Synergy of ferroelectric polarization and oxygen vacancy to promote CO$_2$ photoreduction

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Solar-light driven CO$_2$ reduction into value-added chemicals and fuels emerges as a significant approach for CO$_2$ conversion. However, inefficient electron-hole separation and the complex multi-electrons transfer processes hamper the efficiency of CO$_2$ photoreduction. Herein, we prepare ferroelectric Bi$_3$TiNbO$_9$ nanosheets and employ corona poling to strengthen their ferroelectric polarization to facilitate the bulk charge separation within Bi$_3$TiNbO$_9$ nanosheets. Furthermore, surface oxygen vacancies are introduced to extend the photo-absorption of the synthesized materials and also to promote the adsorption and activation of CO$_2$ molecules on the catalysts’ surface. More importantly, the oxygen vacancies exert a pinning effect on ferroelectric domains that enables Bi$_3$TiNbO$_9$ nanosheets to maintain superb ferroelectric polarization, tackling above-mentioned key challenges in photocatalytic CO$_2$ reduction. This work highlights the importance of ferroelectric properties and controlled surface defect engineering, and emphasizes the key roles of tuning bulk and surface properties in enhancing the CO$_2$ photoreduction performance.

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O₂ reduction into chemical fuels via a solar-energy conversion is an appealing and sustainable strategy towards utilization of renewable energy sources. Photocatalytic processes for CO₂ conversion suffer from high activation energy barriers, rapid electron-hole recombination, and insufficient light utilization in most of the established photocatalysts. In particular, the photocatalytic performance depends strongly on the photogenerated charge separation and transfer kinetics in the bulk and on the surface of photocatalysts. As such, efforts have been made to improve the photocatalytic performance by using cocatalyst to increase the charge separation; surface modification to enrich the reactive sites and formation of heterojunction structures or facet junctions to enhance anisotropic photogenerated charge migration. However, CO₂ conversion efficiencies are still low and not yet sufficient for potential industrial applications.

In ferroelectric semiconductors, the displacement of positive and negative charges allows for spontaneous polarization within the crystal; a strong driving force for bulk charge separation and among others. Ferroelectric SrTiO₃ and BiFeO₃ have been reported to enhance the oxygen production performance of photoanodes. Ferroelectric materials are widely used as capacitors, piezoelectric sensors, and storage devices due to their unique spontaneous ferroelectric polarization. Although ferroelectrics have been proposed as potential photocatalytic materials starting from 2001, the research work up to now are generally focused on the influence of specific surface area or bandgap modification on photocatalysis.

Layered bismuth-based (LRB) semiconductor materials, as one of the most important classes of ferroelectrics, have lately gained considerable interest because of their unique structural properties that favor the formation of an internal static electric field for accelerating interlayer charge transfer. Our group has conducted pioneering work in this specific field. For instance, we demonstrated that ferroelectric polarization and in-turn charge separation was enhanced by post-annealing of ferroelectric SrBi₂Ti₄O₁₃ leading to increased CH₄ and CO production rates. On the other hand, Li et al. revealed that the depolarization field a driving force to disperse photogenerated electrons and holes to the opposite polarization facets in single-domain ferroelectric PbTiO₃ nanoplates. Notably, the depolarization field can be directly increased with the increasing particle size along the polarization direction, further improving the photocatalytic hydrogen evolution reaction activity. Despite the promising results obtained with polarized semiconductors, efforts in understanding and further development of this approach are mainly restricted in thin-film photoelectrodes. Employing effective polarizing routes like corona poling to strengthen the ferroelectric polarization of particulate photocatalysts is of great interest.

The interaction of photocatalysts and reactants is another important property of an efficient photocatalyst. For example, surface defects in oxygen-deficient BOCI have shown the ability to enable CO₂ adsorption and enhance CO₂ hydrogenation. Our group prepared surface oxygen vacancies (OVs) modified Aurivillius phase Sr₃Bi₂Nb₂TiO₁₂ nanosheets leading to promoted CO₂ adsorption and conversion, proven by both computational simulation and experimental evidences. Though the pioneering theoretical work using the two-dimensional Ising model further revealed that the existence of OVs in ferroelectrics might reduce ferroelectric properties (fatigue effect), experimental proof and/or in-depth mechanic understanding of the impact of OVs on ferroelectric domain and overall polarization in promoting photoinduced charge separation are still vacant.

