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# Modulating oxygen vacancy concentration on Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> nanorods for synergistic photo-driven plastic waste oxidation and CO<sub>2</sub> reduction†

Mengping Liu,<sup>‡a</sup> Yu Xia,<sup>‡a</sup> Wen Zhao,<sup>a</sup> Ruiyi Jiang,<sup>a</sup> Xin Fu,<sup>a</sup> Brittney Zimmerle,<sup>b</sup> Lihong Tian<sup>\*a</sup> and Xiaobo Chen<sup>‡\*b</sup>

Sunlight-driven CO<sub>2</sub> reduction coupled with photo-oxidation of plastic waste into value-added chemicals is a very attractive approach towards solving the greenhouse and environmental crisis. Herein, Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> nanorods with regulable O-vacancy concentration have been synthesized by the solvothermal method, aiming to provide abundant active sites for CO<sub>2</sub> adsorption and boost the separation of photogenerated carriers. In a dual-function system, gas production (CO) mainly from the CO<sub>2</sub> reduction-half-reaction reaches 64.7 μmol g<sup>-1</sup> h<sup>-1</sup> on Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> with rich oxygen vacancies (V<sub>O</sub>-BVO-15) in PET hydrolysis solution under 300 W Xe lamp irradiation, 24.5-fold higher than that in 2 M KOH solution. Moreover, a considerable amount of HCOOH product with a conversion rate of 0.7 mmol g<sub>cata.</sub><sup>-1</sup> is also achieved under 5 h of irradiation. Glyoxal (6.9 mmol g<sub>cata.</sub><sup>-1</sup>) and glyoxylate (3.2 mmol g<sub>cata.</sub><sup>-1</sup>) are produced mainly from the PET oxidation-half-reaction. This work presents an in-depth study of the development of Bi–O–V photocatalysts through defect engineering for photocatalytic CO<sub>2</sub> reduction and demonstrates a promising strategy for reuse of plastic waste and realizing carbon cycle with low energy consumption.

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## Introduction

Photocatalytic carbon dioxide (CO<sub>2</sub>) reduction to obtain hydrocarbon solar fuels is one of the promising strategies to solve the energy crisis and complement carbon cycle.<sup>1,2</sup> The construction of novel semiconductor photocatalysts with excellent photocatalytic activity and high stability has been regarded as one of the best strategies to solve the environmental and energy issues. To date, numerous novel semiconductor photocatalysts such as Bi-, W-, and Mo-containing photocatalysts have been designed and fabricated to solve the problems of traditional photocatalysts. In particular, Bi-containing photocatalysts have been widely investigated in photocatalytic applications because of their outstanding electronic and optical properties.

As one of the important Bi-containing compounds, Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> has aroused considerable interest owing to its special lamellar

structure and good light response. To date, numerous efforts have been made to improve its photocatalytic activity through the fabrication of structures with special morphologies and particle sizes.<sup>3–6</sup> However, the structure and morphology have limited influence on its photocatalytic performance. Despite considerable efforts, the practical application of Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> in photocatalysis is still suppressed because of the low light absorption, high recombination rate of photoinduced charge pairs and inadequate surface reactive sites in pristine Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub>.

Oxygen vacancies (V<sub>O</sub>s) are of particular interest for the enhanced adsorption and activation of inert gas molecules and guiding chemical reactions through more efficient pathways that lower the energy barrier.<sup>7</sup> Depending on the coverage and adsorption geometry, O<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub> are activated to their high-energy intermediates.<sup>8</sup> The concept of V<sub>O</sub>s was firstly proposed by Tompkins *et al.* in the 1960s, where V<sub>O</sub>s were considered as a kind of species.<sup>9</sup> Because of the special synthetic conditions and unstable surface structure of photocatalysts, O atoms are prone to move into random positions or even burst out of the crystal lattice.<sup>10</sup> In general, V<sub>O</sub>s are more easily generated by high temperature and/or pressure, chemical reduction, ion doping or light irradiation, which can lead to the bond breaking with lattice distortion and formation of defective states and electronic compensation in photocatalysts, therefore promoting the critical steps in photocatalytic processes. V<sub>O</sub>s are recommended to be one of the most important and prevalent anion defects with a relatively lower formation energy on many

