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# Rational Design of Metal Node-modified Ti-Based MOFs for Selective Photoreduction of Carbon Dioxide to Ethanol by Computational Screening

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In this work, density functional theory (DFT) calculations were conducted to investigate a series of metal node-modied Ti-MOF catalysts using transition metals (Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Os, Ir, Au) introduced into Ti-ATA (ATA = 2-aminoterephthalic acid) for the photocatalytic reduction of CO<sub>2</sub> to C<sub>2</sub> products. CO<sub>2</sub> can be sufficiently activated on Ti(M)-ATA but the adsorption configuration depends on the nature of M. Over Ti(Nb)-ATA, Ti(Ta)-ATA, Ti(Zr)-ATA and Ti(Hf)-ATA, the two \*CHO species undergo C-C coupling to form \*CHOCHO, the important C<sub>2</sub> intermediate. Ti(Nb)-ATA and Ti(Ta)-ATA tend to generate ethanol, while Ti(Zr)-ATA and Ti(Hf)-ATA are more selective to ethylene. Among the Ti(M)-ATA candidates studied, Ti(Nb)-ATA was identified as the most active catalyst for CO<sub>2</sub> reduction to ethanol due to its smallest limiting free energy change (1.12 eV), over which the \*CH<sub>2</sub>CH<sub>2</sub>O reduction to \*CH<sub>2</sub>CH<sub>2</sub>OH was found to be the ratedetermining step. The correlation curve analysis illustrates that the reduction activity of Ti(M)-ATA catalysts is highly dependent on the binding strength of CO<sub>2</sub> and key reaction intermediate such as \*OCHOH. The analysis of electronic and optical properties indicates that the altered energy band structure and charge transfer behavior around the bimetallic nodes of Ti(Nb)-ATA account for its excellent catalytic activity for CO<sub>2</sub> reduction to ethanol.

#### 1. Introduction

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The utilization of fossil fuels for the production of various industrial products emits large amounts of carbon dioxide  $(CO_2)$  into the atmosphere, leading to serious environmental problems.<sup>1,2</sup> Coping these challenges, catalytic conversions of CO2 into valuable chemicals via sustainable strategies offer promising approaches.<sup>3,4</sup> The photocatalytic reduction driven by the renewable solar energy can convert CO<sub>2</sub> into liquid fuels and value-added chemicals such as ethanol, olefins, and carboxylic acids, which is widely recognized as a sustainable and green manner for CO<sub>2</sub> conversion.<sup>5-7</sup> Photocatalytic reduction of CO<sub>2</sub> to C<sub>2</sub> chemicals is economically more valuable and the process involves multi-electron transfer and multi-proton activation processes. However, the insufficient interactions of CO<sub>2</sub> molecules with the active sites of catalysts, the difficulty of CO<sub>2</sub> activation, and retarded C-C coupling kinetics lead to the limited formation of C2 products with lower selectivity and yields.8 Therefore, the rational design of highly efficient and selective photocatalysts with multi-functional active sites to exert the synergistic effects is urgently desire to tune the catalytic activity and selectivity to  $C_2$  products.

Over the past few years, a new class of semiconductor-like crystalline porous materials known as metal-organic frameworks (MOFs) has attracted increasing attention in the field of heterogeneous catalysis, gas storage, and separation.<sup>9,10</sup> MOFs are composed of inorganic metal ions and organic ligand featured with well-defined structures, high porosity, larger surface area, component diversity, and tailorability.<sup>11</sup> Therefore, MOF-based materials possess rich physicochemical properties and unique structural advantages among porous catalytic materials. In particular, the large surface areas and specially designed active sites of MOFs could enrich CO<sub>2</sub> efficiently with superior CO<sub>2</sub> adsorption capacity and stabilize the reaction intermediates, making them promising platforms for the photocatalytic reduction of CO<sub>2</sub> to chemicals and fuels.<sup>12,13</sup>

However, only limited MOF-based photocatalytic systems have been developed for  $CO_2$  reduction and their efficiency to  $C_2$  products is still far from satisfactory. Enhancing the photocatalytic efficiency of MOFs for  $C_2$  formation mainly depends on their ability of generating and maintaining the photogenerated electrons as well as the ability to activate  $CO_2$  and accelerate C-C coupling.<sup>14</sup> Over the past decade, researchers have designed strategies to improve the photocatalytic performance of MOFs as summarized below:

(1) By constructing efficient active sites and using the chelating effect of ligands to immobilize atomically dispersed single/dual metals to promote the photocatalytic reaction.<sup>15-17</sup> For example, our group successfully synthesized a novel Ti-based MOF photocatalyst denoted as Fe/Ti-BPDC (BPDC = 2,2'-bipyridine-5,5'-dicarboxylic acid)

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with atomically dispersed Fe sites, which exhibited high activity and selectivity for CO2 reduction to HCOOH, with a yield of 703.9  $\mu mol~g^{-}$ <sup>1</sup> h<sup>-1</sup> and a selectivity greater than 99.7 %.<sup>18</sup> Illuminated by the experimental work, we proposed a new strategy for designing metal and single-atom-modified dual-atom-modified Ti-BPDC photocatalysts through structural and electronic modulation for CO<sub>2</sub> reduction to C<sub>1</sub> and C<sub>2</sub> products using density functional theory (DFT) calculations.<sup>19,20</sup> The computational results of structure-activity volcano curves show that metal single-atom modified Fe/Ti-BPDC  $(\Delta G_{L} = 0.40 \text{ eV})$  and Pd/Ti-BPDC  $(\Delta G_{L} = 1.17 \text{ eV})$  are optimal candidate catalysts for the photoreduction of CO<sub>2</sub> to HCOOH and CH<sub>3</sub>OH, respectively,19 due to their relatively small limiting free energy changes compared to those reported in the literature.<sup>21</sup> Furthermore, metal dual-atom-modified Ti-BPDCs such as Cu-Sn/Ti-BPDC ( $\Delta G_L$  = 0.20 eV) and Cu-Os/Ti-BPDC ( $\Delta G_L$  = 0.70 eV) show enhanced activity toward the generation of HCOOH and CH<sub>3</sub>OH products from CO<sub>2</sub> photoreduction compared to metal single-atom modified Fe/Ti-BPDC and Pd/Ti-BPDC. In particular, the dual- metal atom-modified Cu-In/Ti-BPDC ( $\Delta G_L$  = 1.37 eV) exhibits improved activity and selectivity towards the generation of C<sub>2</sub> products (mainly C<sub>2</sub>H<sub>4</sub>).<sup>20</sup>

(2) Light absorption efficiency can be improved by choosing the right ligands. For example, in order to improve the optical properties of MIL-125 (Ti) MOFs, researchers successfully shifted MIL-125 (Ti) to visible range by introducing the 2-aminoterephthalic acid (ATA) ligand with broad spectral response, enhancing the visible light absorption of the MOF materials.<sup>22</sup> Sun et al. reported that the MIL-125-NH<sub>2</sub>(Ti) with {110}/{111}-heterojunction yields 10 and 18 times CO and CH<sub>4</sub> products from CO<sub>2</sub> photoreduction compared with the single {001} facet; DFT calculations identified energetically favorable pathways and rate-limiting steps for CO<sub>2</sub> reduction on different low-index surfaces of MIL-125-NH<sub>2</sub>(Ti) in their studies.<sup>23</sup>