In this study, the effect of ferroelectric polarization and surface OV concentration are explored in detail using Bi₃TiNbO₉ nanosheets as proof-of-concept materials, while the generated principle is expected to be extendable to another material system. Surface OVs concentrations were adjusted and corona poling treatment was used to further enhance charge separation. The optimized treatment resulted in improved photocatalytic CO₂ reduction performance yielding CO production rates of 20.91 μmol g⁻¹ h⁻¹, outperforming pristine Bi₃TiNbO₉ nanosheets and those treated by single means. Experimental and theoretical results demonstrated that the photoreponse range, charge separation efficiency, and surface-active sites were improved by corona poling and OVs. Thus, our systematic analysis reveals that ferroelectric polarization and OVs synergistically promote photocatalytic CO₂ reduction. The presented strategy might trigger additional research about tackling pivotal steps in photo(electro) catalysis to further promote CO₂ conversion.

**Results**

**Catalysts characterization.** Bi₃TiNbO₉ crystallizes in the non-centrosymmetric orthorhombic space group A₂₂₄ with unit-cell parameters of a = 5.43 Å, b = 5.39 Å, and c = 25.05 Å. It has a typical Aurivillius-type layered crystal structure formed with alternating [Bi₂O₂]₃⁻ and [TiNbO₇]₃⁻ perovskite slabs along the c axis. Bi atoms are situated within the [TiNbO₇]₃⁻ slabs (Fig. 1a, b), Bi₃TiNbO₉ (BNT) nanosheets were synthesized by a hydrothermal route with NaOH as the mineralizer, followed by treatments with different amounts of glyoxal (BNT-OVX, X = 1, 2, 3) to introduce OVs (Fig. 1a). Then, Corona poling was used to modify BNT and BNT-OV₂, denoted as BNT-P and BNT-OVP, respectively. As indicated by X-ray diffraction (Supplementary Fig. 1), the crystallographic structure is well maintained; neither corona poling nor OV creation caused a phase change of Bi₃TiNbO₉ nanosheets. This is also consistent with the Raman results (Supplementary Fig. 2).

The morphology of as-prepared samples is analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The thickness of nanosheets is measured to be approximately 10–30 nm for all samples (Supplementary Fig. 3a–d and Supplementary Fig. 4a, b), and their specific surface area is about 19–21 m²/g for these samples (Supplementary Fig. 5), further indicating that treatments are non-destructive to catalysts structure. The nanosheet structure of BNT and BNT-P is confirmed by transmission electron microscopy (TEM) (Supplementary Fig. 6a and Fig. 1c). It is noteworthy that both BNT and BNT-P show ferroelectric domains. These domains appear brighter for BNT-P indicating stronger ferroelectric polarization within the respective nanosheets. Diffraction patterns determined by selected area electron diffraction (SAED) of the [200] and [220] zone axis are highly visible and of regular order, revealing that BNT is well crystallized (Fig. 1c). Thus, the dominantly exposed facet of BNT is the [001] facet, according to the layered growth of BNT nanosheets along the c axis. To understand the polarization at the atomic scale, spherical aberration-corrected scanning transmission electron microscopy (ACTEM) was employed to investigate the microstructured domains in BNT-OVP. Atomic-resolution annular bright-field scanning transmission electron microscopy (ABF-STEM) was conducted to survey the surface atomic structure of BNT-OVP (Fig. 1d), which shows a clear and uniform arrangement of Bi, Nb, and Ti atoms. Nb and Ti atoms occupy the central site of the octahedron in the perovskite [Bi₃TiNbO₉] layer, and the direction of their displacement in the unit cell coincides with the direction of the spontaneous polarization. As Bi atoms are much heavier than Nb and Ti, the Bi atomic columns are darker than those of Nb and Ti. The relative displacements of the center Nb⁵⁺ and Ti⁴⁺ cation are presented by vectors pointing from the center of the octahedron to the corner of its four nearest neighboring Bi⁵⁺ cations. The direction of Nb and Ti atoms displacement illustrates...
a clear alignment of the Nb and Ti displacements for each unit cell along [110] direction, indicating a primary monodomain polarization along the [110] direction in BNT-OVP, further revealing the stronger polarization of BNT after corona poling. In sharp contrast to the neat crystal lattice of BNT (Fig. 1e), the thick amorphous edges and atomic defects in BNT-OVP suggest that the surface OVs mainly exist on the edges of the nanosheets\(^{25,26}\) (Fig. 1f and Supplementary Fig. 6b). Still, energy dispersive X-ray (EDX) elemental mapping (Supplementary Fig. 7) confirms the homogeneous distribution of Bi, Nb, Ti, and O across the BNT-OVP nanosheets.

