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Exfoliated 2D Layered and Nonlayered Metal Phosphorous Trichalcogenides Nanosheets as Promising Electrocatalysts for CO₂ Reduction

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Abstract: Two-dimensional (2D) materials catalysts provide an atomic-scale view on a fascinating arena for understanding the mechanism of electrocatalytic carbon dioxide reduction (CO₂ ECR). Here, we successfully exfoliated both layered and nonlayered ultra-thin metal phosphorous trichalcogenides (MPCh₃) nanosheets via wet grinding exfoliation (WGE), and systematically investigated the mechanism of MPCh₃ as catalysts for CO₂ ECR. Unlike the layered CoPS₃ and NiPS₃ nanosheets, the active Sn atoms tend to be exposed on the surfaces of nonlayered SnPS₃ nanosheets. Correspondingly, the nonlayered SnPS₃ nanosheets exhibit clearly improved catalytic activity, showing formic acid selectivity up to 31.6% with -7.51 mA cm^{-2} at -0.65 V vs. RHE. The enhanced catalytic performance can be attributed to the formation of HCOO* via the first proton-electron pair addition on the SnPS₃ surface. These results provide a new avenue to understand the novel CO₂ ECR mechanism of Sn-based and MPCh₃-based catalysts.

Introduction

Electrocatalytic carbon dioxide reduction (CO₂ ECR), which harvests CO₂ as value-added chemicals and fuels using renewable electricity, provides a promising avenue to alleviating carbon emissions.^[1] Formic acid (HCOOH), as a liquid hydrogen carrier with high energy density (1.77 kWh L^{-1}) and hydrogen load (4.35% of its weight), plays an important role in the chemical industry as a feedstock.^[2] Thus, out of many possible products in CO₂ ECR, there is a strong impetus to search for promising materials with good selectivity, high activity, and robust stability for formic acid productions (and other desired products). Sn-based materials have been demonstrated as promising catalysts for electrocatalytic CO₂-to-formic acid conversion, also given their earth-abundant, eco/env-friendly characteristics.^[3] Up to now, a variant form of Sn-based catalysts have been studied for CO₂ ECR, e.g., single metals, alloys, metal oxides, and carbon hybrids materials.^[4] Moreover, more types and morphologies of Sn-based catalysts need further study. Two-dimensional (2D) materials with atomic-scale thicknesses as candidate CO₂ ECR catalysts have shown excellent catalytic activities owing to their high electrical conductivity, amply exposed surface atoms, and high specific surface area.^[5] Additionally, the well-controlled

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crystal structures of 2D materials benefit the understanding of the atomic-scale relationships between active sites and reactivity for CO₂ ECR.^[6] However, 2D metal nanosheets are prone to oxidation, leading to a rapid loss of cyclability.^[7] Moreover, exploring 2D transition-metal dichalcogenides (TMDs) as catalysts demands the use of an ionic liquid as the electrolyte; otherwise, the hydrogen evolution reaction (HER) will surpass the CO₂ reduction during the CO₂ ECR.^[8] Therefore, it is worthwhile exploring new types of 2D nanosheets to produce carbon products such as formic acid through CO₂ ECR, with good selectivity against other competitive reactions.

Metal-phosphorus-chalcogen (MPCh) complexes offer a wide range of layered compounds with a vast spectrum of potential applications, with metal phosphorous trichalcogenides (MPCh₃) being the most widely studied.^[9] Generally, the MPCh₃ materials are categorized into two classes based on the interlayer forces. On one hand, both P₂ pairs and metal atoms are in octahedral coordination and van der Waals forces can stack the layers to form a layered structure (such as CoPS₃, NiPS₃, etc.).^[10] On the other hand, P₂ pairs and metal atoms are located in octahedral and trigonal prismatic coordination, respectively, and the structural units consisting of P₂S₆⁴⁻ anions can be linked together via S–Sn or S–Pb contacts to constitute the nonlayered structure (like SnPS₃ and PbPS₃).^[11] These structural characteristics result in distinct chemical and physical properties, endowing the MPCh₃ materials with rich functionalities for energy storage and conversion.^[12] Although MPCh₃ nanosheets have been widely studied for electrocatalytic HER,^[13] oxygen evolution reaction (OER),^[14] and nitrogen reduction reaction (NRR),^[15] they are rarely explored for CO₂ ECR. In particular, exfoliating layered and nonlayered MPCh₃ nanosheets for CO₂ ECR can be valuable in elucidating the complex active sites-performance relationships for CO₂ ECR on the atomic scale.

