Simultaneously Efficient Light Absorption and Charge Transport of Phosphate and Oxygen-Vacancy Confined in Bismuth Tungstate Atomic Layers Triggering Robust Solar CO₂ Reduction

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ABSTRACT:

The fundamental catalytic limitations for the photoreduction of CO₂ still remain: low efficiency, poor charge transport and short lifetime of catalysts. To address the critical challenges, an efficient strategy based on spatial location engineering of phosphate (PO₄) and oxygen-vacancy (V_o) confined in Bi₂WO₆ (BWO) atomic layers is employed to establish and explore an intimate functional link between the electronic structures and activities of V_o-PO₄-BWO layers. Both theoretical and experimental results reveal, the V_o-PO₄-BWO layers not only narrow the band gap from the UV to visible-light region but also reduce the resistance. The time-resolved photoluminescence decay spectra exhibit the increasing carrier lifetime for V_o-PO₄-BWO layers, indicating the improved charge separation and transfer efficiency. As expected, the V_o-PO₄-BWO layers with the simultaneously efficient light absorption and charge transport properties achieve much higher methanol formation rate of 157 μmol g⁻¹ h⁻¹, over 2 and 262 times larger than that of BWO atomic layers and bulk BWO. This work may reveal that the light absorption and spatial charge transport over atomic layers could benefit CO₂ conversion and shed light on the design principles of efficient photocatalysts towards solar conversion applications.

Keywords: Solar CO₂ reduction, Oxygen vacancy, Atomic Layers, Light absorption, Charge transport

1. Introduction

Photoreduction of carbon dioxide to useful chemicals by use of solar energy is receiving considerable attention to overcome the rising energy crisis and mitigate the increasing emissions of greenhouse gas [1]. Yet, the overall photoconversion efficiency is still very low. Among various catalysts [2], orthorhombic Bi_2WO_6 (BWO), as one of the simplest members of the Aurivillius family, is one promising material that meets the requirements for CO_2 photoconversion: (i) it has a suitable conduction band potential capable of CO_2 photoreduction into renewable fuels with a narrowed band gap; (ii) it has high chemical and thermal stability due to its peculiar structure constructed by alternating fluorine-like layers $(\text{Bi}_2\text{O}_2)^{2+}$ and perovskite layers $(\text{WO}_4)^{2-}$, and (iii) it is naturally abundant and non-toxic [3-10]. However, pristine BWO usually shows low photocatalytic activities owing to the restricted light harvesting capacity, sluggish carrier transport and the low exposed surface active sites [7-10]. Two dimensional (2D) nanostructures are of great interest due to their 2D confined structure which causes exotic physical properties [11-13]. Especially, the ultrathin conducting channels upon 2D atomic layers achieve rapid carrier transport in photocatalysis [13]. Based on the aforementioned concepts, it is highly desirable to explore the synthesis of the optimized BWO atomic layers in efforts to achieve efficient solar conversion.

An important strategy to enhance the catalytic performance of BWO is to engineer its electronic structure by doping strategy, namely, the addition of a small percentage of foreign atoms in the regular crystal lattice, produces dramatic changes in the band gap structure and the electrical properties in semiconductors. To date, doping suitable non-metal (F, I and N) or metal (Zr, Er, and Mo) atoms into BWO crystal lattice for improving its photocatalytic activity have been reported [7-10]. However, the insightful understanding of the effect of non-metallic doping on the band gap structure and photocatalytic performance is still missing. Inspired by the above insight, the incorporation of non-metal phosphate (PO_4) has been considered to be a valid strategy to optimize the catalytic activity. Thus, it is desirable to

explore the role of phosphate doped BWO atomic layers upon the progress in realizing high photoconversion efficiency.

Especially, oxygen-vacancy (O-vacancy) in various semiconductors has been reported to increase solar light harvesting through narrowing the band gap and also serve as the active sites to improve the carrier separation efficiency, thus finally achieving the improved catalytic efficiency [13]. However, the atomic-level insights into the role of O-vacancy is still a challenge. It is thus essential to investigate the geometric and electronic structures of the surfaces of phosphate and O-vacancy confined in BWO atomic layer to explicitly disclose the role of local atomic structure modulation. Combined with the optimization of doping and defect engineering, to gain in-depth atomic-level understanding on the relationship between non-metallic dopant, O-vacancy and CO₂ photoreduction, it would be rather imperative to simplify the catalyst model and bridge them with the optimized catalyst.

