Creation of Sn$_x$Nb$_{1-x}$O$_2$ solid solution through heavy Nb-doping in SnO$_2$ to boost its photocatalytic CO$_2$ reduction to C$_{2+}$ products under simulated solar illumination

Shuang GAO*, Haitao GUAN, Hongyang WANG, Xinhe YANG, Weiyi YANG, Qi LI*

Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, China

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Abstract: Photocatalytic CO$_2$ reduction driven by green solar energy could be a promising approach for the carbon neutral practice. In this work, a novel defect engineering approach was developed to form the Sn$_x$Nb$_{1-x}$O$_2$ solid solution by the heavy substitutional Nb-doping of SnO$_2$ through a robust hydrothermal process. The detailed analysis demonstrated that the heavy substitution of Sn$^{4+}$ by a higher valence Nb$^{5+}$ created a more suitable band structure, a better photogenerated charge carrier separation and transfer, and stronger CO$_2$ adsorption due to the presence of abundant acid centers and excess electrons on its surface. Thus, the Sn$_x$Nb$_{1-x}$O$_2$ solid solution sample demonstrated a much better photocatalytic CO$_2$ reduction performance compared to the pristine SnO$_2$ sample without the need for sacrificial agent. Its photocatalytic CO$_2$ reduction efficiency reached ~292.47 µmol/(g·h), which was 19 times that of the pristine SnO$_2$ sample. Furthermore, its main photocatalytic CO$_2$ reduction product was a more preferred multi-carbon (C$_{2+}$) compound of C$_2$H$_5$OH, while that of the pristine SnO$_2$ sample was a one-carbon (C$_1$) compound of CH$_3$OH. This work demonstrated that, the heavy doping of high valence cations in metal oxides to form solid solution may enhance the photocatalytic CO$_2$ reduction and modulate its reduction process, to produce more C$_{2+}$ products. This material design strategy could be readily applied to various material systems for the exploration of high-performance photocatalysts for the solar-driven CO$_2$ reduction.

Keywords: photocatalytic CO$_2$ reduction; heavy Nb-doping; tin oxide; solid solution; C$_{2+}$ product

1 Introduction

In the past decades, many attempts had been made in the field of photocatalytic CO$_2$ reduction by utilizing metal oxide, oxynitride, sulfide, phosphide, and other semiconductor-based photocatalysts [1–8]. Due to its diverse product types and the advantage of using green solar energy, the photocatalytic CO$_2$ reduction attracted much attention to finding the potential solution for the worldwide crisis of global warming and energy shortage. Despite the significant progress that has been made, two major challenges still exist regarding this topic. One is how to increase the conversion efficiency restricted
by the high energy barrier associated with the activation of CO₂ molecule on the photocatalyst surface [9–11], and the other is how to modulate the reaction pathway to yield desirable products which rely on the photocatalyst surface charge concentration and the related interaction between the active site of photocatalysts and the adsorption status of activated CO₂ molecules [12–16].

It is generally believed that, the adsorption of CO₂ on the photocatalyst surface and the subsequent activation by the formation of bent CO₂ species accompanied by electron transfer play vital roles in overcoming the high energy barrier for its reduction [17] and affecting the product selectivity [18]. Various approaches had been proposed and proved to be effective to enhance the photocatalytic CO₂ reduction efficiency, including impurity doping [19,20], metal deposition [21], heterojunction construction [22], cocatalyst loading [23], and modulating acid-base properties [20,24]. Among them, the creation of defects, such as vacancies or substitutions, could markedly influence the distribution of photogenerated charges to enhance the CO₂ activation [25–27], and serve as surface reactive sites for the reduction reaction [28], which is promising in the design and creation of novel photocatalysts for highly efficient CO₂ reduction.

Due to its environmental friendliness, non-toxicity, relatively low cost, and high surface activity, SnO₂ had been extensively explored for various technical applications, including photocatalysts [29], gas sensors [30], dye-sensitized solar cells [31], and supercapacitors [32]. It had been found that SnO₂ [33] and its composites with other photocatalysts like g-C₃N₄ [34,35], Fe₂O₃ [36], BiVO₄ [37], or MoS₂ [38] could photocatalytically reduce CO₂. However, their photocatalytic CO₂ reduction efficiencies were generally low, and only one-carbon (C₁) products (mostly CO and CH₄) were reported, while multi-carbon (C₂+) products are more attractive due to their higher energy density, easier processing and transportation, and better economical values for the industrial application [39]. Thus, it is of great research interest to develop SnO₂-based photocatalysts with both higher photocatalytic CO₂ reduction efficiency and the capability to produce the C₂+ products.