The central metal atom interacted with its supporting materials, jointly forming the catalytic active sites in 2D transition-metal catalysts. Accordingly, it is necessary to investigate the effects of the metal and supporting material. Recently, researches addressing the transition metal heteroatom co-doped electrocatalysts in CO₂ ECR give a better understanding of the activity origination.^[16] Sulfur (S) atoms exhibit unique properties to regulate the ECR performance by modifying the surrounding structural and electronic environment.^[17] Lu and co-workers synthesized a S-doped Ni–N–C catalyst (Ni–NS–C) by a facile method, which achieved a very high CO₂-to-CO conversion efficiency of 99.7 % under –0.80 V vs. RHE. More importantly, their study revealed that the transition-metal, Ni atoms, played as CO₂ ECR active sites, whereas S atoms improved its electrocatalytic activity synergistically by comparing these two S-doped and S-free catalysts.^[18] These electrocatalytic CO₂ reduction reactions could also be boosted acquired by using the powerful strategy of sulfur activation in Fe–NS–C,^[19] Ni–S–C₇^[20] and so on. Furthermore, the different central earth-abundant transition-metal atoms (Mn, Fe, Co, Ni, Cu, Sn...) have been explored for CO₂ reduction in numerous research groups to investigate the effect of central

metal on catalytic activity and selectivity.^[21] Hence, using different types of MPCh₃ nanosheets as models to study the positions of metal atoms or S atoms is of great significance for understanding the mechanism and activity origination of CO₂ ECR.

Among a large variety of nanosheets preparation techniques, liquid-phase exfoliation (LPE) is a widely used method to sonicate the samples in appropriate solvents to induce fragmentation and delamination of nanosheets from their bulk crystal counterparts.^[22] However, exfoliation of nonlayered materials using LPE requires breaking chemical bonds rather than just van der Waals forces, which greatly increases the difficulty of exfoliation.^[23] Developing effective methods to exfoliate nanosheets from layered and non-layered bulk MPCh₃ is needed for systematically studying the application and reaction mechanism of MPCh₃ on CO₂ ECR.

Herein, we have successfully exfoliated uniform and ultra-thin MPCh₃ nanosheets from layered CoPS₃, NiPS₃, and nonlayered SnPS₃ bulk crystals via wet-grinding exfoliation (WGE) in the presence of isopropanol (IPA). In this work, we not only efficiently and simultaneously synthesized layered and nonlayered ultra-thin MPCh₃ nanosheets, but also revealed the relationship between crystal structures of MPCh₃ nanosheets and the performance of CO₂ ECR. The CO₂ ECR properties of all three nanosheets were studied, and it was demonstrated that SnPS₃ nanosheets clearly exhibit better performance. The selectivity and reaction rate of HCOOH (i.e., FE_{COOH} and j_{COOH}) reach 31.6 % and –7.51 mA cm^{–2} at –0.65 V vs. RHE, respectively. As far as we know, this is the first report using MPCh₃ to produce HCOOH from CO₂. Density functional theory (DFT) calculations further suggested that the formation of HCOO* via the first proton-electron pair addition is energetically more favorable than COOH*, indicating the dominant role of the HCOOH pathway in CO₂ activation. In addition, both scanning transmission electron microscopy (STEM) characterization and DFT calculations showed that WGE can induce atomic defects in CoPS₃ and NiPS₃ nanosheets, which is beneficial for CO₂ ECR. This work provides detailed insight into the fabrication of layered and non-layered 2D nanosheets. It establishes an ideal methodology to design versatile micro-nano structures for understanding the relationships between active sites and catalytic properties at the atomic scale with enhanced catalytic performance.

Results and Discussion

The crystalline structures of monolayer CoPS₃, NiPS₃, and SnPS₃ nanosheet from top and side views are schematically illustrated in Figure 1a. Unlike the layered CoPS₃ and NiPS₃, the SnPS₃ bulk crystals have a distinct nonlayered structure (Figure S1). As reported, CoPS₃ and NiPS₃ exhibit preferential orientation in the (001) direction owing to the layered structure, whereas nonlayered SnPS₃ bulk crystals exhibit a preferential orientation in the (200) direction.^[24] It is interesting to notice that in both layered nanosheets, the transition metal elements (Co and Ni) are located between