The development of the spatial location strategy has strengthened the interest in engineering photocatalysts [5]. Herein, we theoretically and experimentally propose the phosphate (PO₄) and O-vacancy (V_o) confined in Bi₂WO₆ (V_o-PO₄-BWO) atomic layer to be an ideal material model, establishing and exploring an intimate functional link between the electronic structures and activities of V_o-PO₄-BWO layers. This system represents an excellent platform to shed light on the correlation of the phosphate/O-vacancy-photocatalysis relationship through the development of novel oxide atomic layers and the suppressing of the detrimental electron-hole recombination. As expected, the V_o-PO₄-BWO layers achieve the excellent methanol formation rate in comparison of the reported photocatalysts to date [14-28]. Especially, the novelties of this work is aim to the achievement of novel photocatalysts and CO₂ conversion application owing to the following strategies : (i) developing novel V_o-PO₄-BWO layer photocatalyst with simultaneously increasing light absorption and efficient charge transport; (ii) achieving efficient photoreduction reactions over V_o-PO₄-BWO layers, and (iii) proposing the mechanism of solar CO₂ reduction over V_o-PO₄-BWO layers. As a

result, this work opens new avenues towards the design and development of novel materials for solar-driven CO₂ conversion.

2. Experimental section

2.1 Fabrication of PO₄ oxoanion doped Bi₂WO₆ atomic layers

Sodium oleate (50 mg) was dissolved into 20 mL de-ionized water under vigorous stirring to form a homogeneous solution. After 30 min, Bi(NO₃)₃·5H₂O was added into the sodium oleate solution, forming lamellar Bi-oleate complexes. Then, Na₂WO₄·5H₂O and Na₃PO₄ with different stoichiometric ratio of 1%, 3%, 5% and 10%, were added into the mixed solution. After being stirred for 30 min, the solution was transferred into a 30 mL Teflon-lined stainless steel autoclave and maintained at 140 °C for 24 h. Finally, PO₄ oxoanion doped Bi₂WO₆ atomic layers (PO₄-BWO) were obtained and washed several times. In comparison, Bi₂WO₆ atomic layers (BWO) were also synthesized by same process without the addition of Na₃PO₄ and bulk Bi₂WO₆ samples were obtained by use of Bi₂O₃ and WO₃ as raw materials under the heat-treatment at 1173 K for 12 h.

2.2 Fabrication of oxygen-vacancy confined in PO₄-Bi₂WO₆ atomic layers

As-fabricated PO₄ oxoanion doped Bi₂WO₆ atomic layers were introduced into the homemade quartz tube equipped with PO₄-Bi₂WO₆ layers by H₂/Ar mixture gas under the different temperature (50, 100, 150, 175, 200 and 225 °C). Then, oxygen-vacancy confined in PO₄-Bi₂WO₆ atomic layers (V_o-PO₄-BWO) were achieved. In comparison, oxygen-vacancy confined Bi₂WO₆ (V_o-BWO) atomic layers were also synthesized by use of Bi₂WO₆ atomic layers under the same reduction process.

2.3 Characterization

The obtained products were characterized by powder X-ray diffraction (XRD) using Cu Ka (λ = 0.1546 nm) and XRD patterns were obtained at 20~70 2 θ by step scanning with a step size of 0.02°. Transmission electron microscope (TEM) images were captured on the transmission

electron microscopy (TEM, JEM-2010) at an acceleration voltage of 200 kV. Atomic force microscopy (AFM) was employed by DI Innova Multimode SPM system. The chemical states of the sample were determined by X-ray photoelectron spectroscopy (XPS) in a VG Multilab 2009 system with a monochromatic Al K α source and charge neutralizer. The optical properties of the samples were analyzed by UV-vis diffuse reflectance spectroscopy using a UV-vis spectrophotometer (UV-2550, Shimadzu). Low temperature electron paramagnetic resonance (EPR) spectra were obtained using a JEOL JES-FA200 EPR spectrometer. The photoluminescence spectra were measured with a fluorescence spectrophotometer. Raman spectra were recorded on a microscopic Raman spectrometer.

