Vacancy-Defect Modulated Pathway of Photoreduction of CO$_2$ on Quaternary Single Atomically Thin AgInP$_2$S$_6$ Sheets toward Boosting Efficient and Selective Production of Value-Added Olefiant Gas

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Abstract

The quaternary AgInP$_2$S$_6$ atomic layer with the thickness of ~0.70 nm were successfully synthesized through facile ultrasonic exfoliation of the corresponding bulk crystal. The ultrathin sheet exhibits efficiently photocatalytic conversion of CO$_2$ into CO as a major product and minority of CH$_4$ and C$_2$H$_4$ in the presence of water vapor. The sulfur defect engineering on this atomic layer through a H$_2$O$_2$ etch process can excitingly enable to change the CO$_2$ photoreduction reaction pathway to steer dominant generation of ethene (C$_2$H$_4$) important chemical with the yield-based selectivity reaching ~73% and the electron-based selectivity as high as ~89%, and the quantum yield of 0.51% at wavelength of 415 nm. Both DFT calculation and in-situ FTIR demonstrate as the introduction of S vacancies in AgInP$_2$S$_6$ causes the charge accumulation on the Ag atoms near the S vacancies, the exposed Ag sites can thus effectively capture the forming *CO molecules, making the catalyst surface enrich with key reaction intermediates to lower the C-C binding coupling barrier, which facilitates the production of C$_2$H$_4$. Surface photovoltage measurement confirms that atomically ultrathin structure of the exfoliated AgInP$_2$S$_6$ can shorten the transfer distance of charge carriers from the interior onto the surface, thus decrease the recombination in body and improve the catalytic efficiency. This work may provide fresh insights into the design of atomically thin photocatalyst framework for CO$_2$ reduction and establish an ideal platform for reaffirming the versatility of defect engineering in tuning catalytic activity and selectivity.
Introduction

Photocatalytic conversion of CO$_2$ with H$_2$O into solar fuels would be like killing two birds with one stone in terms of saving supplying energy and environment, which occurs mostly on the surfaces of semiconductors through complicated processes involving multi-electrons/protons transfer reactions.$^1$ Photo-driving CO$_2$ hydrogenation into C$_1$ species have been well achieved in recent decade,$^2$ and our group has exploited a series of promising photocatalysts to converse CO$_2$ to selectively form specific hydrocarbons, such as Zn$_2$GeO$_4$ ultrathin nanoribbons for CH$_4$,$^3$ atomically thin InVO$_4$ nanosheets for CO,$^4$ and TiO$_2$-graphene hybrid nanosheets for C$_2$H$_6$,$^5$ and so on. However, the controlled C-C coupling to produce high-value C$_2$ or C$_2+$ products still remains a great challenge. Olefiant gas (Ethylene, C$_2$H$_4$) is a chemical source of particular importance due to its high demand in chemical industry. C$_2$H$_4$ is usually derived from steam cracking of naphtha under harsh production conditions (800–900 °C). It is definitely desirable for realization of C$_2$H$_4$ synthesis through mild and environmentally benign pathways.$^6$

Transition metal thio/selenophosphates (TPS) is a broad class of van der Waals layered structures with two sulfur or selenium layers sandwiching a layer of metal ions and P$_2$ pairs and general compositions of M$_4$[P$_2$X$_6$]$^{4-}$, [M$^{2+}$]$_2$[P$_2$X$_6$]$^{4-}$, and M$^{1+}$M$^{3+}$[P$_2$X$_6$]$^{4-}$, where M$^{1+}$ = Cu, Ag; M$^{3+}$ = Cr, V, Al, Ga etc. X = S, Se.$^7$ Those quaternary compounds exhibit mixed electron–ionic conductivity, promising optical and thermoelectric properties.$^8$ AgInP$_2$S$_6$ is a typical TPS with a rhombohedral structure and contains a sulfur framework with the octahedral voids filled by Ag, In and P–P triangular patterns. Each AgInP$_2$S$_6$ monolayer consists of the [P$_2$S$_6$] anionic complex and two metallic cations (Ag and In) located at the center of sulfur near-octahedral polyhedrons connected one with the other by edges. Semiconducting
AgInP₂S₆ crystal possesses appropriate bandgap structure ($E_g = \sim 2.4$ eV), which is favored for visible light absorption. The low value of the effective mass of electrons and the high value of the effective mass of holes facilitate to accelerate the mobility dynamics of photogenerated electrons onto the surface prior to holes, which may enhance local electron density, benefiting for photo-driving reduction reaction. The centrosymmetry structure of AgInP₂S₆ also enables the photoexcited electrons to distribute on the surface of the layer crystal uniformly, which may remarkably reduce the energy barrier for catalytic molecule activation, alter the catalytic reduction pathway, and enhance yield and enrich species of products.