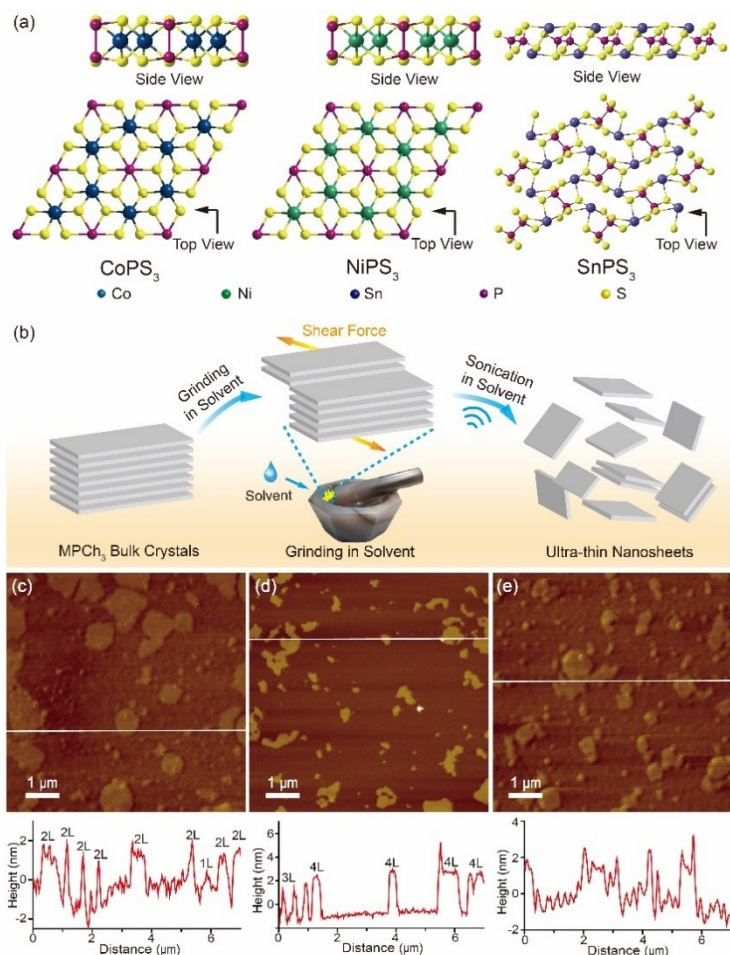


Figure 1. Preparation of $MPCh_3$ nanosheets. a) The crystalline structures of $CoPS_3$, $NiPS_3$, and $SnPS_3$ from top and side views. b) The preparation Scheme for the $MPCh_3$ nanosheets. AFM images and the corresponding height profiles of exfoliated $CoPS_3$ nanosheets (c), $NiPS_3$ nanosheets (d), and $SnPS_3$ nanosheets (e).

atomic layers formed out of nonmetal elements (P and S) and hence are hard to be exposed on the surface, while in the nonlayered $SnPS_3$ nanosheets, the Sn element is located on the surface.

The WGE processes to fabricate $MPCh_3$ nanosheets are schematically shown in Figure 1b. First, we ground the $MPCh_3$ bulk crystals for 30 min using an agate mortar in the presence of IPA. In the second step, the ground samples were added into IPA for sonication and centrifugation to prepare $MPCh_3$ nanosheets dispersions (Figure S2). Compared with the direct LPE, such a pretreatment through grinding produces nanosheets that can significantly reduce the size of $MPCh_3$ bulk crystals (Figure S3) with a shorter sonication time.^[25] The mortar generates a shear force along the layer surfaces to break the van der Waals forces or S–Sn bonds to form ultra-thin $MPCh_3$ nanosheets. In this method, IPA was selected as the solvent, as it exhibited good wettability, high viscosity, and appropriate surface energy matching to that of the $MPCh_3$ bulk crystals.

The resulting $MPCh_3$ nanosheets dispersions were transferred to silicon wafers for atomic force microscopy (AFM) investigations (Figure 1c–e), which suggest the thickness of

the layered and nonlayered $MPCh_3$ nanosheets are within 3 nm. Given that the thickness of single-layered $CoPS_3$ and $NiPS_3$ nanosheets are about 0.7 nm,^[24b,26] the as-prepared layered $CoPS_3$ and $NiPS_3$ nanosheets consist mostly of 1–4 layers according to the thickness distribution (Figure S4). An average lateral size of below 300 nm was observed (Figure S4), consistent with scanning electron microscopy (SEM) images (Figure S5). Furthermore, to the best of our knowledge, this is the thinnest $SnPS_3$ nanosheets achieved from the nonlayered bulk $SnPS_3$. A detailed comparison between the traditional exfoliation methods reported from several literatures and our work has been summarized in Table S1. The results show that we obtained ultra-thin nanosheets with shorter grinding and sonication time without using any toxic solvents, which proves the effectiveness of our WGE method.