<sup>a</sup>Collaborative Innovation Center for Advanced Organic Chemical Materials Constructed by the Province and Ministry, Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, College of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, China. E-mail: tian7978@hubu.edu.cn

<sup>b</sup>Division of Energy, Matter and Systems, School of Science and Engineering, University of Missouri-Kansas City, Kansas City, USA. E-mail: chenxiaobo@umkc.edu

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‡ The authors contributed equally to this work.

oxide surfaces. In this regard, introducing  $V_{\text{O}}$ s on photocatalysts could provide a new perspective to optimize the activity of  $\text{CO}_2$  photoconversion. Though  $\text{Bi}_4\text{V}_2\text{O}_{11}$  is an intrinsic oxygen deficient material, constituted by a  $[\text{Bi}_2\text{O}_2]^{2+}$  layered skeleton spaced by deficient perovskite-like  $\text{VO}_x$  linkages<sup>41</sup> and the oxygen environment around vanadium is adjustable, which results in the unique structure features of  $\text{Bi}_4\text{V}_2\text{O}_{11}$  based compounds,<sup>12–14</sup> few studies focus on investigating the effect of  $V_{\text{O}}$ s on photocatalytic  $\text{CO}_2$  reduction on  $\text{Bi}_4\text{V}_2\text{O}_{11}$ .

The control of the oxidation half reaction is the key to promote charge carrier separation.<sup>15</sup> In the research system of photocatalytic reduction of  $\text{CO}_2$ , a certain amount of hole sacrificial agents, such as triethylamine, triethanolamine, ammonium oxalate, *etc.*, is often added to the reaction, but they are generally expensive and toxic. Plastic is a precious resource that can store a large amount of energy and chemical raw materials, but most of it is simply thrown into landfills, which not only greatly wastes plastic resources, but also causes great damage to the environment.<sup>16</sup> Recently several studies involving photo-reforming of plastics coupled with the photolysis of water to produce hydrogen successfully bring the treatment of waste plastics into the photocatalytic redox system to achieve maximum utilization of energy.<sup>17–20</sup>

Herein, we successfully synthesize  $\text{Bi}_4\text{V}_2\text{O}_{11}$  with gradient oxygen vacancies and first attempt to use plastic waste in the dual-function photocatalytic system, in the search for ways to mitigate the greenhouse effect and explore the degradation of plastic waste to alleviate the earth's "plastic crisis". Our experimental results indicate that the PET photo-oxidation and  $\text{CO}_2$  photoreduction reinforce each other. In a dual-function system, the plastic pollutant PET is oxidated into some high value-added products, avoiding the use of commonly used expensive and often toxic hole sacrificial agents, thus achieving sustainable reduction of  $\text{CO}_2$  to CO and HCOOH. Although this idea is still in the experimental stage, the use of this dual-use technology provides a new pathway to tackle many major environmental challenges such as global warming, and plastic waste.

## Experimental

### Materials

Ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ , AR,  $\geq 98\%$ ), ammonia ( $\text{NH}_3$   $\text{H}_2\text{O}$ , AR, 25–28%) and sodium hydroxide ( $\text{NaOH}$ , AR,  $\geq 96\%$ ) were purchased from Sinopharm Group. Bismuth nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ) and ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) were supplied by Aladdin-Reagent. All chemical reagents were used without further purification.

### Synthesis of defective $\text{Bi}_4\text{V}_2\text{O}_{11}$ nanorods

The typical experimental procedure is as follows: first, 0.34 g urea and 1.30 g  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  were added to 15.0 mL ethylene glycol (EG) marked as solution A under continuous stirring. Second, 0.156 g  $\text{NH}_4\text{VO}_3$  was dissolved in another 15.0 mL ethylene glycol (EG) marked as solution B. Solution B was added to solution A under continuous stirring for 30 minutes, and the

pH value of the final system was adjusted to 9.00 using dilute ammonia water at room temperature under constant magnetic stirring. Subsequently, the formed mixture was poured into a stainless-steel autoclave with a Teflon liner of 50 mL capacity and heated at 180 °C for different reaction times (hours). Finally, the reactor was cooled to room temperature naturally. The resulting samples were washed with deionized water and ethanol several times and dried at 80 °C in an oven overnight. The obtained powders were marked as  $V_{\text{O}}\text{-BVO-}t$ , where  $t$  represents the reaction time.