Doping is an easy process to create defects in various metal oxide photocatalysts to modify their surface chemistry properties and charge distribution/transfer behaviors for targeted reactions or applications [40,41]. It had been demonstrated that doping with cations of high valence into metal oxides could contribute an improved conductivity as well as catalytic activity [42]. For example, the substitution of Ti⁴⁺ by Nb⁵⁺ in TiO₂ lattice could boost the adsorption of CO₂ molecule due to the increased intensity of the Coulomb attraction between the lone-electron pair outside C atom of CO₂ molecule and the surface of photocatalyst, which subsequently enhances the photocatalytic CO₂ reduction performance with a C₂+ product of CH₃CHO as the preferred product [20,43]. Thus, it is of interest to explore if the Nb-doping in SnO₂ could have a similar enhancement effect on its photocatalytic CO₂ reduction performance. Furthermore, the radius of Nb⁵⁺ is ~0.64 Å [44], and that of the Sn⁴⁺ is ~0.69 Å [45]. Their radius closeness and a radius of Nb⁵⁺ slightly smaller than that of Sn⁴⁺ could allow the occurrence of heavy substitutional Nb-doping in the SnO₂ rutile lattice. Thus, the Sn₅Nb₁₋ₓO₂ solid solution with a high Nb content may be created, which should have a better enhancement effect on the photocatalytic CO₂ reduction because the heavy doping of high valence cations could be more effective to induce abundant acid centers and active sites for the reduction reaction than the low doping content, which was usually adopted in the previous reports [46].

In this work, a robust one-step hydrothermal process was developed for the heavy substitutional Nb-doping of SnO₂ to form the Sn₅Nb₁₋ₓO₂ solid solution with a high Nb : Sn atomic ratio of ~2.17 : 1, in which SnO₂ served as the solvent to provide the rutile structure lattice and Nb⁵⁺ substituted Sn⁴⁺ as the solute. The formation of Sn₅Nb₁₋ₓO₂ solid solution largely changed the energy band structure of SnO₂, significantly promoting the separation and transfer of photogenerated charge carriers, and obviously enhanced the adsorption of CO₂ molecules on the photocatalyst surface. Thus, it demonstrated a superior photocatalytic CO₂ reduction efficiency compared to the pristine SnO₂ sample under simulated solar illumination without the need for the sacrificial agent over one magnitude higher. Furthermore, it demonstrated a preferred C₂+ product production with C₂H₅OH as the main product, which could be attributed to the formation of abundant acid centers and the presence of excess electrons on its surface due to the heavy doping of higher valence Nb⁵⁺.

2 Materials and methods

2.1 Chemicals and materials

Ethanol (EtOH, 99%, Sinopharm Chemical Reagent, www.springer.com/journal/40145
Ammonium carbonate ((NH₄)₂CO₃, AR, Shanghai Titan Scientific, China) was used as both the precipitation agent and the sacrificial template. Stannous chloride (SnCl₂, 99%, Shanghai Titan Scientific, China) and niobium chloride (NbCl₅, 99.9%, Shanghai Macklin Biochemical, China) were used as metal salts. Deionized (DI) water was obtained from a water purification system (Chengdu Pure Technology, China) with a resistivity higher than 18 MΩ·cm. All chemicals were used without further purification.

2.2 Synthesis of SnₓNb₁₋ₓO₂ solid solution

The SnₓNb₁₋ₓO₂ solid solution was prepared through a robust one-step hydrothermal reaction. In a typical synthesis process, SnCl₂ (0.02 M) and NbCl₅ (0.04 M) were firstly dissolved in the ethanol to form a mixture solution of 35 mL, while (NH₄)₂CO₃ (0.12 M) was dissolved in the DI water of 35 mL. Then, the aqueous (NH₄)₂CO₃ solution was added slowly to the SnCl₂/NbCl₅ mixture solution. After magnetic stirring for 30 min, it was moved into a hydrothermal vessel and underwent a hydrothermal reaction at 230 °C for 48 h. The collected product was washed with the DI water and ethanol several times, and dried at 60 °C for 8 h in the air. A Xe arc lamp of 300 W (Beijing Perfect Light Technology, China) was utilized to simulate the solar illumination. Surface photovoltage spectroscopy (SPS) was studied by using a home-assembled surface photovoltage measurement system [47]. Electrochemical impedance spectroscopy (EIS) measurement was conducted with a series of frequencies ranging from 0.01 to 100 kHz. Mott–Schottky (M–S) analysis was carried out at the frequency of ~1 kHz to obtain the flat band potential value of samples.

2.3 Characterization of SnₓNb₁₋ₓO₂ solid solution

X-ray diffraction (XRD) patterns were obtained with an Empyrean Alpha-I X-ray diffractometer (Malvern Panalytical, the Netherland). Morphology and chemical element distribution were analyzed by a JEM-2100F transmission electron microscope (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) analysis was conducted on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo Fisher Scientific, USA) with a monochromatized Al Kα X-ray source (1486.71 eV). Quantitative chemical composition analysis was conducted on an inductively coupled plasma optical emission spectroscopy (ICP-OES) 5110 system (Agilent Technologies, USA). Optical absorbance spectra were measured by a UV-3600PLUS spectrophotometer (Shimadzu, Japan).