We next performed STEM studies to investigate the crystalline quality and atomic structure of as-prepared $MPCh_3$ nanosheets. Figures 2a, d, and g show the overview high-angle annular dark-field STEM (HAADF-STEM) images of the $CoPS_3$, $NiPS_3$, and $SnPS_3$ nanosheets, respectively. Electron energy-loss spectroscopy (EELS) maps

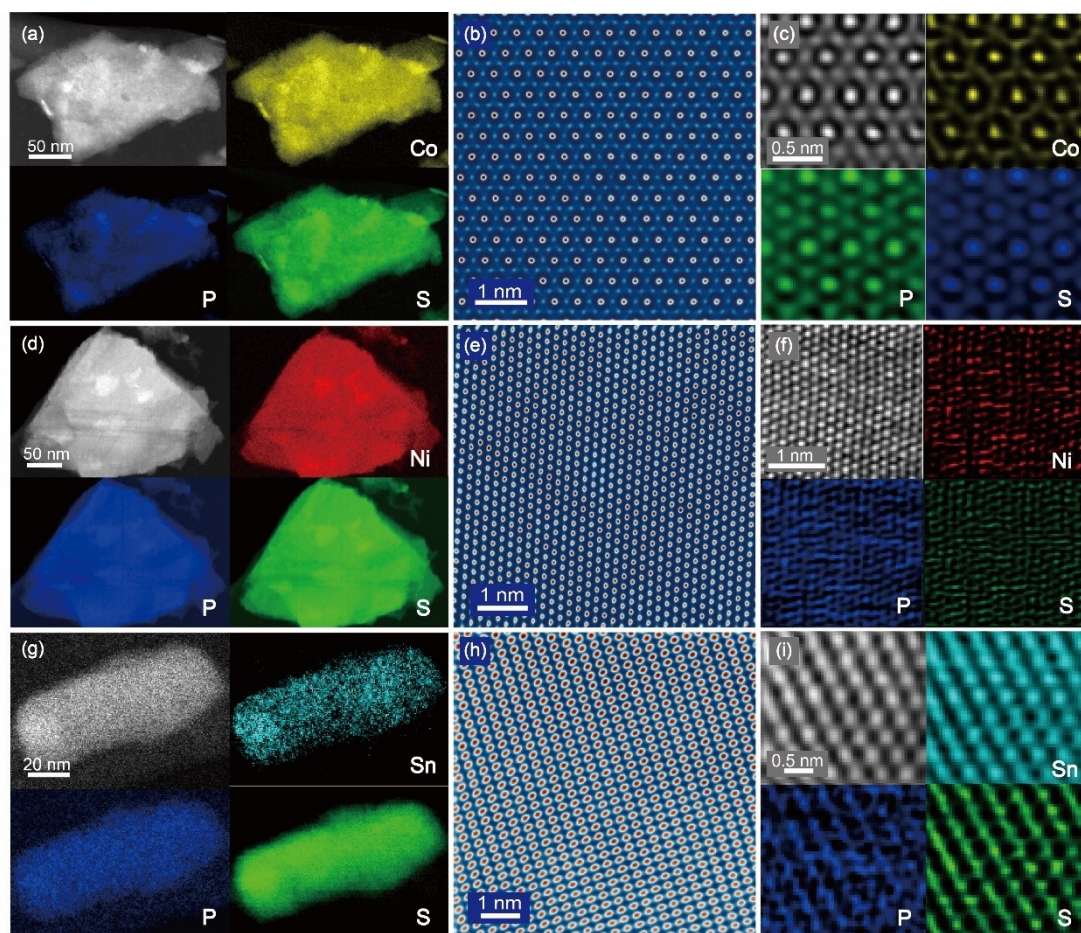


Figure 2. Structure and elemental distribution of the MPCh₃ nanosheets. Overview HAADF-STEM images and corresponding STEM-EELS maps (a, d, and g), the colored atomically resolved HAADF-STEM images (b, e, and h), and atomically resolved HAADF-STEM image and corresponding STEM-EELS maps (c, f, and i), a)–c) CoPS₃ nanosheets, d)–f) NiPS₃ nanosheets, and g)–i) SnPS₃ nanosheet.