UV/vis diffuse reflectance spectra (DRS) demonstrate that BNT and BNT-P primarily absorb light below 400 nm, resulting in a bandgap of approx. 3.17 eV, consistent with the previous report (Supplementary Fig. 8)\(^{27}\). Furthermore, DRS measurements illustrate that light absorption remains unaffected by corona poling, whereas the absorption range was significantly extended after the introduction of OVs when comparing BNT-OV2 and BNT-OVP. Notably, there are two band gaps for BNT-OV2 and BNT-OVP, which are ~3.06 and 2.64 eV. This is consistent with the fact that OVs always cause tail absorption (Supplementary Fig. 9)\(^{28,29}\). Further, the presence of OVs was also confirmed by electron paramagnetic resonance (EPR) spectroscopy. In contrast to BNT and BNT-P, the typical signal at \(g = 2.001\) was observed for BNT-OV2 and BNT-OVP, which is representative for electrons trapped in OVs (Fig. 1g)\(^{23,28}\).

The surface composition and chemical states of related elements are first analyzed by X-ray photoelectron spectroscopy (XPS) (Supplementary Fig. 10a). For samples of BNT-OV2 and BNT-OVP subjected to reductive treatment, an evident shift (~0.15 eV) to smaller binding energies is observed in the high-resolution Nb 3d and Ti 2p core spectra compared with BNT and BNT-P (Fig. 2a). This shift is indicative of a change in the chemical environment of Nb and Ti atoms present in sub-surface layers of the samples, i.e. the number of coordinating oxygen atoms is reduced by OV formation. Furthermore, the core spectra of bismuth (Bi 4f) reveal a less imperceptible shift (Supplementary Fig. 10b), suggesting that OV formation in [Bi\(_2\)O\(_2\)] layers is less likely to occur during reductive treatment. The O 1s XPS spectra shown in Fig. 2b reveal the existence of lattice oxygen (529.9 eV) and surface hydroxyls (531.1 eV). In addition, a peak at 532.5 eV determined for BNT-OV2 and BNT-OVP can be assigned to adsorbed water, in agreement with a strong interaction between OVs sites with water vapor\(^{7,30}\).

Extended X-ray absorption fine structure spectroscopy (EXAFS) of the Nb K-edge was performed to probe the local coordination environment. As shown in Fig. 2c, the Nb K-edge of BNT-OVP slightly shifts to lower energies, implying altered coordination of Nb\(^{5+}\)\(^{31}\). By further analyzing the Fourier transformed (FT) data of the extended fine structure region (Fig. 2d), an octahedral O environment (peak centered at \(R = 1\)–2 Å) and a reduction in Nb-O bond distance of Nb-O in BNT-OVP of 0.07 Å compared with BNT-P were revealed\(^{32}\). EXAFS wavelet transforms (WT) shown in Fig. 2e, f also highlight a shorter radial distance of Nb-O and a generally unsaturated coordination environment in BNT-OVP.

**Photocatalytic performance.** Photocatalytic CO\(_2\) reduction performance is determined in a batch reactor using a gas-solid configuration. Simulated solar light was used for illumination; it was proven that only gaseous products were generated that can be detected by gas chromatography (Fig. 3a, b and Supplementary Fig. 11). Using pristine BNT, CO, and H\(_2\) with production rates of...
Fig. 2 Characterization of the surface composition and chemical states of the samples. XPS spectra of (a) Nd 3d, Ti 2p, and (b) Os of BNT, BNT-P, BNT-OV2, and BNT-OVP. c Normalized Nb K-edge XAFS spectra and (d) Fourier transformed profiles for Nb coordination environments of BNT and BNT-OVP. \( \Delta R \) represents the difference of Nb-O bond distance between BNT and BNT-OVP.

