<sup>3+</sup> impurity levels between MSCs and F-MSCs.  $\Delta E$  represents the kinetic over-potential of the reduction process.

Internal electric fields in photocatalysts can arise from ferroelectric property, which is induced by the polarization effect.<sup>21</sup> With the introduction of F atoms (substitution for oxygen

vacancies) in the surface layer of  $TiO_{2-x}$ , some  $Ti^{3+}$  ions on F-type color centers are oxidized to  $Ti^{4+}$  owing to the strong electronegativity of fluorine,<sup>18</sup> which enhance the ionic polarization effect between color centers and fluorine ions.<sup>20</sup> Furthermore, a substitutional fluorine atom at the crystal surface causes surface lattice deformation, which can destroy the centrosymmetry of  $TiO_2$  crystal. The positive and negative charges with di  $\Box$  erent centers of symmetry can also enhance the polarization effect.<sup>21</sup> As a result, the  $Ti^{3+}$  impurity level has an upsweep in F-MSCs. Under solar light irradiation, some electrons on the  $Ti^{3+}$  impurity band are heated rapidly due to more metallic nature of F-TiO<sub>2-x</sub> after fluorination. The heated electrons have a higher "transient energy" than the work function of the material; as a result, they can escape from the impurity levels of F-TiO<sub>2-x</sub> to take part in the CO<sub>2</sub> reduction (detailed discussion in Figure S10).



**Figure 5.** (a) HRTEM image of F-Pt-MSCs. (b) EPR spectra of fluorinated sample with and without platinum on 77 K. (c) Time course evolution of CH<sub>4</sub> production over different samples in 8 h. (d) *In situ* FTIR spectra of CO adsorption over the samples under adsorption saturation and evacuation by argon for 30 min (insert).

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As expected, F-MSCs displayed significantly enhanced production of CH<sub>4</sub> than MSCs or Degussa P25 titania powders under solar light irradiation (Figure 4a), indicating its outstanding advantages in CO<sub>2</sub> deep photoreduction. First we have to exclude the effect of CO<sub>2</sub> adsorption. The CO<sub>2</sub> adsorption capacity of different samples have been tested, as shown in Figure S11. We can conclude that the CO<sub>2</sub> adsorption plays no key role in the enhancement of CO2PR performance over F-MSCs. The turnover number (TON) of different photocatalysts in CO2PR was shown in Table S1 (details in Supporting Information). As a result, the TON of F-MSCs (0.98) is much higher than that of MSCs (0.095). The low activities of Cal-MSCs and F-Cal-MSCs highlight the importance of Ti<sup>3+</sup> self-doping in enhancing solar light harvesting for CH<sub>4</sub> generation. It is worth mentioning that if argon was used as the reaction gas instead of CO<sub>2</sub>, no CH<sub>4</sub> could be obtained (Figure S12), indicating that CH<sub>4</sub> is resulted from the reduction of CO<sub>2</sub>.<sup>7</sup> In addition to CH<sub>4</sub>, CO was also generated during CO<sub>2</sub> reduction (Figure S13). While CO represented the primary product over other catalysts in previous reports,<sup>6, 9, 36</sup> in our case CH<sub>4</sub> was the main product when F-MSCs were used as the catalyst. In order to characterize in detail the intermediates formed in the CO2PR reaction, the diffuse reflectance infrared Fouriertransform spectroscopy (DRIFTS) analysis was performed.<sup>37, 38</sup> We can infer that the CO2PR reaction on F-MSCs was initiated with the adsorption of CO<sub>2</sub> molecules on the surface oxygen vacancies. Afterwards, under light irradiation, the adsorbed CO2 molecules were activated, generating negatively charged intermediate species such as m-CO32-, b-CO32-, and CO2-. Subsequently, these intermediates underwent the proton coupled electron transfer (PCET) route and generated CO or CH<sub>4</sub> (detailed discussion in Figure S14). The direct photoreduction of CO over F-MSCs was also presented in Figure S15. The CH<sub>4</sub> yield over F-MSCs was also much higher than that of MSCs, indicating that dominant CH<sub>4</sub> production was due to the fast reduction