### Characterization

The crystal structure of the samples was characterized by employing a Rigaku X-ray diffractometer with a  $\text{Cu-K}\alpha$  ( $\lambda = 1.540 \text{ \AA}$ ) radiation source in the  $2\theta$  range of 10–60°. Raman spectroscopy data were collected using a Renishaw InVia Raman microscope with an excitation wavelength of 532 nm. The morphologies were observed on a high-resolution transmission electron microscope (HRTEM, FEI Tecnai F20). The X-ray photoelectron spectroscopy measurement of materials was carried out on a VG Multilab 2000 spectrometer with an  $\text{Al K}\alpha$  X-ray source (Thermo Electron Corporation), and all the spectra were calibrated to the C 1s peak at 284.8 eV. The  $\text{CO}_2$  adsorption experiment was performed on a V-Sorb 2800TP volumetric specific surface area and aperture analyzer. All samples were treated at 120 °C in a vacuum to remove trapped gas and humidity. High purity  $\text{CO}_2$  directly connects the analyzer.  $\text{CO}_2$  adsorption isotherms were determined in the range of 0.01 Pa to 1.8 bar at room temperature. A Micromeritics Autochem II chemisorption analyzer with a thermal conductivity detector was used to conduct  $\text{CO}_2$  temperature programmed desorption ( $\text{CO}_2$ -TPD) on materials. The thermal desorption of chemisorbed  $\text{CO}_2$  was performed in flowing He at a ramp rate of 5 °C  $\text{min}^{-1}$  to a final temperature of 700 °C. Electrochemical measurements were implemented on an electrochemical apparatus (CHI760E, China) in a standard three-electrode system with the as-prepared samples as the working electrode, a Pt wire as the counter electrode and a saturated calomel electrode as the reference electrode. Time-resolved photoluminescence spectra (TRPL) were measured on an FLS980 fluorescence spectrometer (Edinburgh Instruments, UK) with an excitation wavelength of 250 nm.

### Substrate pre-treatment

PET powders were added into 1 L KOH aqueous solution, which was incubated at 40 °C with stirring at 480 rpm for 24 h in air to obtain different concentrations of PET hydrolysis solution.<sup>19</sup> After cooling to room temperature, the mixture was centrifuged at 8000 rpm for 3 min, and the supernatant was then extracted for further use.

### Photocatalytic reaction

The photocatalytic experiment was conducted in a Pyrex glass reactor with a volume of 400 mL (Beijing Perfectlight Technology Co., Ltd, China). Typically, 25 mg catalyst was dispersed into 50 mL 2 M KOH aqueous solution and then 50 mL pre-treated PET solution was added. In order to achieve an

adsorption-desorption balance between the catalyst and the substrate, the system was stirred continuously for 30 min in the dark. Prior to the light irradiation, the above system was vacuum-treated to remove the air completely, and purged with CO<sub>2</sub> (99.999%) with a flow rate of 5 mL min<sup>-1</sup> for 30 min. After that, the reactor was irradiated from the top using a high-pressure xenon lamp as the light source (CEL-HXF300, Beijing Perfect Light Technology Co., Ltd, China). The reaction was kept at constant temperature by a circulating water system. At the given interval, 1.0 mL of gas was taken from the reaction cell and analysed on a gas chromatograph (GC, Zhejiang Fuli Analytical Instrument Co., Ltd, China) equipped with a flame ionization detector (FID, GDX-01 columns). Liquid products were detected by <sup>1</sup>HNMR spectra.