respectively 2.11 and 0.07 \( \mu \text{mol g}^{-1} \text{h}^{-1} \) were measured. BNT-P exhibits higher CO and \( \text{H}_2 \) yields with evolution rates of 10.25 and 0.15 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), respectively. In addition, traces of \( \text{CH}_4 \) were detected (0.62 \( \mu \text{mol g}^{-1} \text{h}^{-1} \)). Thus, corona poling increases the CO yield by \( \sim 5 \) times. Modification of the pristine BNT with OVs as in BNT-OVX (X = 1, 2, 3) also results in enhanced CO\( _2 \) photoreduction activity (Supplementary Fig. 12).\(^7\) The optimized CO and \( \text{H}_2 \) production rates of 5.29 and 0.07 \( \mu \text{mol g}^{-1} \text{h}^{-1} \) are determined for BNT-OVP. Corona poling of OV containing nanosheets (BNT-OVP) finally results in a CO evolution rate of 20.9 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), exceeding the summed rates determined for BNT-P and BNT-OV2 (15.54 \( \mu \text{mol g}^{-1} \text{h}^{-1} \)). This suggests that corona poling and OVs synergistically improve the \( \text{CO}_2 \) reduction activity of BTN-OVP, enabling a significant rate increase, even surpassing that of reported state-of-the-art photocatalysts under similar testing conditions (Supplementary Table 1), such as BiOCl (1.01 \( \mu \text{mol g}^{-1} \text{h}^{-1} \)),\(^{33} \) \( \text{Sr}_2\text{Bi}_2\text{Nb}_2\text{TiO}_{12} \) with OVs (17.11 \( \mu \text{mol g}^{-1} \text{h}^{-1} \)),\(^7\) BiOIO\(_3 \) (17.33 \( \mu \text{mol g}^{-1} \text{h}^{-1} \)),\(^{34} \) and \( \text{Bi}_2\text{O}_3\text{(OH)}(\text{NO}_3) \) (8.12 \( \mu \text{mol g}^{-1} \text{h}^{-1} \)).\(^{11} \) In addition, the production rates of \( \text{CH}_4 \) and \( \text{H}_2 \) increase to 0.96 \( \mu \text{mol g}^{-1} \text{h}^{-1} \) and 0.19 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), respectively. On the basis of the aforementioned results, the solar-to-\( \text{CO}_2/\text{H}_2 \) conversion efficiency and the apparent quantum yield (AQY) with 365, 420, and 450 nm monochromatic irradiation for BNT-OVP are calculated to be about 0.021, 0.74, 0.46, and 0.35\%, respectively. It is important to mention that in all cases the determined production rate of \( \text{O}_2 \) agrees well with the number of electrons required to enable the reductive processes to generate. \( \text{CO}, \text{CH}_4, \) and \( \text{H}_2 \) products (Fig. 3c).

In order to exclude any influence of organic impurities, blank experiments were conducted. Using Ar instead of \( \text{CO}_2 \) purging, CO is detected only in traces (0.25 \( \mu \text{mol g}^{-1} \text{h}^{-1} \)) (Supplementary Fig. 13); instead, a significant increase in \( \text{H}_2 \) production by water splitting is obtained. It is well known that effective suppression of the competing HER is essential to enable \( \text{CO}_2 \) photoreduction. As a matter of fact, \( \text{CO}_2 \) reduction is favorable over water splitting in \( \text{CO}_2 \) containing environment as proven in literatures.\(^{35} \) Additionally, we confirm that in the absence of light and/or photocatalysts, no \( \text{CO} \) is formed (Supplementary Fig. 13). Using labeled carbon dioxide (\( ^{13}\text{CO}_2 \)) to trace the carbon sources, convincing proof is obtained that evolved CO and \( \text{CH}_4 \) indeed originate from the photoreduction of \( \text{CO}_2 \) (Fig. 3c). Notably, for BNT-P and BNT-OVP, the high durability of the polarization-induced electric field is revealed by the stable photocatalytic \( \text{CO}_2 \) reduction performance even after storage of one year (Supplementary Fig. 14). The durability of BNT-OVP is also confirmed for at least four consecutive reaction cycles (Supplementary Fig. 15–18). The favorable activity induced by both corona poling and OVs introduction is shown to be in good agreement with determined \( \text{CO}_2 \) adsorption capacities (Fig. 3d). In fact, \( \text{CO}_2 \) adsorption on BNT-OVP is well reflected by the sum \( \text{CO}_2 \) adsorption capacity of BNT-P and BNT-OV2.
Therefore, it is concluded that CO$_2$ adsorption on OVs is not affected by corona poling. Finally, *in-situ* FT-IR experiments indicate that CO$_2$ is adsorbed as carboxylate (CO$_2$$^-$, 1298 cm$^{-1}$), bidentate carbonate (b-Co$_3$$^-$, 1381, and 1602 cm$^{-1}$), bicarbonate (HCO$_3$$^-$, 1205, and 1418 cm$^{-1}$), and bidentate (2940 and 2981 cm$^{-1}$) that are eventually converted to CO and CH$_4$ upon illumination (Supplementary Fig. 19)\textsuperscript{23,36}. The possible electron/proton transport processes and reaction pathways involved in the CO$_2$ reduction reaction over the as-prepared photocatalysts are proposed in Supplementary Fig. 20.