Photoelectrochemical measurements were conducted with a traditional three-electrode configuration by immersing the working electrode, counter electrode (Pt wire), and reference electrode (saturated Ag/AgCl) in the electrolyte of 1 M Na₂SO₄ (pH = 6.67). The working electrode was prepared by firstly mixing the active material and polyvinyliden fluoride (PVDF) binder in a mass ratio of 9 : 1 and then homogenizing them in N-Methyl-2-pyrrolidone (NMP) to form a slurry. Afterwards, the homogeneous slurry was coated on a titanium mesh substrate with an active area of about 1.5 cm² and dried at 60 °C for 8 h in the air. A Xe arc lamp of 300 W (Beijing Perfect Light Technology, China) was utilized to simulate the solar illumination. Surface photovoltage spectroscopy (SPS) was studied by using a home-assembled surface photovoltage measurement system [47]. Electrochemical impedance spectroscopy (EIS) measurement was conducted with a series of frequencies ranging from 0.01 to 100 kHz. Mott–Schottky (M–S) analysis was carried out at the frequency of ~1 kHz to obtain the flat band potential value of samples.

3. Results and discussion

3.1 Microstructure and morphology of SnₓNb₁₋ₓO₂ solid solution sample

It had been found that the Nb-doping of SnO₂ generally happened by substituting Sn⁴⁺ with Nb⁵⁺ due to the closeness of their radii of Nb⁵⁺ at ~0.64 Å and Sn⁴⁺ at ~0.69 Å. Thus, it could result in only a slight structure distortion during the doping process, which favors the occurrence of the Nb-doping in SnO₂. Figure 1(a) shows
XRD patterns of Sn$_x$Nb$_{1-x}$O$_2$ solid solution and pristine SnO$_2$ samples. As expected, the as-synthesized pristine SnO$_2$ sample possessed a rutile-type crystal structure (JCPDS No. 41-1445). For the Sn$_x$Nb$_{1-x}$O$_2$ solid solution, although its Nb : Sn atomic ratio reached ~2.17 (refer to Table S1 of its composition in the Electronic Supplementary Material (ESM)), it still had the same rutile-type crystal structure as that of the pristine SnO$_2$ sample, and no diffraction peak belonged to the niobium oxide could be observed. Thus, the Sn$_x$Nb$_{1-x}$O$_2$ solid solution with a high Nb : Sn ratio was synthesized by our approach, in which SnO$_2$ served as the solvent to provide the rutile structure lattice and Nb$^{5+}$ ions served as the solute to substitute Sn$^{4+}$ to form the desired Sn$_x$Nb$_{1-x}$O$_2$ solid solution.

The detailed XRD analysis found that its diffraction peaks showed position shifts, compared with that of the pristine SnO$_2$ sample. For example, its (110) peak shifted towards the lower 2θ direction from ~26.58° of the pristine SnO$_2$ sample to ~26.38°, suggesting a lattice spacing increase of its {110} crystal planes from ~0.3351 nm of the pristine SnO$_2$ sample to ~0.3370 nm, while its (101) peak shifted to the higher 2θ direction from ~33.86° of the pristine SnO$_2$ sample to ~34.20°, suggesting a lattice spacing decrease of its {101} crystal planes from ~0.2643 nm of the pristine SnO$_2$ sample to ~0.2616 nm. Rietveld refinements of the obtained XRD data were carried out with the fullproof software to fit their XRD diffraction patterns and obtain their lattice parameters. For the pristine SnO$_2$ sample, its crystal lattice parameters were determined as $a = b = 0.4739$ nm, $c = 0.3185$ nm, and $\alpha = \beta = \gamma = 90^\circ$, and its lattice volume $V$ could be calculated at ~71.53 Å$^3$. For the Sn$_x$Nb$_{1-x}$O$_2$ solid solution sample, its crystal lattice parameters were determined as $a = b = 0.4765$ nm, $c = 0.3130$ nm, and $\alpha = \beta = \gamma = 90^\circ$, and its lattice volume $V$ could be calculated at ~71.07 Å$^3$. Thus, the Sn$_x$Nb$_{1-x}$O$_2$ solid solution sample had a lattice expansion along the $a$ and $b$ directions and a lattice shrinkage along the $c$ direction, compared with the pristine SnO$_2$ sample lattice which was consistent with its lattice spacing changes deduced from XRD peak shifts. Furthermore, its lattice volume decreased compared with that of the pristine SnO$_2$ sample, which
was consistent with the fact that Nb\(^{5+}\) of a smaller radius substituted Sn\(^{4+}\) of a larger radius in the Sn\(_x\)Nb\(_{1-x}\)O\(_2\) solid solution sample.