illustrate that Co/Ni/Sn, P, and S elements are uniformly distributed throughout the entire nanosheets (See information Figure S6 for the corresponding EELS spectra). The colored HAADF-STEM images in Figures 2b, e, and h confirm that the prepared nanosheets preserve an excellent crystal structure even after exfoliation. Moreover, unlike the SnPS₃ nanosheets, some point defects appear in the STEM images of CoPS₃ and NiPS₃ nanosheets, probably due to sonication, grinding, and possible electron-beam damage (Figure S7).^[27] It suggests that atomic defects may be more inclined to be formed in layered MPCh₃ than in nonlayered SnPS₃. We will discuss the effects of vacancies below. Furthermore, atomically resolved EELS maps of MPCh₃ nanosheets with layered and nonlayered structures are acquired, revealing the atomic-scale distribution of different atoms (Figures 2c, f and i). Unlike layered CoPS₃ and NiPS₃ nanosheets, active metal sites of nonlayered SnPS₃ nanosheets tend to be exposed on the surface of nanosheets.^[11a,24b] X-ray photoelectron spectroscopy (XPS) demonstrates the presence of Co, Ni, Sn, P, and S, and a partially-oxidized surface (Figures S8 and S9). For CoPS₃ and NiPS₃, there is a slight red shift in the binding energy for the P 2p_{3/2} and S 2p_{3/2} peaks (131.9 and 162.4 eV for bulk

CoPS₃, 131.9 and 162.5 eV for bulk NiPS₃) compared to bulk crystal (131.3 and 161.8 eV for bulk CoPS₃, 130.6 and 161.4 eV for bulk NiPS₃),^[28] which further confirms the formation of sulfur vacancies in the CoPS₃ and NiPS₃ nanosheets during grinding and sonication.

To investigate the effect of solvent and grinding on the yield of MPCh₃ nanosheets, we employed UV/Vis spectroscopy to study the optical properties of resulting particles, as shown in Figures 3a–c. UV/Vis spectroscopy is based on the Beer–Lambert law, and the absorbance strength can be used to quantitatively characterize the preparation efficiency of WGE. The layered and nonlayered MPCh₃ nanosheets were exfoliated using IPA as the grinding solvent with a higher exfoliation efficiency. This is because the grinding can generate shear forces, which facilitates the exfoliation. Moreover, compared with ethanol and acetone, IPA has a higher viscosity to increase the pre-grinding resistance and further increase the shear force along the layer surface.^[29] In addition, IPA has a smaller contact angle, which indicates better wettability, proving that IPA is a suitable grinding solvent for WGE of MPCh₃ crystals (Figure S10). Under these conditions, the concentration of the CoPS₃, NiPS₃, and SnPS₃ dispersions reach 0.31, 0.65, and 0.22 mgmL⁻¹,