## Results and discussion

### Characterization of defective Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub>

The targeted Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> is synthesized by the solvothermal method in ethylene glycol solvent, and oxygen vacancy concentration is modulated through controlling the reaction time. As shown in Fig. 1a, all diffraction peaks in powder XRD patterns of V<sub>0</sub>-BVO-9, V<sub>0</sub>-BVO-12 and V<sub>0</sub>-BVO-15 are well indexed to Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> without any observable impurity. The strongest peak in the magnified patterns (Fig. 1b) is located at about 28.6° in the former two materials, corresponding to orthorhombic Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> (β-Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub>, JCPDS 42-0135). However, this diffraction peak shifts to 28.7° in V<sub>0</sub>-BVO-15, indicating a possible phase distortion.<sup>11</sup> When the reaction time exceeds 24 h, a small quantity of BiVO<sub>4</sub> impurity is present (marked with an asterisk in Fig. 1a). Raman spectra further provide the fundamental information on the metal-oxygen bond in all as-

prepared Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> materials. The Bi-O stretching modes are too weak to be accessible in low wavenumber. Raman modes of V-O bonds are visible between 600 and 1000 cm<sup>-1</sup> (Fig. 1c). Two distinct split peaks at around 840 and 880 cm<sup>-1</sup> are ascribed to the stretching vibrations of V-O bonds with different bond lengths, monometric V-O tetrahedron and perovskite-like V-O-V bond.<sup>21,22</sup> The weak band at 685 cm<sup>-1</sup> is related to the doubly coordinated (V-O-V) oxygen atom.<sup>21</sup> It is worth noting that the vibrational bands of V-O-V bonds gradually decrease with prolonged reaction time, while the reverse happens to the VO<sub>4</sub> tetrahedron (840 cm<sup>-1</sup>); especially, the additional shoulder at about 800 cm<sup>-1</sup> indicates that the dramatic increase of V<sup>5+</sup> occupied the perfect VO<sub>4</sub> tetrahedral sites in V<sub>0</sub>-BVO-24, probably originating from the BiVO<sub>4</sub> impurity.<sup>23</sup> These results illustrate that the crystalline distortion of as-prepared Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> materials (XRD results) is determined by the structural variation of V-O polyhedra induced by oxygen vacancies.

V 2p and O 1s XPS spectra are recorded to further investigate the surface compositions and chemical interaction with the C 1s level at 284.8 eV as the binding energy (BE) reference. As shown in Fig. 1d, the BE of V 2p<sub>3/2</sub> is located at ~516.3 eV, much lower than the BE of V<sup>5+</sup> (~517 eV),<sup>24</sup> suggesting the presence of V<sub>0</sub>s in all as-prepared Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> materials. In fitted O 1s spectra (Fig. 1e), the main peak at 529.3 eV is ascribed to lattice O<sup>2-</sup> anions in Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub>, and two signals at 1.3 and 2.4 eV higher BE of O<sup>2-</sup> can be assigned to adsorbed -OH and H<sub>2</sub>O on metal sites adjacent to V<sub>0</sub>s in order to maintain charge balance.<sup>25-27</sup> The corresponding intensity of -OH and H<sub>2</sub>O peaks is indirectly proportional to the concentration of oxygen vacancies.<sup>28</sup> Note that the intensity of -OH and H<sub>2</sub>O gradually increases initially but dramatically decreases when the reaction time exceeds 24 h, suggesting the concentration of V<sub>0</sub>s with the order of V<sub>0</sub>-BVO-24



Fig. 1 (a) XRD patterns, (b) the magnified XRD patterns, (c) Raman spectra, (d) V 2p and (e) O 1s XPS spectra, and (f) EPR spectra of V<sub>0</sub>-BVO-9, V<sub>0</sub>-BVO-12 and V<sub>0</sub>-BVO-15.