(3) In addition, metal substitution/doping has been demonstrated to be an effective method to improve the performance of MOF-based photocatalysts. One of the effective strategies is to construct the bimetallic assemblies by partially replacing a node metal in MOFs with another metal. The bimetallic assemblies can harvest visible light and the doped metal cations can act as electronic mediators to promote charge transfer, facilitating the photocatalytic processes.<sup>24</sup> In particularly, partial substitution of metal cations in MOFs can lead to the formation of oxygen-bridged heterometallic structures within the framework, which could exhibit enhanced photocatalytic performance due to the structural flexibility and tunability of the designed MOFs.<sup>25</sup> For example, Ti-substituted NH<sub>2</sub>-UiO-66 (Zr/Ti) was prepared by Li et al. by using the postsynthesis exchange (PSE) method which exhibits good catalytic performance for the photoreduction of  $\ensuremath{\text{CO}}_2$  to formic acid under visible light with a yield of 5.8 mmol mol<sup>-1</sup> for 10 h; DFT calculations and electron spin resonance (ESR) results indicate that the introduction of Ti substituents as a mediator promotes the electron transfer, which improves the photocatalytic performance.<sup>25</sup> In addition, Truhlar et al. used UiO-66 as the basic skeleton and replaced partial Zr atoms in the nodes with metals such as Hf, Th, Ti, U, Ce, etc.; DFT calculations show that the UiO-66(Ce) effectively promotes the electron-hole separation due to the fact that Ce4+ in the material has a low-energy 4f vacancy orbital, which can be used

Based on the literature survey and prior studies in our group, the structures and properties of ligands in MOF materials have important impacts on the photocatalytic performance of CO2 reduction. On the one hand, metal single-atom and dual-atom assemblies can be stably anchored with N-containing ligands within the MOF framework to improve the efficiency of CO<sub>2</sub> activation and conversion.<sup>18-20,27</sup> On the other hand, metal-modified nodes can effectively regulate the light absorptionand electron-hole separation efficiency, and provide special active sites to further tune the activity and selectivity of MOF-based catalysts for CO<sub>2</sub> photoreduction.<sup>25,26,28</sup> However, the directional control of CO<sub>2</sub> reduction products remains challenging, especially for the generation of C<sub>2</sub> products. Due to the complex mechanisms of adsorption/activation of CO2 and cleavage/reconstruction of C=O double bonds over the active sites of catalysts, the principles for the formation and transformation of key intermediates and electron-proton transfer in the reaction processes are still not clear, which make it difficult to regulate the conversion paths and target products.

The limited efficiency of MOF-based photocatalysts in the reduction of CO<sub>2</sub> to C<sub>2</sub> products (e.g., ethanol and ethylene) stems from several intrinsic challenges, among which insufficient activation of CO<sub>2</sub>, slow kinetics of C-C coupling, and generation of key intermediates required for C-C coupling are the major bottlenecks.<sup>29</sup> On the one hand, many MOFs lack robust adsorption sites (e.g., metal active sites or Lewis base sites) to activate the linear structure of CO<sub>2</sub>, which prevents the reduction of CO<sub>2</sub> to the critical \*HCOO or \*COOH intermediate. On the other hand, the C<sub>2</sub> product generation requires multiple electrons, but MOFs usually lack efficient charge transport channels to deliver electrons quickly. In addition, the lack of bimetallic site nodes in some MOF materials leads to weak stability of C-C coupling intermediates. To summarize, the synergistic optimization of CO2 adsorption/activation, electron transfer, intermediate stability, and C-C coupling kinetics inside MOF materials are crucial factors to overcome the inefficiency of MOFbased photocatalysts for the production of C<sub>2</sub> products.

Inspired by our previous experimental studies on Ti-based MOFs and the potential application of 2-aminoterephthalic acid (ATA) ligand in MOFs for photocatalysis,<sup>30,31</sup> the present work systematically investigated the adsorption/activation and reduction of CO<sub>2</sub> to C<sub>2</sub> products (mainly ethanol and ethylene) on a series of metal node-modified Ti(M)-ATA MOFs (ATA = 2-aminoterephthalic acid, M = Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Os, Ir, Au) by means of DFT calculations. By screening these heterometallic node structures via structure-activity correlation, the Ti(Nb)-ATA is identified as the most active photocatalyst for CO<sub>2</sub> reduction to ethanol ( $C_2H_5OH$ ), with a limiting free energy change of 1.12 eV associated with the  $^{*}CH_{2}CH_{2}O \rightarrow ^{*}CH_{2}CH_{2}OH$  step. Electronic property analysis further demonstrates that the computationally designed Ti(Nb)-ATA MOF catalyst via node modification is more favorable for the photocatalytic reduction of CO<sub>2</sub> to C<sub>2</sub> compared to the unmodified Ti-ATA and other Ti-based MOFs such as Ti/BPDC and MIL-125-NH<sub>2</sub>(Ti). In addition, we also find that the node-modified metal in different groups of the periodic table leads to different  $C_2$ products. For example, Ti(Ta)-ATA and Ti(Nb)-ATA tend to generate

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ethanol, while Ti(Zr)-ATA and Ti(Hf)-ATA are more selective to ethylene.

#### 2. Computational models and methods

The present work builds on the recent experimental studies by He et al. in our group, where characterization by X-ray diffraction (XRD) showed that the synthesized Ti-BPDC (BPDC= 2,2'-bipyridine-5,5'dicarboxylic acid) has a high crystallinity; the Ti and O atoms are periodically aligned to form Ti-O layers, and the Ti-O layers connected to the organic ligand are parallel to each other.<sup>18,30</sup> To construct the computational models in this work, we chose 2aminoterephthalic acid (ATA) as the linker instead of BPDC and the aforementioned Ti-MOF as the basic framework. Within the constructed Ti-MOF catalyst, the Ti and O atoms in the nodes of MOF exhibit periodically arranged Ti-O layers, with each Ti atom connected to six O atoms to form Ti-O clusters, in which two of the O atoms belong to the ATA linker and four of the O atoms are from the Ti-O layers, as shown in Fig. 1(a) and (c). A periodic cell of Ti-ATAbased MOF with a lattice constant of 6.44 Å × 21.75 Å × 7.40 Å was built for modelling (Fig. 1(a)). Then, representative metals including Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Os, Ir, and Au were selected as doping metals for node modification (denoted as Ti(M)-ATA) (Fig. 1(b)). According to the literature, bimetallic assemblies with Ti-O-M bridged oxygen structures are formed in typical Ti-ATA MOF materials through metal substitution in the modification processes.<sup>25</sup> Here, when introducing the second metals into Ti-ATA, two possible configurations were considered, i.e. one is the formation of Ti-Ti diagonal structure in one parallelogram of node center which separates the second metals into different parallelograms, and the other is the formation M-M diagonal structure in one parallelogram of node center within MOF, separating the Ti atoms into different parallelograms, as illustrated in Fig. 1(d).