An atomically thin 2D structure is an ideal platform to provide atomic level insights into the structure-activity relationship. Firstly, ultrathin structure allows the photo-generated carriers to easily transfer from the interior to the surface with shortened charge transfer distance, decreasing the bulk recombination. Secondly, large surface exposure renders rich catalytic active sites. Thirdly, transparency resulting from ultrathin thickness helps for light absorption. Creation of vacancy defects in the ultrathin structure can also additionally enrich the reaction intermediates, resulting in low-coordinated atoms on the surface of catalyst, which are known to facilitate to generate multi-carbon species from CO₂ photoreduction.

Herein, we report the synthesis of the AgInP₂S₆ single atomic layer (abbreviated as SAL) of ~0.70 nm in thickness through a facile probe sonication exfoliation of the corresponding bulk crystal (abbreviated as BC). The sulfur vacancy (abbreviated as $V_S$) defects were introduced in the resulting SAL through an etching process with H₂O₂ solution (abbreviated as $V_S$-SAL), which was prospectively utilized for photocatalytic reduction of CO₂ in the presence of water vapor. While BC and SAL dominantly produce CO, the implemented defect engineering changes the reaction
pathway of the CO$_2$ photoreduction on V$_S$-SAL, which allows to steer CO$_2$ conversion into C$_2$H$_4$ with the yield-based selectivity reaching ~73% and the electron-based selectivity as high as ~89%, and the quantum yield of 0.51% at wavelength of 415 nm. Both DFT calculation and *in-situ* FTIR and demonstrate that the key step for the CO production on BC and SAL follows a conventional hydrogenation process of CO$_2$ to form *COOH, which further couples a proton/electron pair to generate *CO. *CO easily liberates from the defect-free AgInP$_2$S$_6$ surface with low absorption energy to become free CO gas. In contrast, the introduction of V$_S$ in AgInP$_2$S$_6$ causes the charge accumulation on the Ag atoms near V$_S$. Thus, the exposed Ag site in V$_S$-SAL can effectively capture the forming *CO, making the catalyst surface enrich with key reaction intermediates to promote C-C coupling into C$_2$ species with the low binding energy barrier. This work may provide fresh insights into the design of atomically thin photocatalyst framework for CO$_2$ reduction and establish an ideal platform for reaffirming the versatility of defect engineering in tuning catalytic activity and selectivity.

**Results**

**Structure characterization of the AgInP$_2$S$_6$ related samples.** BC was synthesized through physical vapor transport in a two-zone furnace, which displays bright yellowis-brown color (Figure S1a). The SAL was produced through mechanical exfoliation in ethyl alcohol solution through a probe sonication technique. The well-defined Tyndall effect of the resulting transparent solution of SAL indicates high monodispersity of the ultrathin sheets (Figure S1b). Etching of SAL with H$_2$O$_2$ solutions allows to deliberately create V$_S$ on the surface of SAL.$^{15}$