2.4 Electrochemical measurement

The as-synthesized powders were initially dispersed in the solvent of ethanol; then the dispersion was uniformly spin-dropped on the indium tin oxide (ITO)-coated glass by a desktop spin coater, then the ITO-coated glasses were heated at 65 °C for 30 min to volatilize the solvent and then the BWO, PO₄-BWO, V_o-PO₄-BWO electrodes as the working electrodes were obtained. The counter and the reference electrodes were the platinum wire and the Ag/AgCl reference electrode, respectively. The electrochemical impedance spectroscopy (EIS) was performed on an electrochemical station in 0.1 M Na₂SO₄ electrolyte.

2.5 Photochemical measurement

Photoreduction of CO₂ was carried out in an air free closed gas circulation system reaction cell made of quartz. The catalyst was dispersed on a quartz cell and then loaded into a Pyrex reaction cell. After that, distilled water was added into the gas closed reaction system. The entire system was then evacuated and filled with pure CO₂ gas. A 300 W Xe lamp was utilized as the solar light source, where a standard AM 1.5G filter was used for solar CO₂ reduction and a $\lambda > 400$ nm filter was employed for visible-light-driven CO₂ reduction. The vessel temperature was kept at about 0 °C by recirculating cooling water system to increase

the solubility of CO₂. The solution products were qualitatively analyzed by gas chromatograph (GC-3240, Shimadzu) according to the standard curves.

2.6 First-principles calculations

The first-principles calculations for Bi₂WO₆ bulks and atomic layers were performed by the plane-wave pseudopotential method implemented in the CASTEP package [29]. The ion-electron interactions were modeled by optimized ultrasoft pseudo-potentials for elements in the compound and the following orbital electrons were regarded as valence electrons, O 2s²2p⁴, Bi 6s²6p³, W 5s²5p⁶5d⁴6s², P 3s²3p³ [30]. The Perdew–Burke–Ernzerhof (PBE) was used to calculate the exchange–correlation effects in the generalized gradient approximation (GGA) [31]. The energy cutoff of plane-wave basis set was 550.0 eV with Monkhorst–Pack k-point meshes spanning less than 0.07/Å in the Brillouin Zone. Geometry optimization was carried out under the threshold energy (10⁻⁶ eV) and force (0.01 eV/Å) convergence criteria [32]. The single-unit-cell thick layer along the [001] projection was used to mimic the as-prepared 1.66 nm thick Bi₂WO₆ sheets, in which 1.5 nm vacuum layer was added to avoid the interaction between adjacent layers [29]. A 2×2×1 supercell has been constructed to study the PO₄ oxoanion-doping and oxygen-vacancy effects on the electronic structure of Bi₂WO₆ atomic layers.

3. Results and discussion

Herein, conceptually novel oxoanion doping and O-vacancy confined in atomic layers is first put forward as an ideal material model for disclosing the role of local atomic structure in photocatalysis (Fig. 1a). To explore the local atomic arrangements of BWO, PO₄-BWO and V_o-PO₄-BWO atomic layers, TEM images (Fig. 1) clearly exhibit sheet-like morphology with average size of 100 nm, while the interplanar spacing of the ultrathin sheet observed from HRTEM is 0.273 nm and 0.272 nm (Fig. 1), which agrees well with the (200) and (020)

Fig. 1 (a) Illustration synthesis of as-prepared BWO, PO_4 -BWO and V_0 - PO_4 -BWO atomic layers in comparison of V_0 -BWO atomic layer. (b-d) TEM image, (e-g) HRTEM image, and (h-j) HRTEM image, and (k-m) illustrations for (b-d) BWO layers, (e-g) PO_4 -BWO layers and (h-j) V_0 - PO_4 -BWO layers as (k) AFM image and (l) the corresponding height profile from (k).

planes of orthorhombic BWO identically, revealing their orientation along the [001] projection. Compared to pristine BWO, the interplanar spacing becomes smaller for the PO₄-BWO and V_o-PO₄-BWO layers. Particularly, a certain extent of pits was observed in HRTEM for V_o-PO₄-BWO layers, indicating the removed of the O atom connecting with Bi atom and confirming the formation of O-vacancy in PO₄-BWO layers. In addition, AFM imaging and the height profile showed an average thickness of 1.66 nm (Fig. 1), indicating the unit cell along the [001] direction [7-10]. Thus, the above results demonstrated the formation of BWO, PO₄-BWO and V_o-PO₄-BWO atomic layers.