**Fig. 1** (a) The optimized structure of Ti-ATA (ATA=2aminoterephthalic acid) framework. (b) Representative 3d (Mn, Fe, Co, Ni, Cu, Zn), 4d (Zr, Nb, Mo, Ru, Rh, Pd), and 5d (Hf, Ta, W, Os, Ir, Au) metals selected as doping metals for node modification in Ti(M)-ATA catalysts. (c) Structure of the 2-aminoterephthalic acid (ATA) linker. (d) Two possible node configurations formed in Ti(M)-ATA catalysts.

All-electronic approach implemented in the Vienna, Ab-initio Simulation Package (VASP) program was Used 100 perform 3 phin polarized DFT calculations.<sup>32,33</sup> The projector-augmented wave (PAW) pseudopotentials were used to deal with the electron-ion interactions. The Perdew-Burke-Ernzerhof (PBE) functional in the generalized gradient approximation (GGA) was used to calculate the exchange-correlation energies of electrons.<sup>34</sup> The Coulomb and exchange interactions were corrected by setting the U<sub>eff</sub> parameter ( $U_{eff}$  = Coulomb U - exchange J) for each transition metal.<sup>35,36</sup> The  $U_{eff}$ parameter for titanium atom was set to 3.0 eV, and that of the remaining metals is given in **Table S1** in the Supporting Information. To include van der Waals (vdW) interactions, the PBE+D3 method was used.<sup>37,38</sup> The valence electrons were described by a plane wave basis set with a cutoff energy of 450 eV. The convergence criteria for all calculated electronic energies and atomic forces were set to 10<sup>-4</sup> eV and 0.03 eV/Å, respectively. Both Ti-ATA and Ti(M)-ATA structures were optimized by a 4 × 1 × 4 k-point for sampling the Brillouin zone in VASP calculations.

The adsorption energy  $(E_{ads})$  of adsorbate onto the catalyst was calculated by the equation of  $E_{ads} = E_{total} - E_{catalyst} - E_{adsorbate}$ , where Etotal, Ecatalyst, and Eadsorbate represent the total energy of the system containing the adsorbate and catalyst, the energy of bare catalyst, and the energy of adsorbate in gas phase, respectively. In order to evaluate the catalytic activity of CO<sub>2</sub> photoreduction over these Ti(M)-ATA catalysts, the free energy change ( $\Delta G$ ) was calculated for each elementary step involved in CO2 reduction process by the formula of  $\Delta G = \Delta E + \Delta E_{ZEP} - T\Delta S$ , <sup>39,40</sup> where  $\Delta E$  is the total electronic energy change obtained by DFT calculations,  $\Delta E_{ZEP}$  is the zero-point energy contribution, T is the temperature at 298. 15 K, and  $\Delta S$  is the entropy change. The zero-point energy and entropy were obtained from vibrational frequency calculations by DFT. The zero-point energies of all adsorbed species are provided in Table S2. In this work, we investigated the reaction pathways for the formation of different  $C_2$  products (mainly  $C_2H_4$  and  $C_2H_5OH$ ) over Ti-ATA and Ti(M)-ATA catalysts, in which protons and photogenerated electrons are added to the reaction intermediates progressively in the presence of a catalyst, ultimately resulting in the formation of C<sub>2</sub> products.

#### 3. Results and discussion

# 3.1 Structural stability of Ti(M)-ATA catalysts and the adsorption of $\ensuremath{\text{CO}}_2$

For clarity, we grouped the introduced second metals (M) into three categories based on their *d* electrons as 3d (Mn, Fe, Co, Ni, Cu, Zn), 4d (Zr, Nb, Mo, Ru, Rh, Pd), and 5d (Hf, Ta, W, Os, Ir, Au). Before exploring the adsorption of CO<sub>2</sub> molecules on the designed Ti(M)-ATA catalysts, we first investigated the structural stabilities of the two types of metal-modified nodes of MOFs (Fig. 1(d)). The calculated DFT energies are presented in Fig. S1, and the results show that Ti(M)-ATA candidates, except Ti(Zn)-ATA, exhibit a periodic enhancement of DFT energies from left to right according to the periodic table of elements. Notably, the absolute energy values of these two different node configurations are not very different. Therefore, we further calculated the substitution energies of bimetallic assembles in Ti(M)-ATA as shown in Fig. S2, and the specific

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values are given in **Table S3**. The results show that considerable negative substitution energies are obtained for Ti(M)-ATA (M= Zr, Nb, Hf, Ta), which range from -0.93 eV to -3.70 eV. However, all other candidate catalysts have positive substitution energy values, indicating that Zr, Nb, Hf, and Ta atoms can bind strongly to the node Ti atom in the MOFs, thus ensuring their high structural stability.

It is worth noting that DFT energy and substitution energy alone are not sufficient to determine the optimal doping model in metal modification. Therefore, we further explored all possible adsorption configurations of CO<sub>2</sub> on the two different node models, considering four different initial adsorption configurations, including \*COO, \*OCO, O\*CO, and O\*OC (\* means adsorption at the doped metal active site). With model structure 1 as shown in Fig. 1(d), after comprehensive structural screening and optimization, it is found that CO<sub>2</sub> is adequately activated on Ti(M)-ATA (M = Nb, Zr, Ta, Hf), with one O atom of  $CO_2$  bonded to the doped metal site in the node and the C atom of CO<sub>2</sub> bonded with the N atom in the ATA ligand, forming a stable \*O(M)-C(N)-O angular adsorption structure, as shown in Fig. 2(a). However, on the catalyst models of Ti(M)-ATA (M = Mn, Fe, Co, Ni, Cu, Zn, Mo, Ru, Rh, Pd, W, Os, Ir, Au), CO<sub>2</sub> shows a linear adsorption configuration and is not bonded to other atoms in the MOF catalysts, as illustrated in Fig. S3. With model

structure 2 as shown in Fig. 1(d),  $CO_2$  exhibits the (Q(Zr)-C(N)-Q)adsorption mode merely on Ti(Zr)-ATA whereas it Shows an intervention adsorption pattern on the rest of the candidate catalysts, as shown in Fig. S4. The adsorption energies of CO<sub>2</sub> on the pristine Ti-ATA and metal-modified Ti(M)-ATA (model structure 1 and model structure 2) were calculated, as shown in Fig. 2(b-d) and Fig. S5, while the specific values of adsorption energies are provided in Table S4. The calculation results show that the adsorption energy values of CO<sub>2</sub> on Ti(M)-ATA (M = Nb, Zr, Ta, Hf) are 0.15, 0.31, -0.10, and 0.26 eV, respectively, which are significantly lower than that obtained over the pristine Ti-ATA catalyst (1.45 eV) and those obtained over other metalmodified Ti(M)-ATA candidate catalysts. Therefore, the Ti(M)-ATA (M = Nb, Zr, Ta, Hf) candidates were chosen for subsequent exploration on reaction pathways and reactivities for CO2 photoreduction to  $C_2$  products. It is worth noting that the adsorption energies of CO<sub>2</sub> on model structure 1 are generally lower than those of model structure 2, as shown in Fig. S5. Based on the calculation results on CO2 adsorption configurations and adsorption energies, the metal-modified model structure 1 exhibits good structural stability, sufficient interactions with CO<sub>2</sub>, and better ability to activate CO<sub>2</sub>, thus was chosen as the representative node-modification model for subsequent study.