Figure 1(b) shows the representative TEM image of Sn\(_x\)Nb\(_{1-x}\)O\(_2\) solid solution sample, which demonstrated that it was composed of nanoparticles with irregular shapes and the average particle size was ~15 nm. Such fine particle size was beneficial for obtaining a relatively high surface area with the active sites. From the Brunauer–Emmett–Teller (BET) analysis results, its specific surface area was determined at ~153.73 m\(^2\)/g, while that of the pristine SnO\(_2\) sample was determined at ~50.98 m\(^2\)/g. These results clearly demonstrated that the formation of Sn\(_x\)Nb\(_{1-x}\)O\(_2\) solid solution through the heavy Nb-doping largely enhanced its specific surface area, which was beneficial for its adsorption and reaction with CO\(_2\) molecules.

Figure 1(c) shows its high-resolution transmission electron microscopy (HRTEM) image. Two sets of lattice planes with \(d\)-spacing values of ~0.34 and ~0.26 nm could be clearly observed, which matched well with the (110) and (101) planes of the rutile phase, respectively. This observation was consistent with the XRD analysis result and further verified that the as-synthesized Sn\(_x\)Nb\(_{1-x}\)O\(_2\) solid solution sample was highly crystallized by the hydrothermal reaction. Figure 1(d) shows its EDS mapping results, which demonstrated that Nb, O, and Sn elements were uniformly distributed in the sample, which was consistent with the fact that the Sn\(_x\)Nb\(_{1-x}\)O\(_2\) solid solution was formed by our approach.

### 3.2 Chemical composition of Sn\(_x\)Nb\(_{1-x}\)O\(_2\) solid solution sample

The XPS analysis was conducted to investigate the chemical composition of synthesized sample. Figure 2(a) shows the representative XPS survey spectra of Sn\(_x\)Nb\(_{1-x}\)O\(_2\) solid solution and pristine SnO\(_2\) samples. As expected, the signals from Sn and O could be found in both samples, while Nb could only be detected in the Sn\(_x\)Nb\(_{1-x}\)O\(_2\) solid solution sample. For both samples, the C 1s peak could be observed due to the wide presence of carbon in the environment. Figure 2(b) shows the high-resolution XPS scan over the Nb 3d peaks of the Sn\(_x\)Nb\(_{1-x}\)O\(_2\) solid solution sample, in which the Nb 3d\(_{3/2}\) and Nb 3d\(_{5/2}\) peaks were found at

![Fig. 2](image-url) (a) XPS survey spectra of Sn\(_x\)Nb\(_{1-x}\)O\(_2\) solid solution and pristine SnO\(_2\) samples. (b) High-resolution XPS scan over Nb 3d peaks of the Sn\(_x\)Nb\(_{1-x}\)O\(_2\) solid solution sample. (c, d) High-resolution XPS scans over Sn 3d and O 1s peaks of Sn\(_x\)Nb\(_{1-x}\)O\(_2\) solid solution and pristine SnO\(_2\) samples, respectively.
~210.1 and ~207.4 eV respectively, consistent with the standard binding energy of Nb in the pentavalent oxidation state [48]. Figure 2(c) compares the high-resolution XPS scans over the Sn 3d peaks of both samples. Both Sn$^{4+}$ 3d$_{3/2}$ (495.4 eV) and Sn$^{4+}$ 3d$_{5/2}$ (487.1 eV) peaks in the Sn$_x$Nb$_{1-x}$O$_2$ solid solution sample shifted slightly to the lower binding energy direction, compared with that in the pristine SnO$_2$ sample. This observation suggested that a conductivity increase happened in the Sn$_x$Nb$_{1-x}$O$_2$ solid solution sample due to the enhanced charge carrier concentration from the substitution of Sn$^{4+}$ by Nb$^{5+}$, which could subsequently improve its surface activity related to photocatalytic reactions. Figure 2(d) compares the high-resolution XPS scans over the O 1s peaks of both samples. For the pristine SnO$_2$ sample, its O 1s peak could be fitted as a combination of two peaks at ~531.9 and ~530.8 eV, which could be assigned to adsorbed O species [49,50] and lattice Sn–O [51], respectively. For the Sn$_x$Nb$_{1-x}$O$_2$ solid solution sample, its O 1s peak could be fitted as a combination of four peaks at ~531.9, ~531.3, ~530.8, and ~530.6 eV, which represented adsorbed O species [49,50], oxygen vacancies [49,50], lattice Sn–O [51], and lattice Nb–O [52,53], respectively. The occurrence of oxygen vacancies in the Sn$_x$Nb$_{1-x}$O$_2$ solid solution sample could be attributed to the substitution of Sn$^{4+}$ by a higher valence dopant of Nb$^{5+}$ in the hydrothermal process, during which the oxygen vacancies were generated to meet the charge balance requirement as described by Eq. (1):

$$\text{Nb}_2\text{O}_5 \rightarrow 2\text{Nb}_{\text{Sn}} + 4\text{V}_0^- + 10e^- + \frac{5}{2}\text{O}_2$$

Thus, XPS analysis results also indicated the formation of the Sn$_x$Nb$_{1-x}$O$_2$ solid solution by substituting Sn$^{4+}$ in the SnO$_2$ rutile structure lattice with Nb$^{5+}$.