Fig. 2 (a) XRD patterns and (b) Raman spectra of (i) BWO, (ii) PO₄-BWO and (iii) V_o-PO₄-BWO atomic layers.

To optimize the crystallographic structures, we doped PO_4 oxoanion into the tungsten sites in the host lattice of two-dimensional BWO sheets, replacing some of the WO_6 oxoanions in BWO with PO_4 oxoanions by a lamellar Bi-oleate intermediate strategy. At an initial stage, the lamellar Bi-oleate complexes were formed by the introduction of the oleate ions [4], confirmed by the small-angle XRD pattern (Fig. S1). After the addition of WO_4^{2-} and PO_4^{3-} , PO_4 -BWO layers with different stoichiometric ratio of 1%, 3%, 5% and 10% were produced. The relative patterns are identical to the standard spectrum of orthorhombic BWO (JCPDS No. 73-2020), indicating that PO_4 doping does not change the crystalline phase of BWO (Fig. 2a). With increasing PO_4 doping amount, the magnified views of two peaks at (020) and (220) show regularly shift toward higher angles compared to that of BWO due to a smaller ionic radius and higher electronegativity of the P in comparison of W, thus making lattice spacing smaller of PO_4 -BWO, indicating that PO_4 has been well inserted into the BWO lattice (Fig. S2/S3). In the Raman spectra (Fig. 2b), the peaks located at the range of $600\sim 1000\text{ cm}^{-1}$ can be indexed to the stretches of the W–O bands. The bands at 790 cm^{-1} and 820 cm^{-1} are associated with antisymmetric and symmetric A_g modes of terminal O–W–O [14-16]. While the peaks lied at the range of $100\sim 400\text{ cm}^{-1}$ can be assigned to the translational mode involving simultaneous motion of Bi and WO_4 [14-16]. In comparison, the peaks located at around 303 cm^{-1} shift to higher vibration frequencies, however, there is no apparent change at about 800 cm^{-1} for BWO, PO_4 -BWO and V_o - PO_4 -BWO layers, confirming the replacing of WO_4 sites by means of PO_4 oxoanions [17]. Based on the analysis of XRD patterns and Raman spectra, there is an obvious shift between BWO and PO_4 -BWO layers, confirming the formation of PO_4 -doped BWO layers. Furthermore, phase transformation or impurity (Fig. S4) was not observed between PO_4 -BWO and V_o - PO_4 -BWO layers after the hydrogen reduction.

To shed light on the existence of PO_4 oxoanions and O-vacancy, the PO_4 -BWO and V_o - PO_4 -BWO atomic layers are obtained by XPS spectra (Fig. 3/Fig. S5). After PO_4 -doping, the

broad signal peak of P 2p state at about 132.9 eV is obviously observed in the PO₄-BWO and V_o-PO₄-BWO layers [7]. It is noted that the binding energies of Bi 4f state and W 4f state in the PO₄-BWO layers and V_o-PO₄-BWO atomic layers shift 0.1 eV and 0.4 eV toward high binding energy compared with that of BWO layers, indicating that the introduction of PO₄ into the lattice matrix of BWO atomic layers may form crystal defect (O-vacancy) [14-17], while the other two weaker peaks located at 36.4 and 34.4 eV correspond to the lower +5 valence of W [16,17]. Two peaks can also be clearly identified from the O 1s core level spectra (Fig. 3c): one peak at 529.8 eV is deemed as the oxygen bond of W–O–W, while the other located at 531.4 eV can be attributed to the coordination of oxygen in O–H [18-20], indicating the decreased contribution of Bi–O as a result of hydrogenation [7-10]. To balance the overall charge of the crystal, the PO₄-BWO layers is likely to form extra hydroxyl groups on the atomic layers, resulting into the creation of O-vacancies. Therefore, these XPS results clearly support the hypothesis that O-vacancies were created in the V_o-PO₄-BWO atomic layers upon hydrogenation. To further confirm the formation of O-vacancy, the BWO, PO₄-BWO and V_o-PO₄-BWO atomic layers exhibit obvious EPR signals. In particular, compared to pristine BWO and PO₄-BWO, the V_o-PO₄-BWO atomic layers show very strong response. However, the PO₄-BWO atomic layers only possess very weak form of resonance at g-value of 2.002. With the increasing of PO₄-doping amounts, the intensities of EPR signals of the PO₄-BWO atomic layers increase. Even more, the intensities of EPR signals of the V_o-PO₄-BWO atomic layers further increase with increasing hydrogen thermal reduction temperatures (Fig. S6). This phenomenon has been reported upon bulk materials, such TiO₂, ZnO, and BiPO₄, etc [21-24]. Nonetheless, the strengthening and broadening of the EPR signals may also be ascribed to the electron-trapped center at the site of oxygen vacancy [24]. In addition, the increased EPR signals confirm the formation of oxygen vacancy in the V_o-PO₄-BWO atomic layers (Fig. 3). Thus, the rational and controllable doping and vacancy modulation remains a challenging task, aiming to the high photocatalytic performance.