**Fig. 2** (a) The optimized stable adsorption configurations of  $CO_2$  molecule on metal-modified model structure 1 of Ti(M)-ATA (M = Nb, Zr, Ta, Hf); (b) The adsorption energies of  $CO_2$  on the pristine Ti-ATA and metal-modified model structure 1 of Ti(M)-ATA (M = Mn, Fe, Co, Ni, Cu, Zn); (c) The adsorption energies of  $CO_2$  on the pristine Ti-ATA and metal-modified model structure 1 of Ti(M)-ATA (M = ATA (M = Zr, Nb, Mo, Ru, Rh, Pd); (d) The adsorption energies of  $CO_2$  on the pristine Ti-ATA and metal-modified model structure 1 of Ti(M)-ATA (M = Ti(M)-ATA (M = Hf, Ta, W, Os, Ir, Au).

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#### 3.2 $CO_2$ reduction mechanisms and catalytic performance of Ti-ATA and Ti(M)-ATA (M = Zr, Nb, Hf, Ta)

Since  $CO_2$  can be sufficiently activated on Ti(M)-ATA (M = Zr, Nb, Hf, Ta), we proceeded to investigate the reaction properties of CO<sub>2</sub> reduction over these candidate catalysts. The reduction of CO<sub>2</sub> to C<sub>2</sub> products can be divided into hydrogenation processes and C-C coupling reaction. In particular, the formation of stable C-C coupling intermediates on the catalyst is a crucial step in the reduction of  $\mathsf{CO}_2$  to  $\mathsf{C}_2$ products, thus we first examined all possible hydrogenation pathways for CO<sub>2</sub> reduction before C-C coupling on pristine Ti-ATA and metal-modified Ti(M)-ATA (M = Zr, Nb, Hf, Ta) candidates, and mapped out the Gibbs free energy diagrams as shown in Fig. 3. The first proton may attack the O or C atom of \*OCO, forming the \*OCOH or \*OCHO intermediate, respectively. For the IVB metals in the periodic table, including single metal Ti, bi-metal Ti(Zr) and Ti(Hf), the \*OCOH intermediate can not be stabilized even after structural optimization and spontaneously transforms into the \*OCHO intermediate. Moreover, it is found that the first hydrogenation step of \*OCO  $\rightarrow$  \*OCHO is thermodynamically quite unfavorable on Ti (Zr) and Ti (Hf), with  $\Delta G$  values of 0.91 and 1.18 eV, respectively, as shown in Fig. 3(b) and (c). Although the hydrogenation of \*OCO to \*OCHO intermediate is slightly uphill ( $\Delta G$  of 0.17 eV) over the pristine Ti-ATA, the  $CO_2$  adsorption/activation process is largely endothermic ( $\Delta G$ of 1.45 eV) on this catalyst, as illustrated in Fig. 3(a). In the next scenario, the continued hydrogenation of \*OCHO to form the

\*OCHOH species is significantly exothermic, releasing the energy of 2.92, 2.77, and 2.81 eV, respectively on the Atta Ti(Zr)-ATA, and Ti(Hf)-ATA. Then, the formed \*OCHOH species needs to overcome large uphill energies ( $\Delta G = 1.48$ , 2.04, and 2.10 eV on Ti-ATA, Ti(Zr)-ATA, and Ti(Hf)-ATA) to dissociate into the key \*CHO intermediate species, releasing a H<sub>2</sub>O molecule simultaneously. Overall, the formation of key \*CHO intermediate on Ti-ATA, Ti(Zr)-ATA, and Ti(Hf)-ATA is quite energy consuming, thus is energetically unfavorable. By contrast, for the VB metals including Ti(Nb) and Ti(Ta), both intermediates can be formed from the first hydrogenation step of \*OCO. Clearly, the \*OCHO intermediate is much more stable than the \*OCOH intermediate, as illustrated in Fig. 3(d) and (e), thus the pathway of further conversion of \*OCOH intermediate is not considered here. Subsequently, the hydrogenation of \*OCHO intermediate on Ti(Nb)-ATA and Ti(Ta)-ATA requires to surmount moderate uphill energies of 0.68 and 0.72 eV, respectively, leading to the formation of \*OCHOH intermediate. In the next step, the continued reduction of \*OCHOH on Ti(Nb)-ATA to form the key intermediate \*CHO is thermodynamically much favorable by releasing an energy of 0.71 eV, whereas the formation of \*CHO species on Ti(Ta)-ATA still needs to overcome an energy rise of 0.35 eV. The above calculation results reveal that the formation of key \*CHO intermediate on the Ti(Nb)-ATA catalyst is thermodynamically more preferred, which plays an important role for subsequent C-C coupling and further reduction to generate C<sub>2</sub> products.



Fig. 3 The calculated Gibbs free energy diagrams for CO<sub>2</sub> reduction steps before C-C coupling on (a) Ti-ATA, (b) Ti(Zr)-ATA, (c) Ti(Hf)-ATA, (d) Ti(Nb)-ATA, and (e) Ti(Ta)-ATA catalysts.

Starting with the formed \*CHO species, all possible pathways and intermediates for the reduction of  $CO_2$  to  $C_2H_4$  or  $C_2H_5OH$  product on pristine Ti-ATA and metal-modified Ti(M)-ATA (M= Zr, Hf, Nb, Ta) were considered, as illustrated in Fig. 4. By comparing the reaction Gibbs free energies, the optimal pathway for  $CO_2$  reduction to  $C_2H_4$  or  $C_2H_5OH$  over

each of the examined catalyst was identified, as shown in Fig. 5(a) and (b), and the optimized structures of relevant intermediates are given in Fig. 5(c) and (d). Other pathways considered and investigated are provided in Fig. S6. In this scenario, we focused on discussing the reaction mechanisms from C-C coupling, as detailed belows:

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(1) According to the free energy diagram in Fig. 5(a), over pristine Ti-ATA, metal-modified Ti(Zr)-ATA and Ti(Hf)-ATA, the two \*CHO species undergo C-C coupling to form the important C<sub>2</sub> intermediate \*CHOCHO (Fig. 5(b)), releasing the energy of 0.98, 1.91, and 1.99 eV, respectively on the three catalysts. Subsequent conversion of \*CHOCHO species leads to the formation of four possible intermediates, namely \*CHOCHOH, \*CHOCH2O, \*CHOHCHO, or \*CH2OCHO. The calculated Gibbs free energies in Fig. S6(a-c) show that the formation of these four intermediates is thermodynamically unfavorable due to the uphill free energy changes, with the \*CHOCHOH species formation having a relatively smaller energy rise than the other three species ( $\Delta G$  = 0.31 (Ti-ATA), 1.17 (Ti(Zr-ATA)), and 1.20 eV (Ti(Hf)-ATA)). The formed \*CHOCHOH intermediate is then reduced by proton-coupled electron transfer to form \*CHOHCHOH, \*CHOCH+H<sub>2</sub>O, \*CHOCH<sub>2</sub>OH, or \*CH<sub>2</sub>OCHOH species. Notably, the  $\Delta G$  values for the formation of \*CHOCH+\*H<sub>2</sub>O on Ti-ATA, Ti(Zr)-ATA, and Ti(Hf)-ATA are -0.78, -1.00, and -1.07 eV, respectively, which are lower than those for the formation of the other three intermediates (Fig. S6(ac)), suggesting that \*CHOCH+\*H<sub>2</sub>O is the preferred intermediate from \*CHOCHOH reduction. In the next step, further reduction of \*CHOCH leads to the formation of \*CH<sub>2</sub>OCH, \*CHOCH<sub>2</sub>, or \*CHOHCH. As demonstrated in Fig. 5(a) and Fig. S6(a-c), the formation of \*CH<sub>2</sub>OCH, \*CHOCH<sub>2</sub>, and \*CHOHCH species is thermodynamically unfavorable due to the uphill free energy changes, but \*CHOCH<sub>2</sub> is relatively more stable than the other two species, with  $\Delta G$  values of 0.67 (Ti-ATA), 0.53 (Ti(Zr)-ATA), and 0.63 eV (Ti(Hf)-ATA), respectively. Subsequently, the \*CHOCH<sub>2</sub> intermediate continues to be reduced to either \*CH<sub>2</sub>OCH<sub>2</sub> or \*CHOHCH<sub>2</sub> species, with the formation of \*CHOHCH<sub>2</sub> species being thermodynamically more favorable, as shown in Fig. S6(a-c). In contrast, the reduction of \*CHOCH<sub>2</sub> to \*CH<sub>2</sub>OCH<sub>2</sub> species is

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thermodynamically unfavorable, with  $\Delta G$  values of  $\Delta G_{1}$ ATA), -0.47 (Ti(Zr)-ATA), and -0.48 eV (ዋዢዙք)-ልፑልነጋቼና ያሸዕጭስ in Fig. 5(a). For the generated \*CHOHCH<sub>2</sub> intermediate, two possible hydrogenation pathways lead to different C<sub>2</sub> intermediates, either the \*CHCH<sub>2</sub> species generation by releasing a H<sub>2</sub>O molecule ( $\Delta G = 0.21$  (Ti-ATA), 0.37 (Ti(Zr)-ATA), and 0.38 eV (Ti(Hf)-ATA)), which is then reduced to \*CH<sub>2</sub>CH<sub>2</sub> (Δ*G* = -0.44 (Ti-ATA), -0.54 (Ti(Zr)-ATA), and -0.61 eV (Ti(Hf)-ATA)), or the generated \*CHOHCH<sub>2</sub> intermediate continues to be hydrogenated into <sup>\*</sup>CH<sub>2</sub>OHCH<sub>2</sub> specie which then further reduces to \*CH<sub>2</sub>OHCH<sub>3</sub>. Finally, the formed \*CH<sub>2</sub>OHCH<sub>3</sub> (\*C<sub>2</sub>H<sub>5</sub>OH) or \*CH<sub>2</sub>CH<sub>2</sub> (\*C<sub>2</sub>H<sub>4</sub>) desorbs from the catalysts. Apparently, the reduction of CO<sub>2</sub> to <sup>\*</sup>C<sub>2</sub>H<sub>4</sub> over Ti-ATA, Ti(Zr)-ATA, and Ti(Hf)-ATA catalysts is more selective (energetically favorable) than \*C<sub>2</sub>H<sub>5</sub>OH according to the calculation results given in Fig. S6(a-c). However, the desorption of formed \*CH<sub>2</sub>CH<sub>2</sub> from catalyst proceeds slowly due to the substantial free energy changes on the three catalysts examined, as shown in Fig. 5(a). Based on the above results, we summarize that the optimal pathway for the photocatalytic reduction of  $CO_2$  to the preferred  $C_2H_4$ product on pristine Ti-ATA, metal-modified Ti(Zr)-ATA and Ti(Hf)-ATA catalysts goes through  $CO_2 \rightarrow OCHO \rightarrow OCHOH$  $\rightarrow$  \*CHO  $\rightarrow$  \*CHOCHO  $\rightarrow$  \*CHOCHOH  $\rightarrow$  \*CHOCH+H<sub>2</sub>O  $\rightarrow$ \*CHOCH<sub>2</sub> → \*CHOHCH<sub>2</sub> → \*CHCH<sub>2</sub> → \*CH<sub>2</sub>CH<sub>2</sub> → \*+C<sub>2</sub>H<sub>4</sub>. According to the free energy diagram in Fig. 5(a), the reduction step of \*OCHOH  $\rightarrow$  \*CHO ( $\Delta G$  = 1.48 (Ti-ATA), 2.04 (Ti(Zr)-ATA), and 2.10 eV (Ti(Hf)-ATA)) has the largest free energy change, which is considered to be the ratedetermining step for the overall reaction. On these three catalysts, the C-C coupling is not difficult to occur with substantially downhill free energy change but the hydrogenation reactions before C-C coupling proceed slowly, especially the generation of key \*CHO intermediate.



**Fig. 4** Possible reaction pathways considered for the reduction of  $CO_2$  to  $C_2$  ( $C_2H_5OH$  and  $C_2H_4$ ) products on (a) Ti-ATA, Ti(Zr)-ATA, Ti(Hf)-ATA and (b) Ti(Nb)-ATA, Ti(Ta)-ATA.