It has been reported that ferroelectric spontaneous polarization largely affects the charge separation of ferroelectric semiconductors\textsuperscript{22,37}. The ferroelectric domains of Bi$_3$TiNbO$_9$ nanosheets are written and read out by Litho-PFM with a “CUGB” pattern. The writing voltage for the CUGB pattern is $-10$ V, and the rest is 10 V. From the hysteresis P–E loops (Fig. 4c and Supplementary Fig. 21a), BNT and BNT-OVP display a strong response of ferroelectric features and 180° phase switch. Besides, BNT-OVP presents remarkably higher remnant polarization and coercive field, which suggests the introduction of the corona polarization and OVs induces a stronger polarization electric field. The decreased saturation polarization causing fatigued ferroelectric characteristics reveals the influence of OVs on the dipole alignment\textsuperscript{38}. The butterfly curves observed for BNT (Supplementary Fig. 21b) confirm its excellent piezoelectric properties. Atomic force microscopy (AFM) shows a clear CUGB pattern (Fig. 4a and Supplementary Fig. 22) attributed to the domain switching after applying switches of ±10 V in different zones of Bi$_3$TiNbO$_9$ nanosheets. Piezo-response force microscopy (PFM) illustrates the negatively and positively polarized domains at different voltages (Fig. 4b). Nevertheless, the unclear phase suggests unstable ferroelectric switching at low voltage (Supplementary Fig. 23). The obtained surface charge images show a heterogeneous charge distribution on the surface of BNT (Supplementary Fig. 24), in line with a polarization-induced electric field formed between bright and dark regions. These results strongly suggest the presence of ferroelectric spontaneous polarization in Bi$_3$TiNbO$_9$ nanosheets, and that corona poling enhances the ferroelectric polarization, which results in more efficient charge separation.

It is remarkable that BNT-OVP displays an apparently larger difference between dark and bright regions and a higher surface charge potential (~45 mV) than that of BNT-P (~14 mV). OVs prevent back switching of ferroelectric domains after corona poling, exhibiting larger remnant polarization, which considerably promotes the charge separation of Bi$_3$TiNbO$_9$ nanosheets (Fig. 4d–f and Supplementary Fig. 25). The surface charge potential of BNT-OVP can be ascribed to the positive polarization and negative polarization with dark and bright regions due to the polarization-induced electric field (Supplementary Fig. 26). It is remarkable that BNT-OVP shows a ~5 mV decrease at the region of positive and negative potentials under the condition of illumination, which is caused by the separation and transferring to two opposite directions of the photogenerated electrons and holes (Supplementary Fig. 26).

The relationship between charge separation efficiency, ferroelectricity, and surface oxygen vacancies is further analyzed by using photocurrent, time-resolved photoluminescence, and Mott-Schottky measurements. As shown in Fig. 4g and Supplementary Fig. 27 and 28, the highest current density of 3 $\mu$A cm$^{-2}$ is observed for BNT-OVP. Moreover, the current response at a longer wavelength observed for BNT-OVP and BNT-OVP demonstrates that the formation of OVs indeed results in photon absorption at a higher wavelength, likely contributing to the enhanced CO$_2$ photoreduction activity. The average lifetime increases from 1.51 ns for BNT, 2.22 ns for BNT-P, 4.14 ns for BNT-OV2, to 7.33 ns for BNT-OVP, which indicates that BNT-OVP has the highest charge separation efficiency (Supplementary Fig. 29 and Supplementary Table 2). Similarly, the carrier density of BNT-P, BNT-OVP, and BNT-OVP is calculated to be $3.46 \times 10^{21}$, $4.44 \times 10^{21}$, $3.89 \times 10^{21}$, and $5.63 \times 10^{21}$, respectively (Fig. 4h and Supplementary Fig. 30), and the flat band
potential was independent of corona poling and/or OV formation (Supplementary Fig. 31, 32). Meanwhile, AFM is employed to identify the charge density in the diffuse part of the electric double layer for BNT-P and BNT-OV2. As shown in Fig. 4i, force-distance curves of BNT-P and BNT-OV2 both display the repulsive forces when the AFM tip made of oxidized Si with a negative charge is close to the surface. Compared with BNT-P, BNT-OV2 shows an obvious larger repulsive force and a strongly negatively charged surface. These results further reveal the high charge separation efficiency of BNT-OVP caused by the synergistic effect of ferroelectric spontaneous polarization and the presence of OVs provides a stronger driving force (Supplementary Fig. 33).

To better understand the effect of OVs on the polarization properties, the system Hamiltonian and Poisson equations are employed based on a two-dimensional film of size $d_x \times d_z$ along the $x$ and $z$ directions. The change system Hamiltonian and spatial variation of the electric field caused by the central ion in the octahedral site displacing and space charge distribution along the $z$-direction is represented by Eqs. (1) and (2), respectively:

$$H = -J \sum_{ij} S_{ij} \pm q_r E_z + H_a + H_b$$

(1)

$$\frac{d^2 \phi}{dz^2} = -q_e f(z)$$

(2)

where $J$ is the coupling coefficient between neighboring dipoles, $S_{ij}$ is the two-dimensional array of pseudospins of the film, $S_{ij}$ is the pseudospin state of one of the neighboring dipoles, $p_0$ is the dipole moment of the central ion, $E_z$ is the electric field along with the $z$ directions and can be obtained from Eq. (2), $H_a$ is the energy flipping between the upward dipole and downward one in the presence of an oxygen vacancy, $H_b$ is the energy term from the couplings of this distorted cage with the neighboring dipoles, $q_e$ is the electrostatic potential, and $q_r$ is the charge concentration, $f(z)$ is the distribution function of oxygen vacancies along the polarization direction ($z$-axis).