Fig. 3 (abc) P 2p, W 4f and O 1s XPS and (d) EPR spectra of (i) BWO, (ii) PO₄-BWO, (iii) V_o-PO₄-BWO atomic layers.

To uncover the innovative property of atomic layers, it is crucial to determine their intrinsic optical properties by UV-visible absorption spectra. Compared to that of the BWO atomic layers (Fig. 4), the light absorption edge of the PO₄-BWO atomic layers is slightly shifted in the blue wavelength range (Fig. S7). With increasing of PO₄ amounts, there is no obvious change in the optical absorption behavior over PO₄-BWO atomic layers. Compared to that of the BWO and PO₄-BWO atomic layers, the light absorption edge of the V_o-PO₄-BWO atomic layers is significantly shifted in the long wavelength range to visible-light region, even the whole spectral region. Especially, the absorbance of the V_o-PO₄-BWO atomic layers is gradually increased with the enhanced thermal reduction temperature (Fig. S8). Moreover, the plots of the transformed Kubelka–Munk function vs. the light energy show the bandgap

narrowing from 3.52 eV for the PO₄-BWO layers to 2.06 eV for the V_o-PO₄-BWO atomic layers, clearly suggesting that the incorporation with PO₄ oxoanion and oxygen vacancy is effective in narrowing the bandgap of the V_o-PO₄-BWO atomic layers.

Fig. 4 UV-Vis diffuse reflectance spectra of (i) BWO, (ii) PO₄-BWO, (iii) V_o-PO₄-BWO atomic layers.

To elucidate the origin of the enhancement of visible-light harvesting by BWO-based atomic layers, a systematic electronic structure analysis was performed by virtue of the First principle calculations. Taking the typical orthorhombic BWO structure, the BWO, PO₄-BWO and V_o-PO₄-BWO atomic layers are initially built, exploring the effect of PO₄-doping and O-vacancy on the electronic structure (Fig. 5). The partial density of states (PDOS) demonstrates that the top of valence band (VB) of bulk BWO is mainly composed of O 2*p*, Bi 6*s*, Bi 6*p* and

Fig. 5 Calculated density of states of (a) V_o - PO_4 -BWO atomic layers, (b) PO_4 -BWO atomic layers, (c) BWO atomic layers and (d) bulk BWO.

small W $5d$ states, while the conduction band (CB) is formed dominantly by W $5d$, O $2p$ and small Bi $6p$ states, similar to the result in other literatures [18-20]. In comparison, the single-unit-cell BWO slab has a larger bandgap and shows an obviously increased DOS at the conduction band edge due to the main contribution of Bi states (comparison of the shadow area in Fig. 5cd). This indicates that more carriers can be effectively transferred to the conduction band minimum (CBM) of the atomically thin perfect BWO sheets (Fig. S9). Upon PO_4 doping, the band gap of BWO layer becomes even slightly larger, which is in consistent with the experimental results. The presence of PO_4 -doping endows the single-unit-cell BWO slab with obviously increased DOS at valence band maximum (VBM). The integrated areas

for DOS in the energy windows of -3-0 eV is 113.37 and 168.58 for pristine and PO₄-BWO, respectively. The larger DOS in the VB around the Fermi energy E_F implies an increase of charge carriers. As O-vacancy forms in the PO₄-BWO slab, a new defect level appears. Comparing with pure BWO and PO₄-BWO sheet, some Bi 6*p* states depart from the CB emerging in the band gap of BWO sheet and the Fermi level shifts upward to the CB and locates in the band gap. These in-gap states near conduction band edge act as barrier of photo-generated electrons and form trapping center. In this case, the electrons can easily be thermally excited into the conduction band under irradiation of solar light, thereby achieving higher conversion efficiency. As a result, the photo-excited electron-hole pairs would spend less time to reach the surface than those generated deep within the bulk BWO, thus decreasing their recombination rates.