(2) In contrast, the mechanisms of CO<sub>2</sub> reduction to C<sub>2</sub> products on Ti(Nb)-ATA and Ti(Ta)-ATA catalysts are different. According to the free energy diagrams given in Fig. 5(c), for Ti(Nb)-ATA and Ti(Ta)-ATA, the two \*CHO species undergo C-C coupling to form \*CHOCHO (Fig. 5(d)), the important C<sub>2</sub> intermediate, releasing the energy of 1.02 and 1.45 eV, respectively on the two catalysts. Further reduction of \*CHOCHO species has different pathways. As illustrated in Fig. S6(d-e), among the four possible intermediates produced from \*CHOCHO reduction, the formation of <sup>\*</sup>CHOCH<sub>2</sub>O is thermodynamically most favorable, with  $\Delta G$ values of 0.45 and 0.46 eV, on Ti(Nb)-ATA and Ti(Ta)-ATA, respectively. The formed \*CHOCH<sub>2</sub>O species can be further reduced to \*CH<sub>2</sub>OCH<sub>2</sub>O, \*CHOHCH<sub>2</sub>O or \*CHOCH<sub>2</sub>OH. From Fig. S6(d-e), it can be seen that \*CHOHCH<sub>2</sub>O formation has a lower Gibbs free energy change than that of \*CH<sub>2</sub>OCH<sub>2</sub>O and \*CHOCH<sub>2</sub>OH. In the next step, the formed \*CHOHCH<sub>2</sub>O species continues to reduce to three possible intermediates including \*CH<sub>2</sub>OHCH<sub>2</sub>O, \*CHCH<sub>2</sub>O+H<sub>2</sub>O or \*CHOHCH<sub>2</sub>OH. Based on the Gibbs free energy diagrams given in Fig. 5(c) and Fig. S6(d-e), it can be observed that the formation of \*CH<sub>2</sub>OHCH<sub>2</sub>O intermediate is thermodynamically much more favorable ( $\Delta G$  = -0.60 (Ti(Nb)-ATA) and -0.42 eV (Ti(Ta)-ATA)), whereas the formation of \*CHCH<sub>2</sub>O+H<sub>2</sub>O and \*CHOHCH<sub>2</sub>OH intermediates shows large free energy rise. Subsequently, the resulted \*CH<sub>2</sub>OHCH<sub>2</sub>O species either continues to reduce to \*CH<sub>2</sub>OHCH<sub>2</sub>OH species which is thermodynamically unfavorable, or to  $^{\ast}\text{CH}_{2}\text{CH}_{2}\text{O}$  and a H\_2O molecule which is thermodynamically favorable. The  $\Delta G$  values for \*CH<sub>2</sub>OHCH<sub>2</sub>O reduction to \*CH<sub>2</sub>CH<sub>2</sub>O+\*H<sub>2</sub>O on Ti(Nb)-ATA and Ti(Ta)-ATA are calculated to be 0.40 and 0.74 eV, respectively. After the release of  $H_2O$  molecule, the remaining \*CH<sub>2</sub>CH<sub>2</sub>O species can be further reduced by proton coupled electron transfer to produce the \*CH<sub>2</sub>CH<sub>2</sub>OH species. As shown in Fig. 5(b), remarkably, the Gibbs free

energy change of this hydrogenation process increases by 1.12 and 1.62 eV for Ti(Nb)-ATA and Ti(Ta)-ATA, respectively. In the last step, further reduction of \*CH<sub>2</sub>CH<sub>2</sub>OH generates either \*CH<sub>2</sub>CH<sub>2</sub>+H<sub>2</sub>O or \*CH<sub>3</sub>CH<sub>2</sub>OH. Unlike Ti-ATA, Ti(Zr)-ATA, and Ti(Hf)-ATA, it is clear that the generation of \*CH<sub>3</sub>CH<sub>2</sub>OH (\*C<sub>2</sub>H<sub>5</sub>OH) on Ti(Nb)-ATA and Ti(Ta)-ATA is energetically more favorable than the formation of  $^{*}CH_{2}CH_{2}$  ( $^{*}C_{2}H_{4}$ ), as shown in Fig. S6(d-e), and the corresponding  $\Delta G$  values for \*C<sub>2</sub>H<sub>5</sub>OH formation on these two catalysts are -0.78 and -0.54 eV, respectively. It is worth noting that there is a small energy change uphill for the desorption of \*CH<sub>3</sub>CH<sub>2</sub>OH species on Ti(Nb)-ATA, however, the \*CH<sub>3</sub>CH<sub>2</sub>OH desorption is not a high energy-consuming step compared to the preceding step of \*CH<sub>2</sub>CH<sub>2</sub>O reduction to \*CH<sub>2</sub>CH<sub>2</sub>OH with a large positive  $\Delta G$  value, as illustrated in Fig. 5(c). To sum up, for the reduction of CO<sub>2</sub> to the preferred C<sub>2</sub>H<sub>5</sub>OH product on Ti(Nb)-ATA and Ti(Ta)-ATA catalysts, the optimal pathway is identified as  $^{*}CO_{2} \rightarrow ^{*}OCHO \rightarrow ^{*}OCHOH \rightarrow ^{*}CHO \rightarrow$ \*CHOCHO → \*CHOCH<sub>2</sub>O → \*CHOHCH<sub>2</sub>O → \*CH<sub>2</sub>OHCH<sub>2</sub>O →  $^{*}CH_{2}CH_{2}O+H_{2}O \rightarrow ^{*}CH_{2}CH_{2}OH \rightarrow ^{*}CH_{3}CH_{2}OH \rightarrow ^{*}+C_{2}H_{5}OH,$ in which the rate-determining step is discovered to be the reduction step of  $^{*}CH_{2}CH_{2}O \rightarrow ^{*}CH_{2}CH_{2}OH$  due to its maximal free energy change ( $\Delta G = 1.12$  (Ti(Nb)-ATA) and 1.62 eV (Ti(Ta)-ATA)) among all of the elementary steps.

Moreover, we also calculated the kinetic barrier of the rate-determining step in the optimal energy pathway for  $CO_2$  reduction to ethanol on Ti(Nb)-ATA and Ti(Zr)-ATA, as shown in **Fig. S7**. In addition to considering the barrier of rate-determining step, the corresponding reaction rate constant was also calculated and provided in **Table S5**. The results show that the  $CO_2$  reduction has an obvious kinetic advantage on Ti(Nb)-ATA than Ti(Zr)-ATA based on Gibbs free energy barrier and reaction rate constant calculation, which further consolidate the above screening results.



**Fig. 5** The calculated Gibbs free energy diagrams of the optimal paths for  $CO_2$  reduction to  $C_2H_4$  product on (a) Ti-ATA, Ti(Zr)-ATA, Ti(Hf)-ATA and to  $C_2H_5OH$  product on (c) Ti(Nb)-ATA, Ti(Ta)-ATA. Structural illustrations of all stable intermediates associated with the optimal paths on (b) Ti-ATA, Ti(Zr)-ATA, Ti(Hf)-ATA and (d) Ti(Nb)-ATA, Ti(Ta)-ATA. The MOF framework structure is omitted for clarity.

Since the adsorption and activation of  $CO_2$  is an extremely important initial step in  $CO_2$  reduction, as demonstrated in the previous studies,<sup>19,20,41</sup> here we correlated the adsorption energy of  $CO_2$  with the limiting free energy change for the generation of  $C_2$  products ( $C_2H_4$  and  $C_2H_5OH$ ) on the four metal-modified Ti(M)-ATA (M = Zr, Hf, Nb, Ta) catalysts, and plotted the corresponding volcano type curve as displayed in Fig. 6(a). The calculation results show that the Ti(Nb)-ATA catalyst has the lowest limiting free energy change and a moderate  $CO_2$  adsorption intensity, which locates at the top of the volcano-type curve. In addition, we note that the stability of \*OCHOH intermediate affects the next step of dehydration to form the key C-C coupling intermediate of \*CHO, and thus we plotted the volcano type curve of  $G_{*OCHOH}$  and the limiting free energy

change on the four metal-modified Ti(M)-ATA (M = Zr, Hf, Nb, Ta) catalysts, as displayed in Fig. 6(b). The results show that the Ti(Nb)-ATA catalyst remains at the top of the volcano curve, further indicating that the moderate stability of \*OCHOH intermediate over Ti(Nb)-ATA is guite favorable for the subsequent generation of \*CHO intermediate. Therefore, the Ti(Nb)-ATA catalyst would be the best candidate for C<sub>2</sub> production among the four candidates studied. These results further clarify that the adsorption strength of CO<sub>2</sub> reactant and key reaction intermediate (e.g.\*OCHOH) directly affects the CO<sub>2</sub> reduction activity, and the relatively mild bonding of \*CO<sub>2</sub> and \*OCHOH over Ti(Nb)-ATA is responsible for the highest activity of Ti(Nb)-ATA among the screened candidate catalysts. This finding is consistent with our previous studies on CO<sub>2</sub> photoreduction over other Ti-MOF-based catalytic materials.19,20