The powder X-ray diffraction (XRD) pattern of BC and SAL agrees with the simulated one from the crystal structure of ICSD 202185 well with the P$_{\bar{3}}$1c space
and no impurity peaks were detected. The stronger SAL peak intensity ratio of (002) to (112) relative to BC indicates that the exfoliation of AgInP$_2$S$_6$ occurs along [001] direction. The field emission scanning electron microscopy (FE-SEM) image shows that BC displays an angular shape with an apparent laminar structure (Figures S3a and S3b). The energy dispersive spectroscopy (EDS) spectra demonstrate the uniform spatial distribution of Ag, In, P, and S (Figures S3c-3f). The TEM image of exfoliated SAL displays light contrast of the extremely thin 2D structure (Figure 1a). A magnified TEM image of a vertically standing sheet shows the single-layer with the thickness of $\sim$0.71 nm (Figure 1b). A typical edge-curling sheet as marked with an arrow also particularly shows the thickness of $\sim$0.72 nm of SAL (Figure 1b'), well in agreement with the AgInP$_2$S$_6$ monolayer along [002] orientation [$d_{(002)} = 6.68 \text{ Å}$]. The corresponding atomic force microscopy (AFM) image of SAL also confirms $\sim$0.66-0.73 nm range in thickness (Figure 1c), demonstrating the single atom layer feature. A high-resolution TEM image of SAL reveals that the interplanar d-spacing between the well-defined lattice fringes were examined 0.54 nm, which can be indexed to (010) (Figure 1d). The selected area electron diffraction (SAED) shows an ordered array of spots recorded from [001] zone axis (Figure 1d, inset), confirming that SAL is of single crystallinity and preferentially enclosed by {002} top and bottom surfaces. The crystallinemodel of SAL from top and side views was schematically illuminated in Figure 1f. With H$_2$O$_2$ solution treatment for optimized 10 seconds, the sulfur atoms, which locate outermost in SAL, can be partially etched away from the surface to form V$_S$. The generation of V$_S$ was confirmed with the electron paramagnetic resonance (EPR) spectra (Figure S4). The TEM image shows that the resulting V$_S$-SAL$_{10}$ displays no any morphology change in ultrathin structure (Figure S5). The corresponding EDS reveals that Ag, In,
and P contents were nearly stoichiometric 1:1:2 of AgInP$_2$S$_6$, except S element less than the stoichiometric ratio (Figure S6). It indicates that H$_2$O$_2$ treatment mainly leads to V$_S$, and has no etching effect on other moieties, which was also verified with the following XPS and the X-ray absorption near edge structure (XANES) spectra. The atomic resolution, aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM) clearly reveals that considerable number of V$_S$ were confined in the sheet (Figure 1e).

Full XPS spectra demonstrate the presence of Ag, In, P, S (Figure S7a). The high-resolution S 2p spectrum of BC shows the S 2p peak falling between 162 and 164 eV (Figure S7b), revealing -2 oxidation state of S. The S 2p peaks of SAL show dramatic low binding energy shift, compared with BC, and V$_S$-SAL$_{10}$ possesses further low-energy shift. The former shift may originate from exfoliation-resulting monolayerization, and the latter from V$_S$. As the decrease of binding energy indicates the enhanced electron screening effect due to the increase of the electron concentration, it implies that the electron density around the S sites increases in the sequence of BC, SAL, and V$_S$-SAL$_{10}$. It reveals that the residual S atoms exist in an electron oversaturated form and possess high electron density. No obvious change of binding energy of P elements was observed (Figure S7c), further demonstrating that the mechanical exfoliation and chemical etching only damage sulfur atoms and have little effect on P moiety. The pre-edge characteristic of the XANES spectra of the S K-edges of three AgInP$_2$S$_6$ were shown in Figure 2a, which could be fitted with components of a spin–orbit split. The spectra indicate the existence of main transitions energies between 2460 and 2500 eV, which originates from the excitation of an electron from a 1S inner orbital to a higher-energy orbital as a result of interaction with an X-ray. In comparison with BC, SAL shows a shift for S K-edge
peaks to lower energy side. This can be explained by the fact that the core electrons of S become more loosely bound after mechanical exfoliation due to the increased screening of the nuclear charge. Through $V_S$ engineering, the S K-edge of $V_S$-SAL$_{10}$ can have a further small moving to lower energy side (Figure 2a). Moreover, the K-edge peak of P between 2100 to 2250 eV exhibits almost no differences among BC, SAL, and $V_S$-SAL$_{10}$ (Figure 2b), which is in good agreement with the above-mentioned XPS results.