### 3. 3 Optical properties and band structure of Sn$_x$Nb$_{1-x}$O$_2$ solid solution sample

The diffuse reflectance measurement was used to investigate the optical properties of the obtained sample, and their light absorbance spectra could be estimated by Kubelka–Munk function as given by Eq. (2):

$$F(R) = \frac{(1 - R)^2}{2R}$$

where $R$ is the diffuse reflectance. Figure 3(a) compares the light absorbance spectra of Sn$_x$Nb$_{1-x}$O$_2$ solid solution and pristine SnO$_2$ samples, which showed that they had similar optical properties. Both had the major light absorbance in the UV light range, while the light absorbance intensity of the Sn$_x$Nb$_{1-x}$O$_2$ solid solution sample was higher than that of the pristine SnO$_2$ sample. Figure 3(b) shows their Tauc plots ($((F(R)hv)^{0.5}$ vs. $hv$) constructed from their light absorbance data, and their band gap values could be determined by extrapolation of the linear part of the Tauc plots to the abscissa of photon energy. It was found that, the band gap values of Sn$_x$Nb$_{1-x}$O$_2$ solid solution and pristine SnO$_2$ samples were ~3.81 and ~3.78 eV, respectively, which suggested that the heavy Nb-doping of SnO$_2$ had no obvious influence on its band gap value.}

Figures 4(a) and 4(b) show the M–S plots of Sn$_x$Nb$_{1-x}$O$_2$ solid solution and pristine SnO$_2$ samples vs. the Ag/AgCl reference electrode measured at 1 and 2 kHz, respectively. Their M–S plots both showed positive slopes, which demonstrated that the formation of Sn$_x$Nb$_{1-x}$O$_2$ solid solution did not change its n-type semiconductor nature. From the intercepts of their M–S plots, their flat band potentials vs. the Ag/AgCl electrode could be calculated at ~−0.74 V for the Sn$_x$Nb$_{1-x}$O$_2$ solid solution sample and ~−0.43 V for the pristine SnO$_2$ sample. Thus, their flat band potentials

![Fig. 3](https://www.springer.com/article/40145) (a) Light absorbance spectra of Sn$_x$Nb$_{1-x}$O$_2$ solid solution and pristine SnO$_2$ samples. (b) Their Tauc plot curves ($((F(R)hv)^{0.5}$ vs. $hv$) constructed from their light absorbance data in Fig. 3(a).
Fig. 4 M–S plots of (a) Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution and (b) pristine SnO$_2$ samples vs. the Ag/AgCl reference electrode measured at 1 and 2 kHz, respectively. (c) XPS valence band spectra of Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution and pristine SnO$_2$ samples. (d) Energy band structure diagrams of Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution and pristine SnO$_2$ samples.

vs. the normal hydrogen electrode (NHE) could be calculated at $\sim$ 0.52 V for the Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution sample and $\sim$ 0.21 V for the pristine SnO$_2$ sample. For n-type semiconductors, their flat band potentials are equal to their Fermi levels, which are generally $\sim$ 0.2 V more positive than their conduction band minimums (CBMs) [54]. Thus, their CBMs could be determined at $\sim$ 0.72 V for the Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution sample and $\sim$ 0.41 V for the pristine SnO$_2$ sample. Thus, their valence band maximums (VBMs) could be calculated at $\sim$ 3.09 V for the Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution sample and $\sim$ 3.37 V for the pristine SnO$_2$ sample, by combining their CBMs and band gap values. Figure 4(c) shows their XPS valence band spectra. It demonstrated that their valence band maximum values could be determined at $\sim$ 3.01 eV for the Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution sample and $\sim$ 3.26 eV for the pristine SnO$_2$ sample, which were consistent with that determined by their band gap values and M–S plots.

Figure 4(d) shows their energy band structure diagrams constructed from these analysis results. Their CBM values were both more negative than the reduction potential of CO$_2$/CH$_3$OH ($\sim$ 0.39 V), CO$_2$/CH$_3$CHO ($\sim$ 0.36 V), and CO$_2$/C$_2$H$_5$OH ($\sim$ 0.33 V), suggesting their feasibility in photocatalytical reduction of CO$_2$ into CH$_3$OH, CH$_3$CHO, and C$_2$H$_5$OH. Although the two samples had similar optical properties and band gap values, the formation of Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution did change the energy band structure of SnO$_2$. Especially, the CBM value of the Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution sample ($\sim$ 0.72 V) was $\sim$ 0.31 V more negative than that of the pristine SnO$_2$ sample ($\sim$ 0.41 V), which could significantly enhance the reduction potential of its photogenerated electrons and subsequently boost its photocatalytic CO$_2$ reduction performance.