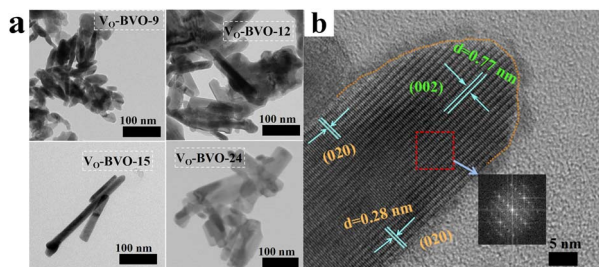


Fig. 2 (a) TEM image of  $V_O$ -BVO-9,  $V_O$ -BVO-12 and  $V_O$ -BVO-15. (b) HRTEM image of  $V_O$ -BVO-15 and selected area electron diffraction graph (the inset).

$< V_O$ -BVO-9  $< V_O$ -BVO-12  $< V_O$ -BVO-15. EPR spectra in Fig. 1f also verify that  $V_O$ -BVO-15 possesses the most  $V_O$ s because of the strongest signal at  $g = 2.002$  originating from the unpaired electrons at oxygen vacancies.<sup>29–31</sup>

Apart from the slight structure distortion, the morphologies of  $Bi_4V_2O_{11}$  are also strongly controlled by the concentration of oxygen vacancies. As shown in Fig. 2a,  $V_O$ -BVO-9 with less  $V_O$ s features irregular nanosheets mixed with seed-like nanorods. With the increase of  $V_O$  concentration, these nanosheets gradually develop into long nanorods with a length of about 100–300 nm and width of 20 nm ( $V_O$ -BVO-15).  $V_O$ -BVO-24 remains a nanorod structure but becomes shorter and wider compared with  $V_O$ -BVO-15. The HRTEM graph of  $V_O$ -BVO-15 exhibits the lattice fringes with an interplanar spacing of 0.77 nm and 0.28 nm in Fig. 2b, assigned to (002) and (020) crystal facets, respectively. The selected area electron diffraction (SAED) of

nanorods shows well-defined electron diffraction spots and further confirms that the lattice distances of (002) and (020) planes are dominant on nanorods (the inset in Fig. 2b). On the edge of the nanorod, a clear disorder layer is observable due to  $V_O$ s.

### Photo-driven $CO_2$ reduction coupled with PET oxidation

The synergistic ox/red reaction of  $CO_2$  and PET on different defective  $Bi_4V_2O_{11}$  samples is evaluated in KOH aqueous solution (pH = 14.16) under full-wavelength light irradiation (intensity:  $150 \text{ mW cm}^{-2}$ ). All gas and liquid products are investigated by GC and  $^1\text{H-NMR}$  spectra in detail. Fig. 3a demonstrates  $CO_2$  reduction on various catalysts in KOH solution (2M) without PET, which is highly related to the oxygen vacancy concentration in catalysts, and the highest CO conversion rate is  $2.6 \mu\text{mol g}^{-1} \text{ h}^{-1}$  on  $V_O$ -BiVO-15 with the most oxygen vacancies. Though the value is far higher than those reported for  $Bi_4V_2O_{11}$  composites ( $< 1 \mu\text{mol g}^{-1} \text{ h}^{-1}$ ),<sup>32</sup> it is still unsatisfactory. An attempt is made to conduct the synergistic catalytic  $CO_2$  reduction and industrial PET oxidation in one system. CO and HCOOH are the main products from  $CO_2$  photoreduction. Fig. 3b compares the conversion rates of CO and HCOOH on  $V_O$ -BiVO-15 in the presence of different PET contents. It is found that the synergistic PET oxidation can significantly improve  $CO_2$  reduction, and  $CO_2$ -to-CO conversion rate increases to  $64.7 \mu\text{mol g}^{-1} \text{ h}^{-1}$  at the optimal PET content of  $20 \text{ g L}^{-1}$ , about 24.5-fold higher than that from the sole  $CO_2$  reduction in KOH solution.  $^1\text{H-NMR}$  spectra of solution before and after photocatalytic reaction are presented in Fig. 3c. The