The UV–vis diffuse reflectance spectra show that the band gap of SAL was determined 2.66 eV, a little larger than that of BC (2.31 eV) (Figure S8), exhibiting strong quantum size effect in the lateral direction. $V_S$-SAL$_{10}$ displays slightly narrowed bandgap (2.57 eV) with respect to SAL. It derives from that introduction of $V_S$ may tailor the electronic structure of SAL through generating impurity states near the conduction band (CB) edge, which can be overlapped and delocalized with the CB minimum edge, leading to a reduced bandgap that may broaden the light absorption edge. The Mott–Schottky plots reveals that the CB edge of $V_S$-SAL$_{10}$ upshifts by ~0.06 eV and ~0.26 eV, relative to that of SAL and BC, respectively, as schematically illustrated in Figure S9. All BC, SAL, and $V_S$-SAL$_{10}$ were thus confirmed to possess suitable bandgaps as well as the appropriate band edge positions for photocatalytic CO$_2$ reduction under visible-light irradiation.

**Photocatalytic performance of the AgInP$_2$S$_6$ related samples toward CO$_2$ photoreduction.** The photocatalytic CO$_2$ conversion was carried out in the presence of water vapor under simulated solar irradiation (Figure 3). CO was detected the major product for BC and SAL (Figures 3a and 3b). BC shows the CO yield of 2.44 μmol g$^{-1}$ for the first hour and a trace amount of CH$_4$ of 0.63 μmol g$^{-1}$ (Figure 3a).
The photogenerated holes in the VB oxidize H$_2$O to produce hydrogen ions by the reaction of H$_2$O $\rightarrow$ 1/2O$_2$ + 2H$^+$ + 2e$^-$. CO is formed by reacting with two protons and two electrons (CO$_2$ + 2e$^- + 2$H$^+ \rightarrow$ CO + H$_2$O), and CH$_4$ formation through accepting eight electrons and eight protons (CO$_2$ + 8e$^- + 8$H$^+ \rightarrow$ CH$_4$ + 2H$_2$O). SAL exhibits 6.9 and 14.3-time enhancement of production of CO and CH$_4$ relative to BC, reaching 17.1 μmol g$^{-1}$ and 9.0 μmol g$^{-1}$ for the first hour, respectively (Figure 3b). The prerogative of atomic ultrathin geometry of SAL may be mainly responsible for the enhanced photocatalytic activity besides larger surface area, allowing charge carriers to move from interior to the surface quickly to conduct catalysis, avoiding the recombination in body. Small amount of C$_2$H$_4$ was also detected for SAL with the yield of 5.3 μmol g$^{-1}$. C$_2$H$_4$ is generated through accepting twelve electrons and twelve protons (2CO$_2$ + 12e$^- + 12$H$^+ \rightarrow$ C$_2$H$_4$ + 4H$_2$O). With the H$_2$O$_2$ etching process, excitingly, C$_2$H$_4$ excitingly becomes the main product for V$_5$-SAL$_{10}$ with the yield of 44.3 μmol g$^{-1}$ (Figure 3c). The calculated yield-based selectivity reaches ~73%, and the electron-based selectivity is as high as ~89%$^{20}$ (Figure 3e). Meanwhile, CO and CH$_4$ minority products were also traced with the yields of 10.9 μmol g$^{-1}$ and 5.6 μmol g$^{-1}$, respectively, both less than the case of SAL. It indicates that the surface of V$_5$-SAL$_{10}$ preferentially promotes the C$_1$ intermediates to C-C couple into C$_2$ product rather than liberate into free CO and CH$_4$ gases. The quantum yield of V$_5$-SAL$_{10}$ was measured 0.51 % at wavelength of 415 nm using monochromatic light (See the details in SI). The etching process time was found determinative for the dominant production of C$_2$H$_4$. The EPR measurement shows that the signal intensity
gradually increases with prolonging etching time from 5 seconds to 15 seconds (Figure S4), indicating being raised number of V₅ in V₅-SAL. Elongation of the etching time from 5s to 10s was favorable for increasing yield of C₂H₄ (Figure S10). However, much long etching time of 15s decreases activity negatively, which may be due to that an excess of V₅ defects may accelerate the recombination of photogenerated carriers.²¹ Reduction experiment of CO₂ preformed in the dark or absence of the photocatalyst shows no appearance of CO and hydrocarbon products, proving that the reduction reaction of CO₂ is driven by light under photocatalyst. Blank experiment with identical condition and in the absence of CO₂ shows no appearance of C₂H₄, CO, and CH₄, proving that the carbon source was completely derived from input CO₂. An isotope labeling experiment using ¹³CO₂ confirms that the produced C₂H₄ originates from the input CO₂ (Figure S11a). The O₂ production was also detected using the similar isotope H₂¹⁸O tracer control experiment (Figure S11b).