3.4 Separation and transfer of photogenerated charge carriers of Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution sample

For semiconductors, the formation of a surface photovoltage signal is theoretically determined by its light absorption capability and the transfer of photogenerated charge carriers [55]. In principle, the photovoltage value could only be observed after the photogenerated charge carriers are separated from each other, so that the signal could provide a better estimation of the potential activities of photocatalysts. Figure 5(a)
shows the SPS of obtained samples to investigate the separation and transfer of photogenerated charge carriers in them under the simulated solar illumination. The Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution sample had a significantly higher surface photovoltage than that of the pristine SnO$_2$ sample, which indicated that the formation of Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution by the heavy Nb-doping could significantly promote the separation and transfer of photogenerated charge carriers due to the formation of oxygen vacancies, and subsequently enhance its photocatalytic performance [25–28].

Figure 5(b) compares their Nyquist plots obtained from the EIS measurements in darkness and under the simulated solar illumination. The arc radius of the Nyquist plot demonstrates the reaction rate occurring on the electrode surface; hence a smaller arc radius represents a higher separation level of photogenerated charge carriers and a faster transfer to an electron acceptor or donor for interfacial charges [56]. In darkness, the Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution sample had a smaller arc radius compared to the pristine SnO$_2$ sample, which verified that the substitution of Sn$^{4+}$ by Nb$^{5+}$ increased its charge carrier concentration. Under the simulated solar illumination, both samples demonstrated that the arc radius decrease due to the generation of charge carriers by the illumination, while the Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution sample also had a smaller arc radius compared to the pristine SnO$_2$ sample. Thus, the formation of Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution through the heavy Nb-doping did enhance the separation and transfer rate of photogenerated charges, which was consistent with the SPS measurement result and beneficial for improving its photocatalytic performance.

3.5 Photocatalytic CO$_2$ reduction performance of Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution sample under simulated solar illumination

Figure 6(a) shows the CO$_2$ adsorption performances by the Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution and pristine SnO$_2$ samples. Within the whole relative pressure range investigated, the CO$_2$ adsorption on the Sn$_{x}$Nb$_{1-x}$O$_2$ solid solution surface was always stronger than that on the pristine

![Image](http://www.springer.com/journal/40145)
SnO$_2$ surface due to the substitution of Sn$^{4+}$ by Nb$^{5+}$ as expected. For example, the CO$_2$ adsorption amount of the Sn$_{Nb1-x}$O$_2$ solid solution sample reached ~8.565 mL/g when the relative pressure was 1.0, which was ~5.7 times that of the pristine SnO$_2$ sample (~1.497 mL/g). To avoid the surface area effect, the CO$_2$ adsorption data was normalized by the corresponding surface area. The CO$_2$ adsorption amount of the Sn$_{Nb1-x}$O$_2$ solid solution sample reached ~0.056 mL/g when the relative pressure was 0.0, which was still ~1.9 times that of the pristine SnO$_2$ sample (~0.029 mL/g). The adsorption of CO$_2$ molecules on the photocatalyst surface is the first step in the photocatalytic CO$_2$ reduction. Thus, it was expected that the Sn$_{Nb1-x}$O$_2$ solid solution sample could have a better photocatalytic CO$_2$ reduction performance compared to the pristine SnO$_2$ sample.

Unlike the previous report [20], no sacrificial agent was used in the photocatalytic CO$_2$ reduction experiment, which could largely reduce the operation cost/complexity and favor its potential practical applications. Figure 6(b) shows the product evolution of photocatalytic CO$_2$ reduction by the Sn$_{Nb1-x}$O$_2$ solid solution sample under the simulated solar illumination for a series of reaction time from 1 to 8 h. Also, Fig. S1 in the ESM displays its magnified version to show the evolution of different products more clearly, especially in the earlier stage of the process. Figure 6(c) shows the product evolution of pristine SnO$_2$ sample under the same reaction conditions. Figures 6(b) and S1 in the ESM summarize the detailed information of the product types and amounts at different reaction time for the Sn$_{Nb1-x}$O$_2$ solid solution and pristine SnO$_2$ samples, respectively. The photocatalytic CO$_2$ reduction products by both samples under the simulated solar illumination were found to be liquid products of CH$_3$OH, CH$_3$CHO, and C$_2$H$_5$OH, while no gas product like CO or CH$_4$ was found. This observation was quite different from the previous reports on the photocatalytic CO$_2$ reduction by SnO$_2$-based photocatalysts to mainly produce CO and CH$_4$ [33–38].