of CO to CH<sub>4</sub>. Our careful calculation suggests that the yield of CH<sub>4</sub> can be increased 13 times from 0.125 with MSCs to 1.63  $\mu$ mol/g h with F-MSCs, and the CH<sub>4</sub> selectivity can be improved from 25.7% to 85.8% (Figure 4b). Remarkably, F-MSCs still have a relatively stable CH<sub>4</sub> yield even after 10-16 h of continuous irradiation (Figure 4c and S16). Even after 16 h continuous illumination, the substitutional F in F-MSCs showed almost no change (Figure 4d), indicating the high stability of the fluorinated photocatalyst. Furthermore, the results of photocurrent, UV-DRS and Mott-Schottky plots over the used F-MSCs confirm the stability of the internal electric fields in F-MSCs (details in Figure S17). For  $TiO_{2-x}$ , the  $Ti^{3+}$  impurity level is approximately located below the CB of 0.11 eV (Figure 2a,d), which is 0.39 eV higher than that of CO<sub>2</sub>/CH<sub>4</sub> potential (-0.63 eV vs -0.24 eV). After fluorination, the kinetic over-potential ( $\Delta E$ ) increased from 0.39 eV to 0.48 eV (Figure 4e), which indicated a stronger reduction potential of F-MSCs than MSCs.<sup>14</sup> In addition to the rutile MSCs, the anatase TiO<sub>2-x</sub> after fluorination also exhibited a distinct upper-shift of impurity levels (details of DFT in Figure S18) and an obvious enhancement of CH<sub>4</sub> generation under solar light irradiation (Figure S19), which demonstrated the general applicability of the fluorination strategy in inducing strong reduction potential for enhanced photocatalytic  $CO_2$  reduction. And the surface fluorination over anatase (without  $Ti^{3+}$ ) cannot greatly improve the CO<sub>2</sub> photoreduction for the CH<sub>4</sub> generation. It is worth noting that the fluorine modified anatase (F-Ti<sup>3+</sup>-Anatase: 5.57  $\mu$ mol/h/g) shows a relatively higher CH<sub>4</sub> yield than most of the recently reported photocatalysts in CO<sub>2</sub> reduction, as shown in Table S2.

The photocatalytic activity over F-MSCs with different F doping level was studied to reveal the role of the concentration of  $Ti^{3+}$ . With the increase of the concentration of F, the CH<sub>4</sub> production yield over F-MSCs (m%) increased first and then decreased, as shown in Figure S20. All the fluorination modified catalysts show an obviously enhanced CH<sub>4</sub> production compared

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with MSCs, which further confirms the modulation of the reduction potential of TiO<sub>2-x</sub> by fluorination for the efficient and selective CH<sub>4</sub> generation from CO<sub>2</sub> photoreduction. Seen from the F 1s XPS spectra of Figure S21, compared with the peak of MSCs, the characteristic peaks of F-MSCs (m%) are all obviously enhanced and moved to the higher binding energy, confirming the introduction of substitutional F in MSCs. With the increase of the concentration of F from 4.7% to 8.5%, the relative intensity of the characteristic peak of surface Ti-F (683.7 eV) increased from 24.1% to 43.7%. Interestingly, the concentration of F has a great influence on the Ti<sup>3+</sup> content in MSCs, as shown in Figure S22. We have demonstrated that the after-treatment of fluorination can decrease the Ti<sup>3+</sup> concentration due to the substitution of F for oxygen vacancy and the building of internal electric field. When the F amount was fixed at 4.7%, there was a distinct decrease of Ti<sup>3+</sup> in F-MSCs, compared with that of MSCs. It indicates that the F atoms preferentially displace surface or subsurface oxygen vacancies and build an internal electric field in the process of fluorination, resulting in a rapid decrease in Ti<sup>3+</sup> concentration. With the continued increase of F from 4.7% to 6.3%, the Ti<sup>3+</sup> concentration starts to pick up, but still less than the original value of MSCs. With the increase of F, the surface Ti-F increased gradually, which would induce some new defects appearing on the surface of the catalyst, owing to the oxygen deficiency or interstitial fluorine induced by the excessive fluorination.<sup>39</sup> As a result, the  $Ti^{3+}$  increases with the increase of F from 4.7% to 6.3%. When the amount of F reaches 8.5%, the newly generated Ti<sup>3+</sup> EPR signal over F-MSCs has exceeded the original signal of MSCs. The excessive  $Ti^{3+}$  is likely to become a new electron-hole recombination center, which is not conducive to the occurrence of CO<sub>2</sub> photoreduction. Therefore, the F-MSCs (8.5%) display a decreased CH<sub>4</sub> production yield compared with that of F-MSCs (5.5%). Despite all this, the activity of all the fluorinated catalysts was much higher than that of blank samples.