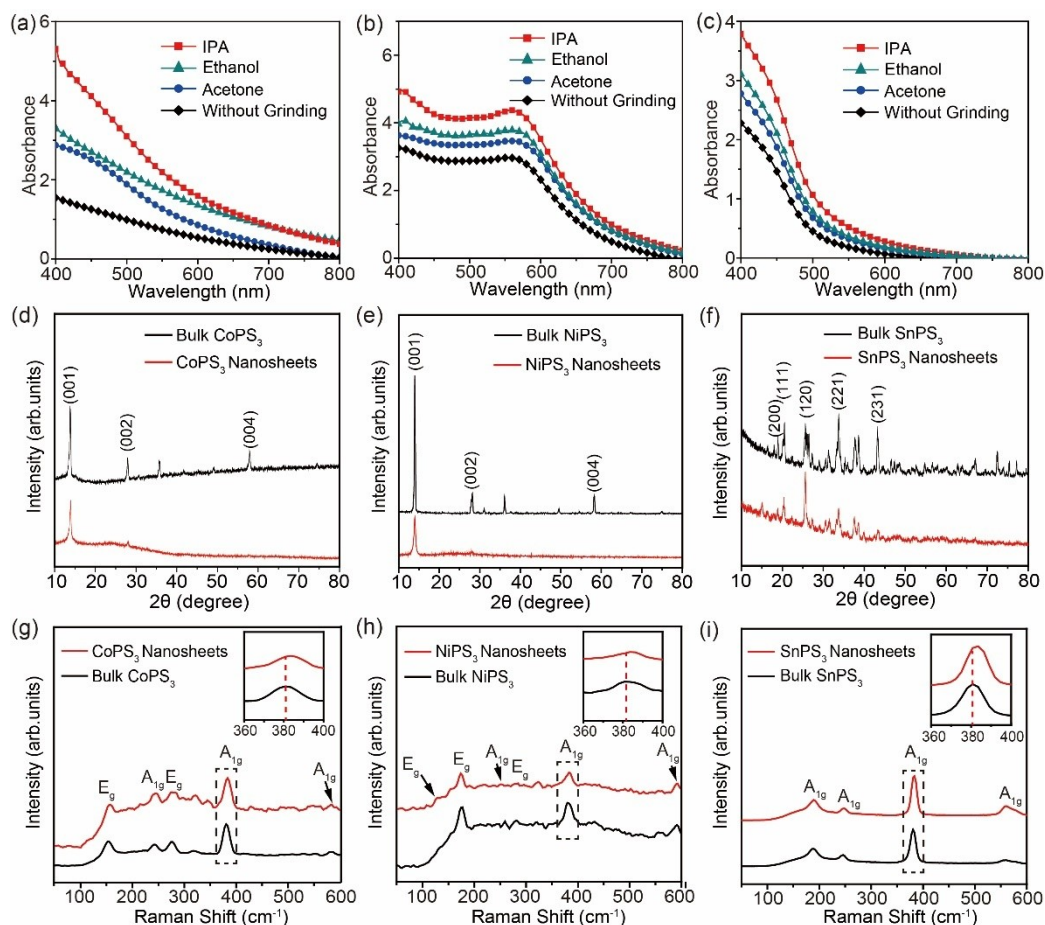


Figure 3. Properties of MPCh₃ nanosheets. UV-vis absorption spectra of the CoPS₃ (a), NiPS₃ (b), and SnPS₃ (c) prepared in different grinding solvents (IPA, ethanol, and acetone) and without grinding. XRD patterns of bulk CoPS₃ and CoPS₃ nanosheets (d), bulk NiPS₃ and NiPS₃ nanosheets (e), bulk SnPS₃ and SnPS₃ nanosheets (f) on the glass substrate. Raman spectra of bulk CoPS₃ and CoPS₃ nanosheets (g), bulk NiPS₃ and NiPS₃ nanosheets (h), bulk SnPS₃ and SnPS₃ nanosheets (i), and the corresponding enlarged Raman spectra (inset).

respectively, suggesting a corresponding synthesis yield of 3.1%, 6.5%, and 2.2%, respectively, measured by the commonly used weighing method.^[30] We also investigated the effect of acetone as a grinding solvent on the MPCh₃ nanosheets (Figure S11). The results show that the grinding solvent has little effect on the lateral size and thickness of the nanosheets.

The crystal structures of MPCh₃ were subsequently studied using X-ray diffraction (XRD) with 2θ ranging from 10° to 80°. The peaks in Figure 3d and e can be attributed to the monoclinic CoPS₃ (space group *C2/m*) (PDF No.78-0498)^[31] and NiPS₃ (space group *C2/m*) (PDF No.78-0499).^[32] Figure 3f confirms that monoclinic SnPS₃ bulk crystals (PDF No.27-1475) have the space group *P2₁/n*.^[33] CoPS₃, NiPS₃, and SnPS₃ nanosheets exhibit significantly reduced intensities, which proves the ultra-thin 2D structures. Raman spectra of CoPS₃, NiPS₃, and SnPS₃ are displayed in Figure 3g–i with an excitation laser line of 532 nm. Raman peaks within 50 to 600 cm⁻¹ originate from A_{1g} and E_g vibrational modes of the P₂S₆ units. The Raman peaks corresponding to A_{1g} vibrational mode of CoPS₃, NiPS₃, and SnPS₃ nanosheets show a slight shift of 2 cm⁻¹

due to the exfoliation of MPCh₃ bulk crystals, which demonstrates the successful exfoliation of the nanosheets from layered and nonlayered MPCh₃ bulk crystals.^[34]

The CO₂ ECR performance of the MPCh₃ nanosheets were evaluated using a custom-built flow cell at fixed potentials between -0.45–-0.75 V vs. RHE (Figure 4a).^[35] The faradaic efficiency (FE) and current density (*j*) for all the products with different applied potentials are presented in Figure 4b and Table S2. Hydrogen (H₂) is formed from HER, which is a competing reaction against CO₂ reduction, e.g., NiPS₃ and CoPS₃ catalysts show insignificant CO₂ ECR activity with the majority product being H₂ (Table S3 and S4), CoPS₃ catalysts display higher selectivity towards H₂ at low applied potentials. When the applied potential becomes more negative, the performance of NiPS₃ and CoPS₃ catalysts is comparable. In addition, the calculated results confirmed that NiPS₃ and CoPS₃ are better HER catalysts (Figure S12). SnPS₃ shows better inhibition of HER as compared to CoPS₃. Besides, only CO and HCOO⁻ are detected when using SnPS₃, the FE_{CO} decreased according to the increased overpotential. Importantly, the selectivity and reaction rate of HCOO⁻ (i.e., FE_{HCOO⁻} and *j*_{HCOO⁻}) for