**Mechanism of the excellent photocatalytic performance of the V₅-SAL.** DFT simulations were performed to explore the V₅-mediated catalytic selectivity mechanism toward CO and C₂H₄ on AgInP₂S₆. CO₂ molecules are initially adsorbed on the catalyst surface where H₂O molecules dissociate into hydroxyl and hydrogen ions at the same time. The free-energy profile for the photocatalytic CO₂-to-hydrocarbon process with the lowest-energy pathway on the perfect AgInP₂S₆ surface was calculated, as shown in Figure 4. The key step for CO production is the hydrogenation of CO₂ to form *COOH, and the free-energy change of the step is 0.48 eV. Subsequently, the reaction intermediate (*COOH) further couples a
proton/electron pair to generate CO and H₂O molecules. An adsorption energy of -0.07 eV of the produced *CO on the defect-free AgInP₂S₆ surface implies the physical adsorption on the catalyst (Figure S12a). It means that *CO molecules can easily liberate from BC and SAL to become free CO gas, allowing high CO catalytic selectivity. Additional parts of *CO were continuously reduced by the incoming electrons and the successive protonation process to transform into CH₄.¹⁹,²² While the charge density of the valence band (VB) for pristine AgInP₂S₆ is evenly located on all the S and Ag atoms, contrastingly, the charge density of the VB is mainly located on the Ag atoms near the Vₛ for Vₛ-AgInP₂S₆, (Figure S13). That is to say, the presence of Vₛ in Vₛ-AgInP₂S₆ causes the charge enrichment on the Ag atoms near the Vₛ, which would benefit for stabilizing the reaction intermediates. For Vₛ-SAL, Vₛ can act as a trap for the *CO molecule, that is, the *CO molecule can chemically adsorb at exposed Ag sites with an adsorption energy of -0.25 eV (CO can only physically adsorb on the exposed P and In sites with distance of 2.56 and 3.20 Å, See Figure S13b-13d). The higher CO onset desorption temperature on Vₛ-SAL₁₀ than SAL affirms the stronger absorption (Figure S14). The absorbed *CO can be further protonated to successively form a series of key reaction intermediates with unsaturated coordination, which was confirmed with in-situ FTIR measurement (Figure S15). The other *CO molecules produced on the surface diffuses toward Vₛ and couple with those reaction intermediates to produce C₂H₄. The C₂H₄ free energy diagrams are summarized in Figure 4c, while the corresponding C-C coupling barriers are presented in Figure 4b. The different C-C coupling energy barriers were evaluated for three unsaturated reaction intermediates (*COH, *CHOH, and *CH₂) (Figure 4b). The coupling energy barrier with a value of 0.84 eV (*CO-CHOH) is lower than that of other coupling pathways (*CO-COH, 1.01 eV and *CO-CH₂, 1.84 eV), hence the
C$_2$H$_4$ will be produced via CO-CHOH coupling and hydrogenation. The whole free energy diagram shows that the process of $^*$CO to $^*$COH is regarded as the potential determining-step (0.86 eV). It should be especially emphasized that the detected small amount of C$_2$H$_4$ on SAL possibly originates from potential existence of the tiny number of V$_S$ in SAL, resulting from mechanically detaching sulfur atoms from SAL during the probe sonication exfoliation process. The reaction process for reduction of CO$_2$ into C$_2$H$_4$, CO, and CH$_4$ over V$_S$-SAL under light illumination is thus proposed in Figure S16.