The displacement of the central ion in the $(x, z)$-plane is denoted as $u_{xz}$, the associated dipole moment is $p_{xz}$, where $p_{xz} = q u_{xz}$ and $q$ is the electron charge. The overall polarization can be estimated from the following expression:

$$P_x = \frac{\sum_{xz} p_{xz}}{d_x d_z}$$

(3)

It is clear that the introduction of OVs impedes the displacement of the central ion increasing the coercive field ($E_c$), and the domain switching needs extra energy to allow the deviated ions to return to their original positions, which maintains a larger polarization intensity after poling. These results provide a theoretical perspective of the synergistic effect of OVs and poling field in promoting the separation of photocarriers.

The domain switching in Bi$_3$NbTiO$_9$ nanosheets induced by corona poling was analyzed by COMSOL simulations. The simulations provide evidence that domains tend to gradually switch to be aligned when exerting a poling voltage, inducing a...
strong electric field around the nanosheets (Fig. 5a–c). Thus the separation efficiency of photogenerated charge carriers can be improved with the increase of electric field intensity of spontaneous polarization under illumination. After the polarization voltage was removed, most domains trend to switch back, and a decrease of the polarization strength in the nanosheets can be observed. Introducing OVs are capable of retarding the back switching of domains, thus resulting in a higher persistent remnant polarization-induced electric field, as illustrated in Fig. 5c. More importantly, the positively polarized charge can bend down the energy band promoting the reduction reaction, while the negatively polarized charge can bend up the energy band enhancing the oxidation reaction, which can effectively improve the photocatalytic CO2 reduction activity of Bi3NbTiO9 nanosheets. With the increase of poling voltage, the domains gradually switch to be aligned, resulting in a higher persistent remnant polarization-induced electric field, which provides a stronger driving force for charge separation and higher photocatalytic activity.

It has been reported that ferroelectric polarization can lead to atom reconstruction on the surface of polar materials. To get an in-depth understanding of the influence of ferroelectric spontaneous polarization on the position of formed OVs in Bi3NbTiO9, density functional theory (DFT) calculations were conducted towards OV formation energy (\(\Delta E_{fvac}\)) in the direction (d) perpendicular and (e) parallel to the ferroelectric polarization in the Nb/Ti-centered octahedral of Bi3NbTiO9 with dipole moment correction. Charge difference of CO2 adsorbed and adsorption energy (\(\Delta E_{ads}\)) on (f) Bi3NbTiO9 and (g) Bi3NbTiO9 with OVs (charge accumulation is in blue and depletion in yellow) with dipole moment correction.

![COMSOL simulations on Bi3NbTiO9 sheets under the process of corona poling and density functional theory (DFT) calculations.](image)

**Fig. 5** COMSOL simulations on Bi3NbTiO9 sheets under the process of corona poling and density functional theory (DFT) calculations. COMSOL simulation of polarization-induced electric field on Bi3NbTiO9 sheets: (a) un-poled, (b) intermediate poled, (c) fully poled. The red arrow represents the polarization direction of a single domain. Formation energy (\(\Delta E_{fvac}\)) of OV in the direction (d) perpendicular and (e) parallel to the ferroelectric polarization in the Nb/Ti-centered octahedral of Bi3NbTiO9 with dipole moment correction. Charge difference of CO2 adsorbed and adsorption energy (\(\Delta E_{ads}\)) on (f) Bi3NbTiO9 and (g) Bi3NbTiO9 with OVs (charge accumulation is in blue and depletion in yellow) with dipole moment correction.

are dominantly two nonequivalent oxygen sites in the Nb/Ti-centered octahedra in Bi3NbTiO9, namely, one in the direction perpendicular and one in the direction parallel to the ferroelectric polarization, which are labeled as OI and OII, respectively. The OV formation energy (\(\Delta E_{fvac}\)) of OII (1.092 eV) is significantly lower than that of OI (2.955 eV), indicating that OII is easier to be absent to form OV (Fig. 5d, e), which is consistent with our HRTEM images. According to the Ising model and theoretical calculation, the OVs in the polarization direction will produce a pinning effect on the domain to hinder the switching of the domain, thus affecting the in-plane polarization and the separation of electrons and holes in this direction. Due to the existence of ferroelectric spontaneous polarization along [110], OII in BNT-OVP is more conducive to the formation of OVs to maintain stability when glyoxal is added. The oxygen vacancies defecting in the polarization direction eventually show a pinning effect on the domains, maintaining superb ferroelectric spontaneous polarization as a stronger driving force to greatly improve the separation efficiency of photogenerated carriers, which is the key to promote the catalytic performance of the photocatalyst.