Fig. 3 (a) Photocatalytic  $CO_2$  reduction in 2 M KOH solution using  $V_O$ -BVO- $t$  catalysts without PET; (b) CO yield in dual-functional system with different concentrations of PET substrate; (c)  $^1\text{H-NMR}$  spectra of PET ( $20 \text{ g L}^{-1}$ ) hydrolysis products before and after photocatalytic reaction; (d) photocatalytic reaction in different atmosphere with PET ( $20 \text{ g L}^{-1}$ ). (e) Gas products from cyclic experiments of photocatalytic  $CO_2$  reduction synergistic PET ( $20 \text{ g L}^{-1}$ ) oxidation on  $V_O$ -BVO-15. (f) The XRD pattern of the used  $V_O$ -BVO-15.



hydrolysis products of industrial PET in KOH solution (before photochemical reaction) are identified to be composed of a large amount of ethylene glycol (EG, c) and a little phthalic acid (a) and acetic acid (d) after removing the insoluble terephthalic acid (TPA, b) by filtration, which could be reused as feedstocks in the synthesis of PET.<sup>20</sup> After photocatalytic reaction, new signals of formic acid (i), glyoxal (ii), and glyoxylate/glycoaldehyde (iii) are visible. Accordingly, the HCOOH (i) product originates from CO<sub>2</sub> reduction with a yield of 0.7 mmol g<sub>cata.</sub><sup>-1</sup> under 5 h of irradiation.

Products (ii) and (iii) are ascribed to the PET oxidation-half-reaction, which are not detected in the absence of light irradiation or catalysts. The CO<sub>2</sub> bubbling consumedly improves the PET oxidation, compared with an Ar or O<sub>2</sub> atmosphere. As shown in Fig. 3d, the production rate reaches 6.9 mmol g<sub>cata.</sub><sup>-1</sup> for glyoxal (ii) and 3.2 mmol g<sub>cata.</sub><sup>-1</sup> for glyoxylate (or glycoaldehyde) (iii), almost 15 and 64 fold those under an O<sub>2</sub> atmosphere, respectively. These results indicate that CO<sub>2</sub> bubbling is highly effective in promoting the selective photo-oxidation of PET components to organic chemicals on V<sub>O</sub>-BVO catalysts.

The stability of V<sub>O</sub>-BVO-15 in a synergistic reaction of CO<sub>2</sub> reduction and PET oxidation is investigated by quantifying CO product in four cycle experiments with each run for 5 h. Fig. 3e displays that CO evolution yield had no obvious decline in four cycle experiments. The XRD pattern of the used V<sub>O</sub>-BVO-15 well corresponds to Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> without noticeable impurity in Fig. 3f. The used V<sub>O</sub>-BVO-15 still retains a similar morphology (nanorods) to the fresh one (Fig. S1†). The above results indicate a good durability of V<sub>O</sub>-BiVO-15 in long-term photocatalytic synergistic reaction of CO<sub>2</sub> reduction and PET oxidation.

### Role of V<sub>O</sub>s in enhanced photocatalytic activity

From the photocatalytic kinetic viewpoint, the adsorption of substrate, *e.g.*, CO<sub>2</sub> on a catalyst is an important prerequisite for product efficiency.<sup>33</sup> Fig. 4a illustrates that the order of CO<sub>2</sub> uptake capacity is V<sub>O</sub>-BVO-9 (0.0667 mmol g<sup>-1</sup>) < V<sub>O</sub>-BVO-12 (0.1169 mmol g<sup>-1</sup>) < V<sub>O</sub>-BiVO-15 (0.1603 mmol g<sup>-1</sup>) at 298 K and 1.8 bar, probably ascribed to the gradually increased surface areas analysed by N<sub>2</sub> adsorption-desorption isotherms (Fig. S2, ESI†). CO<sub>2</sub>-TPD measurements are performed to determine the strength distribution of basic sites on all catalysts. Except for the weak physical adsorption for CO<sub>2</sub> in 50–150 °C,<sup>34,35</sup> the strong chemical adsorption appears at 400–600 °C in Fig. 4b. V<sub>O</sub>-BiVO-9 with less V<sub>O</sub>s only shows a peak at about 420 °C. With the