Surface photovoltage spectroscopy (SPV) was employed to study separation and transport behavior of photoinduced charge carriers of the studied AgInP$_2$S$_6$. More negative SPV signal change reflects higher concentration of photogenerated electrons before and after light illumination. All BC, SAL, and V$_S$-SAL$_{10}$ show the SPV response under light illumination (Figures 5 and S17), corresponding to band-to-band transition. The SAL and BC exhibit 20 ~ 30 mV and 5 ~ 10 mV negative change before and after light illumination, respectively. More negative SPV signal change of SAL than BC exactly demonstrates that the atomically thin structure enables to alleviate the bulk electron-hole recombination to achieve high-concentration accumulation of photogenerated electrons on the surface. The V$_S$-SAL$_{10}$ display obviously dramatic change of 50 ~ 60 mV, indicating that introduction of V$_S$ can further favor the carrier separation and allow much increment of electron concentration on the surface. The excess surviving electrons are not only the necessary prerequisite to photoconversion of CO$_2$, but also can promote CO$_2$ adsorption and activation on the surface of the photocatalyst.

Photoluminescence (PL) decay profiles show that the SAL (~ 1.32 ns) possesses longer PL lifetime than BC (~ 0.40 ns) (Figure S18), demonstrating that the
atomically thin structure can indeed shorten transfer distance of the carriers and decrease recombination chance of electron and hole in the body. VS-SAL\textsubscript{10} exhibits the longest PL lifetime (~1.50 ns), confirming that the surface VS can serve as surface separation centers for charge carriers and further promote the charge separation, therefore offering more opportunities for photocatalytic CO\textsubscript{2} reduction. Transient photocurrent shows that the photocurrent intensity of SAL was enhanced with steadily repeating course due to promoted charge separation, compared with BC (Figure S19a). The highest photocurrent intensity of VS-SAL\textsubscript{10} implies that the VS also makes effective contribution for saving carriers. Electrochemical impedance spectra (EIS) reveal that VS-SAL\textsubscript{10} manifests the smallest semicircle in Nyquist plots (Figure S19b), suggesting the lowest charge-transfer resistance, which permits fast transport of photoinduced charge.

**Discussion**

In summary, single atomically-thin AgInP\textsubscript{2}S\textsubscript{6} layers were successfully synthesized through a facile probe sonication exfoliation of BC. The atomically thin structure of SAL, relative to BC, enables more charge carriers to mobile from the interior onto the surface and survivingly accumulate onto the active sites to improve the photocatalytic activity. While SAL exhibits obvious conversion efficiency with CO as the major product, the presence of VS in VS-SAL changes the CO\textsubscript{2} photoreduction pathway to allow the dominant generation of C\textsubscript{2}H\textsubscript{4}. This work not only paves an effective approach for selectively producing multi-carbon product from CO\textsubscript{2} photoreduction but also provides a new insight for catalyst design through vacancy defect engineering.
Methods

Synthesis of BC, SAL and V₅-SAL. The AgInP₂S₆ crystals have been synthesized by physical vapor transport (PVT) in a two-zone furnace. Stoichiometric amounts of high-purity elements (mole ratio Ag : In : P : S = 1:1:2:6, around 1 g in total) were sealed into a quartz ampoule with the pressure of 1*10⁻⁴ Torr inside the ampoule. The length of the quartz ampoule was about 15–18 cm with the 13mm external diameter. The ampoule was kept in a two-zone furnace (680 → 600 ℃) for 1 week. After the furnace was cooled down to room temperature, the AgInP₂S₆ crystalline powders could be found inside the ampoule (Figure S1a). SAL were prepared by sonication-assisted liquid exfoliation processes from synthetic AgInP₂S₆ crystalline powders. SAL was immersed in H₂O₂ solutions with the of concentrations 0.1 mol/L inside which SAL were allowed to react with H₂O₂ for 5, 10, 15 s, referred to V₅-SAL₅, V₅-SAL₇₀ and V₅-SAL₁₅, respectively, at 25 °C. All the obtained samples were carefully washed and dried before use.