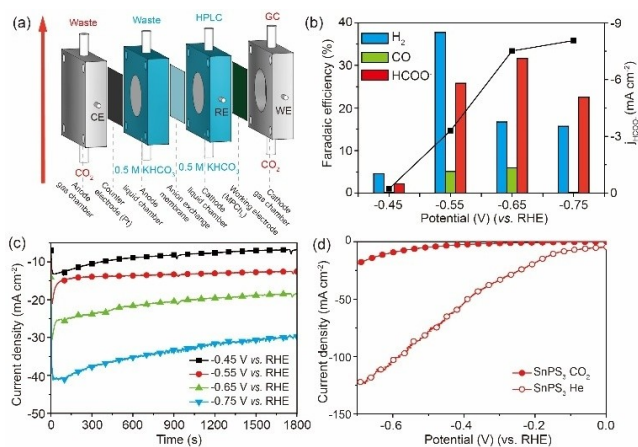


Figure 4. CO₂ ECR performance. a) Scheme of the custom-built flow cell, b) faradaic efficiency of major products and current density of formic acid, and c) chronoamperometry curves using SnPS₃ catalyst at different applied potentials, d) LSV curves of SnPS₃ catalyst in CO₂-saturated and He-saturated 0.5 M KHCO₃ solution.

SnPS₃ nanosheets ramps up to 31.6% and -7.5 mA cm^{-2} at -0.65 V vs. RHE, respectively. As to the best of our knowledge, this is the first experimental report using MPCh₃ for CO₂ reduction to HCOO⁻. The corresponding chronoamperometry curves at different potentials are shown in Figure 4c. The linear sweep voltammetry (LSV) traces performed under a Helium (He) and CO₂-saturated electrolyte solution are depicted in Figure 4d. Under the He atmosphere, the cathodic current density is assigned to HER. The result suggests the cathodic current is severely suppressed in the CO₂-saturated solution.^[36] To further verify the active forms of our catalysts, the chemical composition of the SnPS₃ catalysts before and after CO₂ ECR were examined by XRD pattern and XPS spectra. In the XRD pattern (Figure S13a), the result shows that the peaks at 30.6°, 32.0°, 44.9° arise from the (200), (101) and (211) planes of tin metal (JCPDS card No. 04-0673)^[37] were

not detected, only the strong peak of the substrate and the weak peak of SnPS₃ were observed. The XPS spectra are consistent with XRD characterization (Figure S13b and c), Sn 3d XPS spectra of SnPS₃ catalysts can be deconvoluted into peaks at 486.6, 495.1 (Sn⁴⁺), 486.1, 494.4 (Sn²⁺). No tin metal (485.2 and 493.7 eV) was observed before and after the catalysis.^[37] Therefore, the experiment can exclude the emergence of tin metal in the CO₂ ECR.

To further elucidate the mechanism of CO₂ ECR to CO and HCOO⁻ on the MPCh₃ (M=Co, Ni, and Sn) nanosheets, we carried out DFT calculations. CO₂ molecules are initially adsorbed on the SnPS₃ surface, on which H₂O molecules dissociate into hydroxyl and hydrogen ions simultaneously. The free-energy profiles for different adsorbed ligands with the lowest-energy pathway on the surface of SnPS₃ nanosheets were calculated, as shown in the Figure 5a. The formation of HCOO* via the first proton-electron pair addition is energetically more favorable than that of COOH*, indicating the dominant role of the HCOOH pathway in CO₂ activation. Furthermore, the energy diagram for HER on SnPS₃ is also shown in the Figure 5a. To explain the selectivity of the CO₂ ECR, it is widely accepted that the difference between limiting potentials for CO₂ reduction and H₂ evolution ($\Delta U = U_L(\text{CO}_2) - U_L(\text{H}_2)$, where $U_L = -\Delta G_0/e$) is a reasonable descriptor.^[38] A large positive ΔU value denotes a higher selectivity. Therefore, based on our calculations, it is clear that the selectivity of different products follow the trend HCOO⁻ > H₂ > CO, where the corresponding ΔU is 0.36 (between HCOO⁻ and H₂) and 0.11 (between H₂ and CO) eV, respectively. This is consistent with our experimental observations. In addition, the free-energy diagrams for CO₂ reduction to HCOO⁻ and CO on CoPS₃ and NiPS₃ surfaces were also calculated and shown in the Figures 5b–e, with the considered structural geometries for different defect concentrations considered shown in Figure S15. Due to the structural geometry for these two materials, namely the transition metal atoms are (Co and Ni) located between non-metallic element (P and S) layers (as shown in Fig-