increase of V<sub>O</sub>s, the peak becomes stronger and wider and shifts to higher temperature for V<sub>O</sub>-BiVO-12 and V<sub>O</sub>-BiVO-15. In addition, a sharp peak at higher temperature between 500 and 600 °C is probably attributed to the formed CO<sub>3</sub><sup>2-</sup> with Bi<sup>3+</sup> in the CO<sub>2</sub>-TPD spectrum of V<sub>O</sub>-BiVO-15.<sup>34,35</sup> The quantity of various basic sites is determined by the integral of peak area and displayed in Table S1.† Obviously, V<sub>O</sub>-BiVO-15 possesses the most basic sites for CO<sub>2</sub> adsorption among the three catalysts owing to the highest concentration of V<sub>O</sub>s, which are beneficial for CO<sub>2</sub> adsorption and activation.

In addition, UV-Vis DRS spectra present gradually enhanced light absorption from V<sub>O</sub>-BVO-9 to V<sub>O</sub>-BVO-15 due to the increase of V<sub>O</sub> concentration (Fig. 5a),<sup>36,37</sup> in accordance with the colour change from yellowish-green to yellowish-brown (the inset in Fig. 5a). Moreover, a bump correlative to the V<sub>O</sub>-induced defect state becomes more obvious between 600 and 700 nm,<sup>32,38</sup> which probably forms an intermediate energy level for charge transfer. The corresponding optical band gap is determined by the Kubelka-Munk formula to be 2.48 eV (V<sub>O</sub>-BVO-9), 2.41 eV (V<sub>O</sub>-BVO-12) and 2.36 eV (V<sub>O</sub>-BVO-15), respectively (inset in Fig. 5a).<sup>30</sup> XPS valence spectra demonstrate an almost similar valence band maximum (VBM) at 1.67 eV for the three samples (Fig. S3, ESI†). As a result, the conduction band minimum (CBM) calculated according to  $E_{CB} = E_{VB} - E_g$  exhibits a slight positive-shift due to gradually narrowed band gap, *i.e.*, -0.81 eV for V<sub>O</sub>-BVO-9, -0.74 eV for V<sub>O</sub>-BVO-12 and -0.69 eV for V<sub>O</sub>-BVO-15, as shown in Fig. 5b, which are sufficient for CO<sub>2</sub> reduction to CO and HCOOH.

To confirm V<sub>O</sub>s promoting charge carrier migration, electrochemical experiments including photocurrent response and EIS spectra are performed. Fig. S4 in the ESI† demonstrates the stable and reproducible on-off current on all samples with/without light irradiation. The photocurrent density on V<sub>O</sub>-BVO-15 is about 1.31 and 1.62 times that of V<sub>O</sub>-BVO-12 and V<sub>O</sub>-BVO-9, respectively, indicating the fastest photogenerated

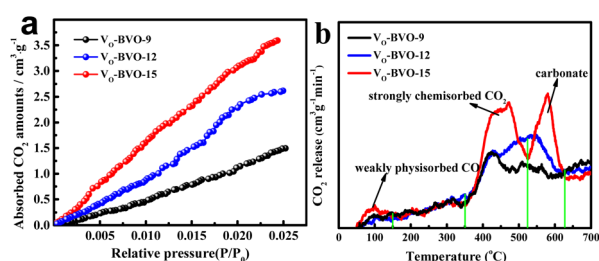


Fig. 4 (a) CO<sub>2</sub> absorption-desorption isotherms and (b) CO<sub>2</sub>-TPD curves of V<sub>O</sub>-BVO-9, V<sub>O</sub>-BVO-12 and V<sub>O</sub>-BVO-15.