Characterizations. X-ray diffraction (XRD) (Rigaku Ultima III, Japan) was used to investigate the purity information and crystallographic phase of the as-prepared powder samples. The XRD pattern was recorded by using Cu-ka radiation (λ = 0.154178 nm) at 40 kV and 40 mA with a scan rate of 10° min⁻¹. The morphology was characterized by the field emission scanning electron microscopy (FESEM, FEI NOVA NANOSEM 230). The transmission electron microscopy (TEM) and fine resolution transmission electron microscope (HRTEM) images were taken on a JEM 200CX TEM apparatus. X-ray photoelectron spectroscopy (XPS; K-Alpha, Thermo
Fisher Scientific) was standardized according to the binding energy of the adventitious C 1s peak at 284.8 eV, which was used to inspect the chemical states. A UV-vis spectrophotometer (UV-2550, Shimadzu) was hired to record the UV-visible diffuse reflectance spectra and switched to the absorption spectrum on the basis of the Kubelka–Munk connection at room temperature. Fourier transform infrared (FTIR) spectroscopy was examined using a Nicolet NEXUS870 (USA) spectrometer. The photoluminescence decay profile was described by the single-particle confocal fluorescence spectroscopy measurement (PicoHarp300). Surface photovoltage spectroscopy (SPV) was detected through AFM (Asylum Research, MFP-3D-SA, USA) analysis with the photo-assisted (a 405 nm laser excitation) Kelvin probe force microscopy (KPFM). Photoelectrochemical measurements were detected by a CHI660E electrochemical workstation using a standard three-electrode system in 1 mM NaSO₄ solution. Soft X-ray absorption spectra (XAS) were collected from the Soft X-ray Spectroscopy beamline at the Australian Synchrotron(AS, Australia), part of ANSTO.

**Measurement of Photocatalytic Activity.** For the photocatalytic reduction of CO₂, 4–5 mg of sample was uniformly dispersed on the glass reactor with an area of 4.2 cm². A 300 W Xenon arc lamp was used as the light source of photocatalytic reaction. The volume of reaction system was about 460 ml. Before the irradiation, the system was vacuum-treated several times, and then the high purity of CO₂ gas was followed into the reaction setup for reaching ambient pressure. 0.4 mL of deionized water was injected into the reaction system as reducer. The as-prepared photocatalysts were
allowed to equilibrate in the CO$_2$/H$_2$O atmosphere for several hours to ensure that the adsorption of gas molecules was complete. During the irradiation, about 1 mL of gas was continually taken from the reaction cell at given time intervals for subsequent CO, CH$_4$ and C$_2$H$_4$ concentration analysis by using a gas chromatograph (GC-2014C, Shimadzu Corp., Japan).

**The external quantum efficiency (EQE):** The quantum yield was calculated according to the below equation:

\[
E_Q = \frac{\text{N(electron)}}{\text{N(photon)}} = \frac{[N(\text{CO}) \times 2 + N(\text{CH}_4) \times 8 + N(\text{C}_2\text{H}_4) \times 12]}{\text{N(photon)}} \times 100\%
\]

where \(N\) (electron) signify two electrons are required to produce one molecule CO in unit time. The \(N\) (photon) is figured out according to the equation:

\[
N(\text{photon}) = \frac{[\text{Light intensity} \times \text{Illumination area} \times \text{Time}]}{[\text{Average single photon energy} \times N_A]}
\]

A light-emitting diodes (LEDs) provides the monochromatic incident light with identical condition. The light intensity of LEDs with 415 nm wavelength is 10.5mW/cm$^2$, the illumination area is controlled to 4.91 cm$^2$, \(N_A\) is the Avogadro constant, and the average single photon energy is calculated according to the equation:

\[
E(\text{photon}) = \frac{hc}{\lambda}
\]

in which \(h\) is the Planck constant, \(c\) indicates speed of light, and \(\lambda\) is the wavelength.