**Fig. 6** Volcano-type curves between (a)  $CO_2$  adsorption energy, (b)  $G_{*OCHOH}$  and limiting free energy change for  $C_2$  products generation on Ti(M)-ATA (M = Zr, Hf, Nb, Ta) catalysts.

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In addition, we note that CO<sub>2</sub> molecules can be adequately activated when the doped nodal metals are IVB and VB group metals and could provide favorable active sites for CO<sub>2</sub> adsorption and activation. For IVB group metalmodified Ti-ATA, such as Ti(Zr)-ATA and Ti(Hf)-ATA, CO2 photocatalytic reduction tends to generate C<sub>2</sub>H<sub>4</sub> product and share similar reaction pathways. On the contrary, for VB group metal-modified Ti-ATA, such as Ti(Nb)-ATA and Ti(Ta)-ATA, CO<sub>2</sub> photoreduction to C<sub>2</sub>H<sub>5</sub>OH product is energetically more preferred. The calculated limiting free energy change  $(\Delta G_1 = 1.12 \text{ eV})$  over Ti(Nb)-ATA for C<sub>2</sub>H<sub>5</sub>OH generation is even smaller than that ( $\Delta G_{L} = 1.37 \text{ eV}$ ) obtained over the dual metal -atom-modified Cu-In/Ti-BPDC catalyst which was identified to be a good catalyst for  $C_2$  ( $C_2H_4$ ) generation in our previous DFT work.<sup>20</sup> Therefore, it can be proposed that Ti(Nb)-ATA is a promising candidate catalyst for the photocatalytic reduction of CO<sub>2</sub> to C<sub>2</sub> product, especially C<sub>2</sub>H<sub>5</sub>OH. Overall, the calculation results indicate that the ATA ligand with Ti-O-Nb dual-metal-node structure as well as with a broad absorption spectrum effectively improve the photocatalytic efficiency for CO<sub>2</sub> reduction to C<sub>2</sub> products, which are also essential for regulating the catalytic activity and product selectivity of Ti-MOF-based photocatalysts.

The CO<sub>2</sub> photoreduction was typically carried out in the aqueous solution. Under the same conditions, \*H species could be adsorbed on the active site and reduced by the proton-electron pair (H<sup>+</sup> + e<sup>-</sup>), which would affect the photocatalytic efficiency of CO<sub>2</sub> reduction. Here, we calculated the Gibbs free energy diagram of hydrogen evolution reaction (HER) on the Ti(Nb)-ATA catalyst, as shown in Fig. S8(a), which shows that the \*H species is more favorably adsorbed on the Nb atom in the node of Ti(Nb)-ATA. It is worth noting that the limiting free energy change of HER on Ti(Nb)-ATA is calculated to be 1.29 eV, which is higher than that (1.12 eV) of CO<sub>2</sub> reduction, thus the competitive effect of HER is minor. In addition, we also calculated the Gibbs free energy diagrams of CO and HCOOH production from CO<sub>2</sub> reduction on Ti(Nb)-ATA, as shown in Fig. S8(b), and the results show that the stability of \*CHO intermediate is higher than that of CO and HCOOH products, thus the ethanol formation pathway through the CHO\* intermediate is mainly considered in this work.

#### 3.3 Electronic structure and optical property analysis of Ti-ATA and Ti(M)-ATA (M = Zr, Nb, Hf, Ta)

In order to gain fundamental insights into the optical properties of the node-modified Ti-ATA catalysts, we further analyzed the electronic structures of pristine Ti-ATA and the

best active catalyst identified, Ti(Nb)-ATA, by calculating the total and projected density of states (TDOS and PDOS) and band structures, as shown in Fig. 7(a)-(b). The results of other catalysts (Ti(M)-ATA (M = Zr, Hf, Ta)) are provided in Fig. S9(a)-(b). The indirect band gap of unmodified Ti-ATA is 1.54 eV. Compared to the unmodified Ti-ATA, the band gap of metal-modified Ti(Nb)-ATA (1.25 eV) and Ti(Ta)-ATA (1.31 eV) (VB metals in the periodic table) becomes significantly narrower and several new energy bands appear near the Fermi energy level. By contrast, the band gap of Ti(Zr)-ATA (1.77 eV) and Ti(Hf)-ATA (1.79 eV) (IVB metals in the periodic table) is wider and there are no new energy bands near the Fermi energy level. Importantly, a new energy band consisting of transition metal d orbitals is generated near the Fermi energy level of Ti(Nb)-ATA. This energy band has an important contribution near the Fermi energy level and can be used as a doping energy level to promote the separation of photoelectrons and holes by trapping electrons, thus increasing the stability of reaction intermediates and lowering the barriers in the reduction of  $CO_2$  to  $C_2H_5OH$  via photocatalysis. Charge separation is a key step in photocatalysis to convert light energy into chemical energy, and its efficiency directly impacts the performance of the catalyst. In order to further improve the activity and selectivity of CO<sub>2</sub> photoreduction to ethanol, we constructed bimetallic active sites by introducing a second metal component into the metal node of Ti-ATA, effectively regulated the energy band structure of the MOF material, and optimized the separation efficiency of photogenerated electrons. To further analyze the electron transfer behavior during the photocatalytic process, we further calculated the valence band maxima (VBM) and conduction band minima (CBM) of Ti-ATA and Ti(M)-ATA (M = Zr, Hf, Nb, Ta), as shown in Fig. 7(c) and S9(c). For the unmodified Ti-ATA, the VBM is mainly located in the  $\pi$ -bond orbitals of the ligand, whereas the CBM is mainly located in the Ti-oxo cluster. For Ti(Nb)-ATA, electrons are transferred from the excited ATA ligand to the Nb portion, and subsequently, the Nb ions transfer electrons to Ti, forming photocatalytically active Nb ions. The calculation results infer that the modified Ti nodes may act as electronic mediator to facilitate the transfer of electrons from the ATA ligand to Nb site. The emergence of new energy levels in Ti(Nb)-ATA effectively inhibits the rapid electron-hole complexation and provides a more stable platform for photogenerated electrons with superior photocatalytic performance for CO<sub>2</sub> reduction to C<sub>2</sub> products. In addition, according to Bader charge analysis (Fig. S10), the doped metal atoms transfer electrons to bridging oxygen atoms between the Ti atom and doped metal atoms,

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which leads to the accumulation of negative charges around the doped metal center. This result indicates that there is a significant charge transfer in the Ti-O-M (M = Zr, Hf, Nb, Ta) structure, with the Nb dopant transfer the most charge, as evidenced in Fig. S10. Thus, doping another metal into the Ti-MOF can result in a significant charge distribution at the nodes of MOF materials. Overall, the electronic structure characteristics of pristine Ti-ATA and metal-modified Ti(M)-ATA (M = Zr, Hf, Nb, Ta) are generally consistent with the



**Fig. 7** The calculated (a) total and projected density of states (TDOS and PDOS), Fermi energy level set to zero. (b) energy band structures of pristine Ti-ATA and metal-modified Ti(Nb)-ATA. (c) The calculated valence-band maximum (VBM) (left side) and conduction-band minimum (CBM) (right side) of pristine Ti-ATA and metal-modified Ti(Nb)-ATA.