Although the Sn$_{Nb1-x}$O$_2$ solid solution sample and the pristine SnO$_2$ sample had similar photocatalytic CO$_2$ reduction products, their performances were quite different. The Sn$_{Nb1-x}$O$_2$ solid solution sample demonstrated a much better photocatalytic CO$_2$ reduction efficiency than the pristine SnO$_2$ sample. For example, the production of the Sn$_{Nb1-x}$O$_2$ solid solution sample after 8 h under the simulated solar illumination reached ~42.0 µmol/g for CH$_3$OH, ~106.0 µmol/g for CH$_3$CHO, and ~1043.0 µmol/g for C$_2$H$_5$OH, while that of the pristine SnO$_2$ sample was only ~52.8 µmol/g for CH$_3$OH, ~13.7 µmol/g for CH$_3$CHO, and ~21.5 µmol/g for C$_2$H$_5$OH. Thus, the total CO$_2$ reduction amount by the Sn$_{Nb1-x}$O$_2$ solid solution sample reached ~2340.0 µmol/g after 8 h of treatment, which was 19 times that of the pristine SnO$_2$ sample (~123.2 µmol/g). Table S4 in the ESM summarizes the reported photocatalytic CO$_2$ reduction performances by different SnO$_2$-based photocatalysts without using sacrificial agent, compared with our Sn$_{Nb1-x}$O$_2$ solid solution and pristine SnO$_2$ samples. It could be seen that, the pristine SnO$_2$ sample had better or similar photocatalytic CO$_2$ reduction performances, compared with these SnO$_2$-based photocatalysts reported, while that of the Sn$_{Nb1-x}$O$_2$ solid solution sample was much higher than various photocatalysts previously reported in pieces of literature [33–38], when no sacrificial agent was used during the photocatalytic CO$_2$ reduction.

Figure S2 in the ESM shows the product evolution of photocatalytic CO$_2$ reduction by the Sn$_{Nb1-x}$O$_2$ solid solution sample under the simulated solar illumination with the reaction time of 8 h for four consecutive runs. Also, Table S5 in the ESM summarizes the detailed information of the product types and amounts by the Sn$_{Nb1-x}$O$_2$ solid solution sample for these four consecutive runs. It was found that, the photocatalytic CO$_2$ reduction products (C$_2$H$_5$OH, CH$_3$CHO, and CH$_3$OH) and the preferred product selectivity to C$_2$+ products were the same for these four consecutive runs, and their total reduction efficiency only decreased moderately. Figure S3 in the ESM shows XRD patterns of the Sn$_{Nb1-x}$O$_2$ solid solution sample before and after the photocatalytic CO$_2$ reduction experiment under the simulated solar illumination, which demonstrated that no obvious difference could be observed between them. The good structure stability during the photocatalytic CO$_2$ reduction was consistent with its relatively good cycling photocatalytic CO$_2$ reduction performance stability, which is beneficial for its potential applications.

3. 6 Photocatalytic CO$_2$ reduction process and performance enhancement mechanism of Sn$_{Nb1-x}$O$_2$ solid solution sample

From literature [3,9,17–20,29,57] and our investigation...
results, the possible reactions involved in the photocatalytic CO2 reduction process by the SnxNb1−xO2 solid solution and pristine SnO2 samples with the water as the reductant and without the sacrificial agent under the simulated solar illumination could be proposed as shown in Eqs. (3)–(13):

\[
\text{Sn}_{x}\text{Nb}_{1-x}\text{O}_2 + \text{SnO}_2 + h\nu \rightarrow h^+ + e^- (3) \\
\text{CO}_2 + e^- + \text{H}^+ \rightarrow \text{HCOO}^- (4) \\
\text{HCOO}^- + \text{H}^+ + e^- \rightarrow \text{CO} + \text{H}_2\text{O} (5) \\
\text{CO} + e^- + \text{H}^+ \rightarrow \text{CHO} (6) \\
\text{'CHO} + 2e^- + 2\text{H}^+ \rightarrow \text{'CH}_3\text{O} (7) \\
\text{'CH}_3\text{O} + e^- + \text{H}^+ \rightarrow \text{CH}_3\text{OH} (8) \\
2\text{'CH}_3\text{O} + 2e^- + 2\text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} (9) \\
\text{CH}_3\text{OH} + h^+ \rightarrow e^- + \text{H}_2\text{CO} + 2\text{H}^+ (10) \\
\text{H}_2\text{CO} + h^+ \rightarrow \text{'CHO} + 2\text{H}^+ (11) \\
2\text{'CHO} + 4e^- + 4\text{H}^+ \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} (12) \\
\text{CH}_3\text{CHO} + 2e^- + 2\text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{OH} (13)
\]