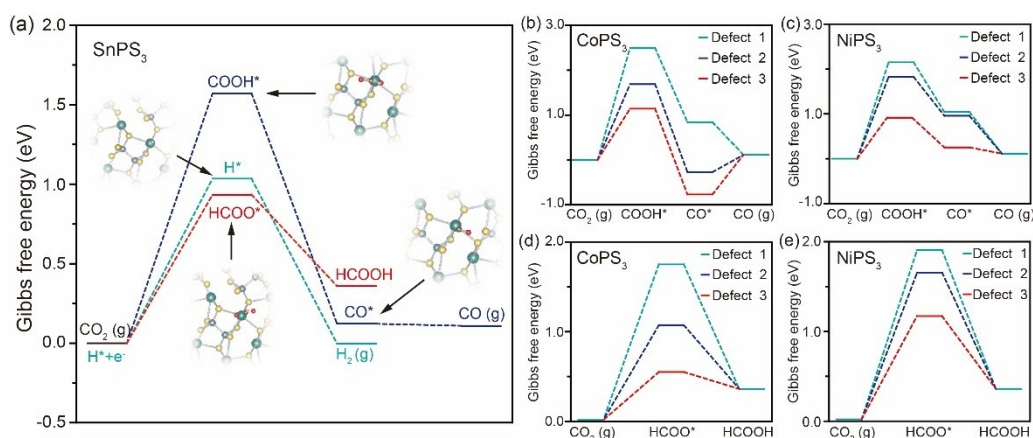


Figure 5. Theoretical investigations. Calculated potential free energy diagrams for HER and CO₂ reduction to HCOOH, CO on the a) SnPS₃ surface. The calculated Gibbs free energy diagram for electroreduction to CO on b) CoPS₃ surface and c) NiPS₃ surface, to HCOOH on d) CoPS₃ surface and e) NiPS₃ surface.

ure 1a), they are hardly exposed on the surface. Therefore, the perfect monolayers CoPS₃ and NiPS₃ barely react with the adsorbates, whereas the presence of sulfur vacancies may foster this reaction.^[39] The corresponding Gibbs free energies illustrated in Figures 5b–e reveal that the HCOO[−] production is more favorable than CO production on CoPS₃ and NiPS₃ surfaces, especially at higher sulfur vacancy concentrations. This confirms that WGE is a promising method for engineering highly active CO₂ ECR catalysts, like MPCh₃ nanosheets by in situ incorporations of sulfur vacancies.

Conclusion

In summary, ultra-thin MPCh₃ nanosheets from layered CoPS₃, NiPS₃, and nonlayered SnPS₃ bulk crystals were successfully exfoliated based on the WGE method. SnPS₃ nanosheets exhibit enhanced CO₂ reduction with good selectivity towards formic acid production, whereas CoPS₃ and NiPS₃ display higher selectivity towards H₂. We demonstrated that ultra-thin nanosheets with a thickness of a few atomic layers can be successfully exfoliated for both van der Waals bonded layered and chemically bonded nonlayered MPCh₃ materials. The relationship between crystal structures and defects of the resulting MPCh₃ nanosheets and their performance of CO₂ ECR were quantitatively evaluated based on experiments and theoretical calculations. The selectivity and reaction rate of HCOOH (i.e., FE_{HCOOH} and j_{HCOOH}) increase step by step, and reach 31.6% and -7.51 mA cm^{-2} at -0.65 V vs. RHE, respectively, which marks the first report using MPCh₃ to produce HCOOH. DFT calculations suggest that the exposed active Sn atoms of SnPS₃ nanosheets give rise to enhanced CO₂ ECR with good selectivity against HER and sulfur vacancies are essential for the catalytic properties observed in as-prepared CoPS₃ and NiPS₃ nanosheets. Our work establishes a feasible method to engineer 2D materials for CO₂ ECR and other electrocatalytic reactions with desired activity and selectivity, which paves the way to tailor the performance of 2D catalytic materials towards future industrial applications.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords: 2D Materials · CO₂ ECR · Exfoliation · MPCh₃ Nanosheets · Nonlayered

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