Finally, we calculated the optical absorption spectrum of Ti-ATA and Ti(Nb)-ATA, as shown in Fig. 8(a-b). The optical absorption of Ti-ATA and Ti(Nb)-ATA is mainly located in the ultraviolet region. However, the light absorption activity of the modified nodes was slightly improved. Due to the narrow band gap, the response of Ti(Nb)-ATA in visible and infrared bands is slightly stronger than that of Ti-ATA. The absorption spectra of other Ti(M)-ATA (M= Zr, Hf, Ta) were also calculated, as shown in Fig. S11. In addition, the work function ( $\Phi$ ) is an important parameter to measure the electron gain/loss ability of materials, which is defined as the minimum energy required for electrons to escape from the interior of materials to the surface.<sup>42,43</sup> In DFT calculation, the work function is obtained from the electrostatic potential distribution, which is calculated by the equation of  $\Phi = E_V - E_f$ , where  $E_v$  and  $E_f$  are the potentials of vacuum energy level and Fermi energy level, respectively. As shown in Fig. 8(c-d), the work function of Ti-ATA is calculated to be 4.23 eV (Fig. 8(c)). After the introduction of Nb atom in Ti node, the work function is reduced to 2.91eV (Fig. 8(d)). The work function of other Ti(M)-ATA catalysts is also lower than that of the pristine Ti-ATA (Fig. S12). The values of work function, vacuum energy level and Fermi energy level for Ti-ATA and Ti(M)-ATA are provided in Table S6. Further observation reveals that the decrease of work function is caused by the up shift of Fermi level. As mentioned above, the electrons in the Nb atom transfer to the O atom of node, and the Fermi level of Ti(M)-ATA is enhanced by the Nb-O bonding. The reduced work function is conducive to the transfer of electrons from Ti(M)-ATA to the surfaceadsorbed species in the photocatalytic reaction, delivering improved photocatalytic activity.

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Fig. 8 The optical absorption spectra for (a) Ti-ATA and (b) Ti(Nb)-ATA. The electrostatic potential profiles of (c) Ti-ATA and (b) Ti(Nb)-ATA.

### 4. Conclusions

In summary, by means of DFT calculations, we systematically investigated the structure and stability of a series of metal node-modified Ti(M)-ATA (Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Os, Ir, Au) MOF catalysts and their applications in the photocatalytic reduction of CO<sub>2</sub> to C<sub>2</sub> chemicals. Our results show that Ti(M)-ATA (M = Zr, Hf, Nb, Ta) can sufficiently activate CO<sub>2</sub>, and the energetically optimal pathway in the reduction of CO<sub>2</sub> to C<sub>2</sub> products has been determined by reaction route screening. Over Ti(Nb)-ATA, Ti(Ta)-ATA, Ti(Zr)-ATA and Ti(Hf)-ATA, the two \*CHO species undergo C-C coupling to form \*CHOCHO, the important C<sub>2</sub> intermediate. Ti(Nb)-ATA and Ti(Ta)-ATA tend to generate ethanol, while Ti(Zr)-ATA and Ti(Hf)-ATA are more selective to ethylene. Remarkably, Ti(Nb)-ATA is the best photocatalyst for C<sub>2</sub>H<sub>5</sub>OH production among all candidates studied, and the corresponding optimal reduction pathway is identified as: \*CO<sub>2</sub>  $\rightarrow$  \*OCHO  $\rightarrow$  \*OCHOH  $\rightarrow$  \*CHO  $\rightarrow$  \*CHOCHO  $\rightarrow$ \*CHOCH<sub>2</sub>O  $\rightarrow$  \*CHOHCH<sub>2</sub>O  $\rightarrow$  \*CH<sub>2</sub>OHCH<sub>2</sub>O  $\rightarrow$  \*CH<sub>2</sub>CH<sub>2</sub>O+H<sub>2</sub>O  $\rightarrow$  \*CH<sub>2</sub>CH<sub>2</sub>OH  $\rightarrow$  \*CH<sub>3</sub>CH<sub>2</sub>OH  $\rightarrow$  \*+C<sub>2</sub>H<sub>5</sub>OH, in which the hydrogenation of \*CH<sub>2</sub>CH<sub>2</sub>O species is the rate-determining step for the overall reaction with a limiting free energy change of 1.12 eV. By analyzing the correlation, it is found that the catalytic activity of these metal node-modified catalysts is highly dependent on their binding strength to CO<sub>2</sub> reactant and key reaction intermediate (e.g. \*OCHOH).

In addition, the analysis of electronic and optical properties indicates that the altered energy band structure and charge transfer feature at the bimetallic node of Ti(Nb)-ATA are responsible for its superior catalytic activity towards the  $CO_2$  reduction to  $C_2H_5OH$  compared to the pristine Ti-ATA and other metal-modified Ti(M)-ATA candidates. The

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facile nature of metal substitution or doping in Ti-MOFs and their structural flexibility and diversity enable us to design a variety of Ti-based MOF photocatalysts with desirable properties. Our findings will stimulate further in-depth study of Ti-based MOF materials experimentally and open up new avenue for developing Ti-MOF-based catalysts for CO<sub>2</sub> photoreduction, especially for the synthesis of C<sub>2</sub> chemicals.

#### Author contributions

Shuang Wang: methodology, data acquirement, writing – original draft preparation. Xiaowa Nie: conceptualization, supervision, methodology, data analysis, project administration, writing – review & editing. Chunshan Song: investigation, writing – review & editing. Xinwen Guo: supervision, resources, project administration, writing – review & editing.

#### **Conflicts of interest**

There are no conflicts to declare.

#### Data availability

The data supporting this article have been included as part of the Supporting Information.

#### Author contributions

Shuang Wang: conceptualization, methodology, data acquirement, writing – original draft preparation. Xiaowa Nie: conceptualization, supervision, methodology, data analysis, writing – review & editing. Chunshan Song: investigation, writing – review & editing. Xinwen Guo: supervision, resources, project administration, writing – review & editing.

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#### Data availability

The data supporting this article have been included in the Supporting Information.