Enlightened by the above analysis, controllable synthesis of the V_o-PO₄-BWO atomic layers is desirable to improve the photoreduction efficiency of CO₂. To disclose the role of the phosphate and O-vacancy among BWO atomic layers in affecting photocatalysis, it is indispensable to implement the CO₂ photoreduction. In the dark, there is no any product over these samples. Upon 300 W Xe lamp with a standard AM 1.5G filter, the methanol yield gradually increased with the photolysis time, and the total yield of methanol of the V_o-PO₄-BWO atomic layers was 777 $\mu\text{mol g}^{-1}$, corresponding to approximately 157 $\mu\text{mol g}^{-1} \text{ h}^{-1}$ of the methanol formation rate, which was larger than that of the V_o-BWO, PO₄-BWO and BWO atomic layers and bulk BWO (Fig. 6ab/Fig. S10). Especially, the methanol formation rate of the V_o-PO₄-BWO atomic layers was 36 $\mu\text{mol g}^{-1} \text{ h}^{-1}$ under visible-light irradiation ($\lambda > 400 \text{ nm}$), which was identified by GC-MS spectrometry to confirm the evolution of methanol (Fig. S11). Compared to BWO layers, the PO₄-BWO layers presented the slight enhancement of the methanol yield rate. However, the O-vacancy confined in BWO (V_o- BWO) layers exhibited the obvious improvement of the methanol yield rate in comparison of BWO and PO₄-BWO

layers, while it is still lower than that of the $V_o\text{-PO}_4\text{-BWO}$ layers. After the ten cycles of repetition tests (Fig. 6c), there is no obvious loss of CO_2 photoreduction over the $V_o\text{-PO}_4\text{-BWO}$ atomic layers, presenting prospective signs for practical solar fuels generation. To evaluate the charge separation and transfer efficiency, the electrochemical impedance spectra, steady-state photoluminescence (PL) spectra and time-resolved PL decay curves were presented (Fig. 6def). From EIS spectra, the $V_o\text{-PO}_4\text{-BWO}$ layers features significantly smaller radius than that of the $\text{PO}_4\text{-BWO}$ layers, BWO layers, and bulk counterpart, demonstrating that a fast interfacial charge transfer property in the $V_o\text{-PO}_4\text{-BWO}$ layers. Since the low resistance is associated with efficient carrier mobility [33-37], the carrier mobility of the $V_o\text{-PO}_4\text{-BWO}$ layer was also improved, thus, indicating the efficient charge transfer over the $V_o\text{-PO}_4\text{-BWO}$ layers. Moreover, the intensity of steady-state PL emission spectra result into the pronounced PL emission quenching, implying greatly suppressed radiative electron-hole recombination [38-42], in line with the observed the highest photocatalytic activity of the $V_o\text{-PO}_4\text{-BWO}$ layers. To gain a deeper understanding of the efficiency of the photoexcited charge separation, we resorted to the time-resolved PL spectra for tracking in real time the charge carrier dynamics in nanosystems. Through fitting the decay spectra, the lifetime of $V_o\text{-PO}_4\text{-BWO}$ layers (134.3 ns) is longer than that of $\text{PO}_4\text{-BWO}$ (87.9 ns) and BWO (75.1 ns) layers and bulk BWO (15.6 ns). The longest PL lifetime implies lowest charge carrier recombination rate for the $V_o\text{-PO}_4\text{-BWO}$ layers. From the electron dynamics perspective, it is essential to infer that such a dramatic lifetime increase in $V_o\text{-PO}_4\text{-BWO}$ layers accounts for the enhanced conversion efficiency. Especially, in comparison of BWO, the $\text{PO}_4\text{-BWO}$ layers do not significantly change the optical absorption, nevertheless reduce the resistance, overcoming the intrinsically poor charge transport properties of BWO layers without compromising light absorption. It is worth mentioning the $V_o\text{-PO}_4\text{-BWO}$ layers not only narrow the band gap but also reduce the resistance. Therefore, the critical advance is the

use of $V_o\text{-PO}_4\text{-BWO}$ layers to achieve the highest solar reduction of CO_2 into methanol owing to simultaneous enhancements in wide-range-light-absorption and efficient charge separation.