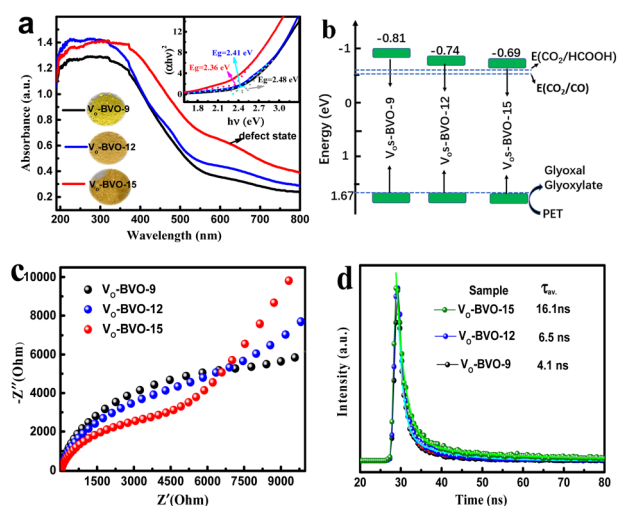


Fig. 5 UV-Vis spectra and  $(ah\nu)^2$  functions as  $h\nu$  curves (a), schematic diagram of the energy band structure (b), electrochemical impedance spectra (c) and TRPL spectra (d) of V<sub>O</sub>-BVO-9, V<sub>O</sub>-BVO-12 and V<sub>O</sub>-BVO-15.

electron transfer on V<sub>O</sub>-BVO-15. In electrochemical impedance spectra (EIS) (Fig. 5c), the semicircle radius in the high frequency region diminishes with the increase of V<sub>O</sub> concentration on the catalyst, which also elucidates the decreasing electron transfer resistance on the electrode interface with increasing V<sub>O</sub>s.<sup>39</sup>

The TRPL spectra are studied to further understand the charge transfer process. The collected spectra are displayed in Fig. 5d, and the PL decay lifetime ( $\tau$ ) components and corresponding intensity ( $A$ ) are extracted by curve fitting using a two-exponential function and shown in Table S2.<sup>†</sup><sup>40</sup> Both short lifetime  $\tau_1$  and long lifetime  $\tau_2$ , related to intrinsic fluorescence from radiative decay and non-radiative coupling, respectively, prolong with the increase of oxygen vacancy concentration. The resultant average lifetime ( $\tau_{av}$ ) gradually increased, *i.e.*, 4.1 ns for V<sub>O</sub>-BVO-9 < 6.5 ns for V<sub>O</sub>-BVO-12 < 16.1 ns for V<sub>O</sub>-BVO-15, indicating that oxygen vacancies effectively promote charge carrier separation; especially, non-radiative recombination related to defects is dramatically suppressed due to the intensity ( $A_2$ ) drop from 16% on V<sub>O</sub>-BVO-9 to 6.5% on V<sub>O</sub>-BVO-15. This is presumably associated with the special Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> structure that V<sub>O</sub>s generally reside in V–O layers ( $\langle 110 \rangle$  direction).<sup>41</sup> The increase of V<sub>O</sub> concentration greatly improves the oxygen ion migration in Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub>, thus enhancing the conductivity (electrochemical results) and decreasing non-radiative recombination.

## Conclusions

In this work, for the first time, Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> photocatalysts with modulating V<sub>O</sub>s are used in a dual-functional system to photocatalyse carbon dioxide reduction and plastic waste oxidation. V<sub>O</sub>s significantly promote the light adsorption, and charge separation and provide abundant sites for CO<sub>2</sub> capture, thus synergistically improving the photocatalytic CO<sub>2</sub> reduction and PET oxidation. In a dual-function system, CO<sub>2</sub>-to-CO conversion rate increases to 64.7  $\mu\text{mol g}^{-1} \text{h}^{-1}$  at the optimal PET content of 20 g L<sup>-1</sup>, about 24.5-fold higher than that from the sole CO<sub>2</sub> reduction in KOH solution. Despite this, a considerable amount of HCOOH is also produced with a yield of 0.7 mmol g<sub>cata.</sub><sup>-1</sup> under 5 h of irradiation. In the oxidation-half-reaction, considerable glyoxal and glyoxylate are produced by oxidation of glycol coming from PET hydrolysis. As a result, this study provides a novel strategy to reuse plastic waste and promote carbon cycle with low energy consumption.

## Conflicts of interest

There are no conflicts to declare.

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