**Computational details:** The density functional theory (DFT) calculations were made with the Vienna Ab Initio Simulation Package$^{24,25}$ (VASP) code. The
exchange-correlation interactions and the ion-electron interactions were solved by the Perdew-Burke-Ernzerhof (PBE) functionals\textsuperscript{26,27} and the projector-augmented wave (PAW) method\textsuperscript{28}, respectively. The monolayer AgInP\textsubscript{2}S\textsubscript{6} was a model with a 2 × 2 supercell. A plane-wave cutoff of 450 eV was adopted and the maximal force on all-atom was below 0.02 eV/Å. The distance between periodic units in the vertical direction was larger than 16 Å. The DFT-D2 method of Grimme\textsuperscript{29} was used in all calculations to accurately describe long-range Van der Waals (vdW) interactions. The climbing-image nudged elastic band (CI-NEB) method\textsuperscript{30} incorporated with spin-polarized DFT was used to locate the minimum-energy path. The intermediate images of each CI-NEB simulation were relaxed until the perpendicular forces were smaller than 0.1eV/Å.

The free energies of each reaction intermediates were determined according to $G = E + ZPE - TS$. The electronic energies (E) can be directly obtained from DFT computations. The zero-point energy (ZPE) and entropy correction (TS) were calculated from vibration analysis by standard methods. The computational hydrogen electrode (CHE) model\textsuperscript{31} was used to treat the free energy change of each reaction step involving a proton-electron pair transfer. In this model, the free energy of a proton-electron pair at 0 V vs RHE is equal to half of the free energy of hydrogen molecule.
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Acknowledgement
The authors wish to acknowledge the support of National Key R &D Program of China (2018YFE0208500), 973 program (2017YFA0204800), NSF of China (21972065, 21773114, and 21773027), the Fundamental Research Funds for the Central University (020414380167), NSF of Jiangsu Province (No. BK20171246), the Hefei National Laboratory for Physical Sciences at the Microscale (KF2020006), the Program for Guang-dong Introducing Innovative and Enterpreneurial Team (2019ZL08L101) and The university Development Fund (UDF01001159).

Author contributions
Y. Z., Y. X. and Z. Z instructed this work. L. S. and J. W. carried out the DFT calculation. W. G., H. H., X. Li, Z. C., Y. Y., and Q. S. performed the experiments and co-wrote this manuscript. X. W. contributed the PL spectrum measurement.

Competing interests: The authors declare on Competing Financial or Non-Financial Interests.
Fig. 1 TEM images of (a) SAL, (b) vertically standing and (b’) laying single piece SAL, (c) AFM image of SAL showing an average thickness of ~ 0.69 nm. (d) HRTEM image and the EDS. (e) HAADF-STEM image of V₅-SAL₁₀, in which the atomically dispersed V₅ are highlighted with the yellow circles. (f) The crystalline models of SAL from top and side views.
Fig. 2 (a) S and (b) P K-edge XANES spectra of BC, SAL, and Vs-SAL_{10}.
Fig. 3 Photocatalytic gases evolution amounts as a function of light irradiation times of (a) BC, (b) SAL, and (c) V₅-SAL. (d) Photocatalytic activity for the first hour. (e) Table illustration for the yield and electron-based selectivities of photocatalytic CO₂ conversion.
Fig. 4 (a) Gibbs free energy diagrams for CO₂ reduction to CO over perfect AgInP₂S₆. (b) Three kinds of possible C-C coupling pathways over AgInP₂S₆ containing V₅. (c) Gibbs free energy diagrams for CO reduction to C₂H₄ over AgInP₂S₆ with V₅. The insets show the corresponding optimized geometries for the reaction intermediates during the CO₂ reduction process. Sulfur, phosphorus, indium, silver, carbon, oxygen, and hydrogen atoms are yellow, purple, lilac, gray, black, red, and white, respectively.
Figure 5. Height images of (a) V₅-SAL₁₀, (b) SAL and (c) BC; The SPV images (d) V₅-SAL₁₀, (e) SAL and (f) BC in (a), (b) and (c), respectively, are differential images between potential images under light and in the dark. All scale bars represent 0.5 μm. The surface photovoltage change by subtracting the potential under dark conditions from that under illumination (SPV, ΔCPD = CPD dark – CPD light) of (h) V₅-SAL₁₀, (i) SAL and (j) BC.