Fig. 6 (ab) Methanol yields, (c) cycled test of methanol production of $V_o\text{-PO}_4\text{-BWO}$ layers, (d) electrochemical impedance spectra, (e) steady-state PL spectra and (f) time-resolved PL decay curves of (i) bulk BWO, (ii) BWO atomic layers, (iii) $\text{PO}_4\text{-BWO}$ layers and (iv) $V_o\text{-PO}_4\text{-BWO}$ atomic layers.

To in-depth elucidate the pertinent mechanisms of solar CO₂ reduction over BWO, PO₄-BWO and V_o-PO₄-BWO atomic layers, it is worthy to proposing the photoreduction mechanisms. As we know the photocatalytic reduction of CO₂ was performed over BWO nanostructures [25-28]. It was reported that the oxygen vacancies with abundant localized electrons are of particular interests for the enhanced adsorption and activation of inert gas molecules [43]. Especially, CO₂ by the activation of oxygen vacancies can be indirectly activated to H₂CO₃, HCO³⁻ or CO³⁻ ions, which would transform the inert linear CO₂ molecules to more reactive bent C–O bonds and lower the corresponding reduction potential by >0.42 eV [43-45]. Moreover, the surface O-vacancies have energy positions closer to the conduction band, thus, the photoinduced long-wavelength absorption is most likely caused by the trapped electrons at surface states [46,47]. According to the above-mentioned analysis, the electrons from the valence band are excited into the conduction band (CB) under solar light irradiation, leaving a hole in the valence band (VB). Especially, the photogenerated electrons in the CB may be trapped at the O-vacancies, resulting into the efficient spatial charge transfer and separation over the V_o-PO₄-BWO atomic layers (Fig. 7). However, the relative low CO₂ photoreduction activities of the BWO layers and the PO₄-BWO layers are ascribed to the serious recombination of the photogenerated electrons and holes (Fig. 7). Although the methanol yielding of the V_o-BWO layers is higher than that of the BWO layers and the PO₄-BWO layers, it is still lower than that of the V_o-PO₄-BWO layers due to the limited charge transfer and separation (Fig. S12). Based on this propose, the photogenerated electrons and holes on the V_o-PO₄-BWO layers can react with CO₂ and H₂O, and transform into CH₃OH and O₂. However, in-situ formed O₂ is detrimental to the undesirable oxidation of CH₃OH over the V_o-PO₄-BWO layers. To avoid this defect, the formed O₂ could be swept off from the aqueous solution under the continuous CO₂ purging, thus maintaining the stability of the V_o-PO₄-BWO layers with the abundant oxygen vacancies. As a result, we are able to design a

general alternative to atomic layer materials with simultaneously efficient light absorption and charge transport triggering robust solar CO₂ reduction.

Fig. 7 (a) Photoreduction mechanism and (b) schematic illustration of V_o-PO₄-BWO atomic layers triggering robust solar CO₂ reduction.

4. Conclusion

In summary, as a proof-of-concept prototype, the spatial location engineering of phosphate and O-vacancy confined in BWO atomic layers to extend their light absorption and overcome their intrinsically poor charge transport properties, was employed to optimize CO₂ photoreduction. Theoretical/experimental results reveal that the V_o-PO₄-BWO atomic layers with a new donor level and increased states of density, not only narrow the band gap from the UV to visible light region but also reduce the resistance. The time-resolved photoluminescence decay spectra exhibit the increasing carrier lifetime for V_o-PO₄-BWO atomic layers, indicating the improved electron-hole separation and transfer efficiency. As

expected, the V_o-PO₄-BWO atomic layers with strong light absorption and efficient charge transport, achieve the highest methanol formation rate of 157 $\mu\text{mol g}^{-1} \text{h}^{-1}$, over 2 and 262 times larger than that of the PO₄-BWO atomic layers and bulk BWO. This work may reveal that the efficient light absorption and spatial charge transport over atomic layers could benefit CO₂ conversion and shed light on the physicochemical design principles of efficient photocatalysts towards solar conversion applications.

Supporting Information

XRD patterns, SEM and TEM images, XPS and EPR spectra, UV-Vis spectra, calculated band structures, CO₂ reduction, GC-MS spectra and photoreduction mechanisms.

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