Besides their different photocatalytic CO2 reduction amounts in orders of magnitude, their product selectivity of the photocatalytic CO2 reduction was also quite different. For the SnxNb1−xO2 solid solution sample, its CH3OH production amount reached the maximum of ~67.0 µmol/g after 4 h of reaction and then decreased to ~42.0 µmol/g after 8 h of reaction, which could reflect the competition between the production of CH3OH (Eq. (8)) or CH3CH2OH (Eq. (9)) from the ‘CH3O intermediate, and also the further oxidation of CH3OH to formaldehyde (H2CO) and formyl (‘CHO) by h+ (Eqs. (10) and (11)) [20,57] to produce CH3CHO (Eq. (12)). Its CH3CHO production amount gradually increased to ~37.5 µmol/g after 1 h of treatment to ~45.0 µmol/g after 2 h of treatment, then largely reduced to ~21.6 µmol/g after 4 h of treatment, and did not change obviously at ~21.5 µmol/g after 8 h of treatment, which was only ~2% of that produced by the SnxNb1−xO2 solid solution sample under the same treatment conditions (~1043.0 µmol/g). The primary photocatalytic CO2 reduction product by the pristine SnO2 sample was CH3OH. Its maximum production amount of ~109.0 µmol/g occurred after 4 h of reaction and then decreased to ~52.8 µmol/g after 8 h of reaction. In the meantime, the production of CH3CHO could be detected at 13.7 µmol/g only after 8 h of treatment. Thus, this observation demonstrated that the further oxidation of CH3OH to formaldehyde (H2CO) and formyl (‘CHO) by h+ (Eqs. (10) and (11)) for the production of CH3CHO (Eq. (12)) mainly happened between 4 and 8 h during the photocatalytic CO2 reduction process by the pristine SnO2 sample. Interestingly, the total CO2 reduction amount by the pristine SnO2 sample decreased from ~152.2 to ~123.2 µmol/g when prolonging reaction time from 4 to 8 h, which suggested that a part of the reduction products must be oxidized back to CO2. This behavior was deleterious to the photocatalytic CO2 reduction, and may be related to the higher oxidation capability of photogenerated holes in the pristine SnO2 sample from its VBM value (~3.37 V) higher than that of the SnxNb1−xO2 solid solution sample (~3.09 V).

The formation of SnxNb1−xO2 solid solution through the heavy substitutional doping of Nb5+ to replace Sn4+ could result in the formation of abundant acid centers with positive charges and provide excess electrons due to the higher valence of Nb5+ [20]. These abundant acid centers could attract the lone-electron pair outside of the O atom of CO2 molecules from the Coulomb force [20], to largely enhance CO2 adsorption on the surface as demonstrated by the CO2 adsorption performance comparison, while the excess electrons in the SnxNb1−xO2 solid solution sample could promote the activation of CO2 [58]. Thus, the SnxNb1−xO2 solid solution sample had better adsorption and activation of CO2 molecules on its surface compared to the pristine SnO2 sample, which were the first steps towards their subsequent reduction. Next, the formation of SnxNb1−xO2 solid solution through the heavy Nb-doping had a favorable change on the band structure to endow it with a more negative CBM value (stronger photogenerated electron
reduction potential) and a less positive VBM value (weaker photogenerated hole oxidation potential), which promotes the photocatalytic reduction process to occur. Then, its better separation and transfer of photogenerated charge carriers could largely boost the photocatalytic efficiency. Furthermore, abundant CO2 adsorption/activation centers could increase the density of •CH3O intermediate on the SnxNb1−xO2 solid solution sample surface, which makes it easier for two 'CH3O intermediate species to encounter to form C2H5OH as shown in Eq. (9). Thus, the SnxNb1−xO2 solid solution sample demonstrated a superior photocatalytic CO2 reduction performance compared with the pristine SnO2 sample with a different photocatalytic CO2 reduction process and different product selectivity.

4 Conclusions

In summary, a novel defect engineering approach was proposed to synthesize the SnxNb1−xO2 solid solution by the heavy substitutional Nb-doping of SnO2 through a robust one-step hydrothermal process, which was found to largely enhance the photocatalytic CO2 reduction performance under the simulated solar illumination without the need for the sacrificial agent. The formation of SnxNb1−xO2 solid solution lifted both its conduction band and valence band, which could significantly enhance the reduction potential of its photogenerated electrons and reduce the oxidation potential of its photogenerated holes. Furthermore, it promoted the separation and transfer of photogenerated charge carriers, enhanced the adsorption of CO2 molecules on the photocatalyst surface, and created abundant acid centers and the presence of excess electrons on its surface through the heavy Nb-doping. All these factors were beneficial for the photocatalytic CO2 reduction, so the SnxNb1−xO2 solid solution demonstrated a photocatalytic CO2 reduction efficiency 19 times that of the pristine SnO2 sample and desirable product selectivity for the preferred C2+ product production. This work demonstrated that the heavy doping with the high valence cations in the metal oxides to form the solid solution may be a promising defect engineering approach of enhancing the photocatalytic CO2 reduction and modulating its reduction process to produce the desirable C2+ products, which could be readily applied to various photocatalyst systems to advance the development of solar-driven CO2 reduction.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

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