To highlight another advantage of fluorination of TiO<sub>2-x</sub>, we loaded Pt nanoparticles on the surface of MSCs and followed by post-fluorination using a similar procedure for F-MSCs to produce a control sample of F-Pt-MSCs. The TGA and C1s XPS spectra of the samples before and after modification indicate the absence of carbon impurities during the fluorination and Pt loading treatment (Figure S23a,b). The UV-DRS spectrum of the MSCs treated in the isopropanol (IPA) indicate that the solvothermal treatment (without NH<sub>4</sub>F) does not affect the Ti<sup>3+</sup> (Figure S23c). Analyses by TEM and HRTEM suggested that the Pt nanoparticles were highly dispersed on the surface of MSCs (Figure 5a). After Pt loading, the Ti<sup>3+</sup> concentration was about the same as that of F-MSCs (Figure 5b), which ensured the formation of internal electric field in F-Pt-MSCs. As predicted, the F-Pt-MSCs exhibited a significantly higher activity for the CH<sub>4</sub> generation from CO<sub>2</sub> photoreduction than F-MSCs, Pt-MSCs and other references (Figure 5c). We have shown the original samples that treated in the same conditions, i.e. without  $NH_4F$  by the IPA only involved solvothermal method in the Figure 5c (MSCs (IPA only)). The low activity of MSCs (IPA only) indicates the solvothermal treatment (without NH<sub>4</sub>F) cannot enhance the CO2PR performance. The quantum yield (QY) of F-Pt-MSCs was 0.038% (Table S3). Most importantly, the F-Pt-MSCs could keep a very stable CH<sub>4</sub> generation rate even after continuous illumination for 8 hours. However, the conventional Pt-MSCs has an unstable activity for the CH<sub>4</sub> generation, owing to poisoning of the Pt surface by the adsorption of the by-product of CO.40 To investigate the cause of the high stability of F-Pt-MSCs, we have studied the adsorption and desorption of CO on various samples using in situ infrared spectroscopy (Figure 5d). The peaks in the range of  $2100 \sim 2200 \text{ cm}^{-1}$  could be ascribed to the characteristic adsorption of CO molecules on TiO<sub>2</sub>,<sup>41, 42</sup> and the small peak at about 2030 cm<sup>-1</sup> could be assigned to CO adsorption on the Pt surface.<sup>43</sup> After purging with Ar gas, only the characteristic peak of CO

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adsorption on the Pt remained in the IR spectra (inset of Figure 5d). Moreover, the peak intensity of F-Pt-MSCs was very close to that of Pt-MSCs, implying the fluorination could not decrease the CO adsorption on Pt. In our case, the Pt NPs not only act as the electron trapping agent but also become the active sites in CO2PR. According to our previous DFT calculations,<sup>44</sup> the hydrogenation of \*CO and \*COH require the highest energy barrier (the total free energy in these two steps on Pt(111) is 0.74 eV), which become the rate limiting steps in CO2PR. Considering the fact that the F-Pt-MSCs not only showed the enhanced charge separation efficiency (highest reacted electrons' number in Table S4), but also possessed elevated CB level, the F-Pt-MSCs could provide sufficient electrons with strong reduction potential to promote the deep reduction of \*CO to generate  $CH_4$  in CO2PR. Hence, we believe that the enhanced photocatalytic activity of F-Pt-MSCs is not due to direct inhibition of Pt poisoning. Rather, it is mainly caused by the deep reduction from CO to  $CH_4$ , which decreases the standing time of CO on Pt and thereby reduces the possibility of CO poisoning on Pt.