To better understand the OVs’ role on charge behavior and adsorption/activation processes of CO2 molecules, the charge difference of Bi3NbTiO9 and Bi3NbTiO9 with OV for CO2 adsorption is theoretically determined. In the presence of OVs, a much stronger charge interaction is observed between CO2 and Bi3NbTiO9. The adsorption energy of CO2 increases from 0.99 to
1.808 eV after the introduction of OV, further revealing a strong interaction between CO2 and OVs (Fig. 5f, g), which is conducive to the following reduction processes.

**Discussion**

In summary, Bi$_4$Ti$_3$NbO$_9$ nanosheets were synthesized via a one-pot hydrothermal approach with the assistance of NaOH as a mineralizer. Subsequent modification by the creation of surface oxygen vacancies and treatment by corona poling resulted in a considerable improvement on the following crucial photocatalytic steps: (i) extending the photoresponse to the visible-light region; (ii) promoting the separation and migration of photoinduced electrons and holes to opposite directions; and (iii) providing a large number of reactive sites to effectively absorb and activate CO$_2$ molecules. Particularly, the OVs were demonstrated to show an apparent quantum yield (AQY) with the equations below:

\[
\eta = \frac{G°(CO)}{G°(CH₄)} \times \left( \frac{R(\text{CH₄}) + R(\text{H₂})}{R(\text{CO}) + R(\text{H₂})} \right) \times \left( \frac{\Delta G°(\text{CH₄})}{\Delta G°(\text{CO})} \right) = \eta_{\text{aq}} \times \eta_{\text{aq}} \times \eta_{\text{aq}}
\]

where $R(\text{CH₄})$ and $R(\text{H₂})$ are the rate of CO$_2$, CH$_4$, and H$_2$ evolution, and $\Delta G°(\text{CH₄})$ and $\Delta G°(\text{CO})$ represent the change in the Gibbs free energy that accompanies the reduction of CO$_2$ to CO and CH$_4$, respectively. According to the linear relationship between $\eta$ and the illumination area ($4 \text{ cm}^2$), respectively.

**Photoelectrochemical tests**. Photocurrent and Mott-Schottky plots of samples were measured with the CHI-660E electrochemical system (Shanghai, China) using a three-electrode system setup. Details of the electrochemical cell (ECS) were employed to be a reference electrode and a platinum wire act as counter electrode. The series of photocatalyst films were coated on indium-tin-oxide (ITO) glasses as a working electrode. The electrolyte solution was 0.1 M Na$_2$SO$_4$ solution. The as-prepared samples were irradiated by a xenon lamp (300 W) with an AM1.5 filter to adjust intensity of 100 mW cm$^{-2}$. The measurements were conducted at room temperature at an open-circuit potential. The working electrodes were prepared using a dip-coating process. In short, 10 mg of photocatalysts were dispersed in 1 ml of ethanol to be an even slurry. After that, the suspensions were dropped on 15 mm x 30 mm indium-tin-oxide (ITO) glasses and dried at 373 K for 10 h to remove ethanol.

**Photocatalytic CO$_2$ reduction test**. The reduction products of CO$_2$ were detected using a closed circulation system (Labsolar-III AG, Beijing Perfect light Technology Co., Ltd, China) (Supplementary Fig. 38). 50 mg of obtained photocatalyst dispersed on a quartz dish and 1.3 g of NaHCO$_3$ were separately placed in the upper and lower in a reaction cell, which was then vacuum pumped. Subsequently, 5 mL of H$_2$SO$_4$ (4 M) was injected in the above reactor to react with NaHCO$_3$ for producing CO$_2$ gas (1 atm). Then, they were irradiated by a 300 W Xe lamp with an AM1.5 G filter (100 mW cm$^{-2}$ in intensity) with keeping the reactor temperature $\sim$ 20 °C. Then, 1 mL of the gaseous product was sampled and inspected using gas chromatography (GC9790II, Zhejiang full Analytical Instrument Co.) with a thermal conductivity detector. Meanwhile, 1 mL of gas and 20 μL of liquid were detected by GC-7860Plus gas chromatography (Shanghai Yiyou Electronic Technology Co.) to analyze liquid products. 1 atm high purity Ar and 5 mL of water were injected into the reactor instead of 1.3 g of NaHCO$_3$ and 5 mL of H$_2$SO$_4$ to detect the possible influence of organic impurities on the surface of photocatalysts under the same experimental conditions. With the same experimental conditions, the light source was not turned on and photocatalyst was not added to the reactor in the blank experiment for dark and no photocatalyst, respectively.