In order to reveal the key parameters that determine the products' yield and selectivity in  $CO_2$  photocatalytic reduction (CO2PR), the main products' yield, reacted electrons' number and selectivity for CH<sub>4</sub> over different photocatalysts in CO2PR are summarized in Table S4. Apparently, both the F-MSCs and F-Pt-MSCs show enhanced CH<sub>4</sub> yield and selectivity; on the contrary, the main product of MSCs and F-Cal-MSCs is CO and the mixture of CO and H<sub>2</sub>, respectively. Based on the Mott-Schottky plots (Figure 2c,d and Figure S5b,c), there's no doubt that all of the above samples possessed suitable reduction potential which could trigger both the CO2PR reaction and hydrogen evolution reaction (HER) (eqs. (4)~(6) in Supporting Information) in thermodynamics.<sup>14</sup> Therefore, the distinct difference of products yield acquired by different photocatalysts was illustrated in both surface catalytic reaction and charge separation

efficiency. As for the MSCs and its fluorination derivatives, there exists abundant surface oxygen vacancies (Figure 1b and Figure 5b). Hence, the CO<sub>2</sub> molecules tend to be adsorbed and activated on these oxygen vacancies<sup>45, 46</sup> and the competitive hydrogen evolution reaction could be greatly suppressed. However, after the calcination treatment in air, the oxygen vacancies of Cal-MSCs would vanish, in this case, the H<sub>2</sub>O molecules tend to be adsorbed and generate H<sub>2</sub> in the photocatalytic reaction, hence the F-Cal-MSCs show the highest hydrogen yield (Table S4). Thereafter, the surface catalytic reaction towards CH<sub>4</sub> was determined by the charge separation efficiency and enlarged reduction potential of the photocatalyst.<sup>47</sup> The conduction band of F-MSCs was elevated by the polarization effect of the lattice interval F, therefore, F-MSCs possessed more negative reduction potential compared with MSCs, which could trigger the 8electron CH<sub>4</sub> generation reaction. In addition, F-Pt-MSCs with enhanced charge separation efficiency, which could further improve the generation of  $CH_4$  and show the highest yield and selectivity (Table S4). In sum, F-MSCs and F-Pt-MSCs not only contain surface oxygen vacancies but also display elevated reduction potential, thus could promote the CO2PR for enhanced selective CH<sub>4</sub> formation both thermodynamically and kinetically.

In conclusion, we have developed an effective fluorination strategy to enhance the reduction potential of  $TiO_{2-x}$  while maintaining the efficient solar light harvesting. The interaction between  $Ti^{3+}$  and substitutional fluorine contributed to the establishment of internal electric fields in  $TiO_{2-x}$ , which led to the upsweep of  $Ti^{3+}$  impurity level. The fluorinated  $TiO_{2-x}$  showed a high  $CH_4$  production yield and excellent selectivity for  $CO_2$  photoreduction under solar light irradiation. Our research provides a novel metal-free strategy for deep photoreduction of  $CO_2$  and efficient generation of  $CH_4$ , which is expected to have its high impact in addressing both environmental and energy challenges.

# ASSOCIATED CONTENT

# **Supporting Information**.

The Supporting Information is available free of charge on the ACS Publications website at DOI:

# XXXX

Experimental procedures, summary of different catalytic systems, and additional

characterizations (file type, i.e., PDF)

# Notes

The authors declare no competing financial interest.

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