\[
\text{The calculation of solar-to-CO/CH}_4/\text{H}_2 \text{ conversion efficiency (η) and apparent quantum yield (AQY)}
\]

\[
\text{η} = \eta_{\text{aq}} \times \eta_{\text{aq}} \times \eta_{\text{aq}}
\]

where $\Delta G°(\text{CO})$, $R(\text{CH}_4)$, $R(\text{H}_2)$, $\Delta G°(\text{CO})$, $\Delta G°(\text{CH}_4)$, $\Delta G°(\text{H}_2)$, and S denote the rate of CO$_2$, CH$_4$, and H$_2$ evolution, and $\Delta G°$ represents the change in Gibbs free energy that accompanies the reduction of CO$_2$ to CO ($257 \times 10^3$ mol$^{-1}$) and CH$_4$ ($818 \times 10^3$ mol$^{-1}$), respectively. $\eta$ is the apparent quantum yield (AQY) with the equation below:

\[
\text{AQY} (\%) = \left( \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \right) \times 100% = \left( \frac{\text{number of evolved CO molecules} + \text{number of evolved CH}_4 \text{ molecules}}{\text{number of incident photons}} \right) \times 100%
\]

The apparent quantum yield (AQY) of BNT-OVP were determined to be about 0.74%, 0.46%, and 0.35%, respectively.

**The calculated charge carrier densities**. The information of carrier density ($N_d$) in semiconductor photocatalysts can be reflected by Mott-Schockley plots based on the following equations:

\[
C^{-2} = \frac{2}{\varepsilon_0 \varepsilon_r \kappa q} \left( E - E_{FB} - \frac{kT}{q} \right)
\]

where $C$ is the differential capacitance, $\kappa$ represents the dielectric constant of semiconductor, $\varepsilon_0$ means the permittivity of vacuum, $q$ is the elementary electron charge, $E$ is the electrode potential, $E_{FB}$ is flat band potential, $k$ represents Boltzmann’s constant, $T$ is the absolute temperature. According to the linear relationship between $C$ and $E$, the carrier concentration can be obtained from the slope of the straight line.

**COMSOL simulation of polarized electric field**. The geometrical characteristics were chosen as 100 nm x 100 nm x 20 nm, where the same domain is uniformly distributed. The space potential caused by domain interactions is approximately determined by the following equation:

\[
D = e_D E + P
\]

where $D$ is electric displacement, $e_D$ is the permittivity of vacuum, $E$ is electric field strength, and $P$ is polarization strength.
Density functional theory (DFT) calculations. To get in-depth cognition on the presence of oxygen vacancies in charge behavior enhanced adsorption and acti-
vation processes of CO2 molecules, electronic band structure, structure relaxation, and single-point energies were investigated by the density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) with the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) exchange and correlation functional. Cut-off energy at 500 eV K-point sampling in the Brillouin area using the Monkhorst-Pack method was used to conduct the framework of the projector-augment wave. The convergences of energy and force were separately set as 1 × 10−5 eV and 0.04 eV Å−1, and the minimum density of the point is 2n × 0.04 Å−3. The vacuum layer is set at 15 Å in the nonperiodic direction in the structural model to insure that the periodic mirrors have no interaction in this direction. The adsorption energy (Eads) for CO2 molecules was determined by the following formula

\[ E_{\text{ads}} = E_{\text{tot}} - (E_{\text{mol}} + E_{\text{BNT}}) \]

in which \(E_{\text{tot}}, E_{\text{mol}}, E_{\text{BNT}}\) represent the total energy of the adsorption structures, the energy of isolated molecules, and the energy of BNT structure, respectively.

Data availability
The data that support the findings of this study are available from the corresponding author upon request.

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Author contributions
H.J.Y. performed most of the experiments and wrote the first version of the paper; Y.H.Z. and H. W.H. co-supervised H.J.Y. regarding the work. Y.H.Z., H.W.H. and T.Y.M. co-initiated the research and co-revised the paper; F.C., X.W.L., and Q.Y.Z. carried out the DFT calculations; K.Y.W. help carry out the COMSOL simulation; S.Q.S. and E.Y.M. helped to analyze the results. B.M. and G.M. took part in the revision of the paper. All the authors discussed the results and commented on the paper.

Competing interests
The authors declare no competing interests.

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