High-yield Electrochemical Production of Large-sized and Thinly-layered NiPS₃ Flakes for Overall Water Splitting

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Achieving large-sized and thinly layered two-dimensional metal phosphorus trichalcogenides with high quality and yield has been an urgent quest due to their extraordinary physical/chemical characteristics for multiple applications. Nevertheless, current preparation methodologies suffer from uncontrolled thicknesses, uneven morphologies and area distributions, long processing times and inferior quality. Here, we report a sonication-free and fast (in minutes) electrochemical cathodic exfoliation approach that can prepare large-sized (typically ~ 150 μm²) and thinly layered (~ 70 % monolayer) NiPS₃ flakes with high crystallinity and pure phase structure with a yield approximately 80 %. During the electrochemical exfoliation process, the tetra-n-butylammonium salt with large ionic diameter are decomposed into gaseous species after the intercalation and efficiently expand the tightly stratified bulk NiPS₃ crystals, as revealed by in situ and ex situ characterizations. Atomically thin NiPS₃ flakes can be obtained by slight manual shaking rather than sonication, which largely preserves in-plane structural integrity with large size and minimum damage. The obtained high quality NiPS₃ offers a band-new and ideal model for overall water splitting due to its inherent fully exposed S and P atoms that are often the active sites for HER and OER. Consequently, the bifunctional NiPS₃ exhibits outstanding performance for overall water splitting.
1. Introduction

Two-dimensional (2D) ternary metal phosphorus trichalcogenide (MPT) materials have received tremendous attention in recent years because of their distinctive structures and novel physical/chemical characteristics.\(^1\) Among the MPTs, large-sized and thinly layered (LSTL) NiPS\(_3\) flakes with high quality, which have distinctive properties due to an atomically thin structure, are the most sought-after materials in the scientific community. The remarkable charge-discharge performance, magnetic ordering property, intermediate range of bandgaps (~1.6 eV), and preeminent electrochemical activity of this material, facilitates a wide range of applications in batteries,\(^2\) electronics,\(^3\) optoelectronics,\(^4\) and catalysis.\(^5\) However, despite tremendous effort, the production of LSTL NiPS\(_3\) with high quality remains a formidable challenge because of production difficulties, i.e., the inability to produce on a large scale, at an acceptable expenditure and in a reproducible manner.

The chemical vapor deposition method reported by He and coworkers is the predominant approach for directly preparing LSTL NiPS\(_3\) on a laboratory-scale.\(^4,5\) Unfortunately, the scope of this technique is limited because of the lack of large-scale fabrication and layer-controlled growth, and large number of defects (up to 7.6 % S vacancies).\(^5\) Mechanical exfoliation using Scotch tape can produce NiPS\(_3\) flakes with high quality and crystallinity; these flakes are mainly used for fundamental studies.\(^6\) Nevertheless, practical applications of this method are greatly restricted because of the lack of scalability and random thickness and size of the obtained NiPS\(_3\) flakes. Liquid-phase exfoliated bulk 2D crystals has recently emerged as an effective measure for preparing high-quality and atomically thin 2D flakes, such as Li intercalation,\(^1a,7\) and ultrasonic methods.\(^8\) The approach of Li intercalation requires large amount of time, and the process is extremely sensitive to ambient conditions. In addition, this approach may induce a phase transition, and the residual Li can promote a doping effect in the products. To date, the ultrasonic method is the unparalleled approach to harvest monolayer NiPS\(_3\) flakes.\(^2,5a,5b,5d,5e,9\) Unfortunately, this method generally involves prolonged interaction of forces at all directions,
ineluctably disintegrating the bulk crystals into an undersized area distribution (commonly < 0.06 μm²) with extensive defects, uneven morphology and inferior quality. Hence, the design and development of a feasible and scalable technique to produce large quantities of high-quality and solution-processable LSTL NiPS₃ is highly desired.

Herein, for the first time, we report the massive production of large-sized and mono-layered NiPS₃ flakes with high quality by electrochemical cathodic exfoliation of bulk NiPS₃ crystals. The exfoliated NiPS₃ flakes have unprecedented sizes (area ~150 μm²) with an atomic level thickness (monolayer ratio: ~70 %) and have extremely low degree of oxidation and defects with the intrinsic structure preserved. In comparison with other fabrication techniques, this electrochemical method has several merits, such as scalable production, structural integrity with large size, affordable cost, solution-processability and reproducibility. More importantly, exfoliated NiPS₃ flakes via cationic intercalation are not contaminated with oxygen groups. To the best of our knowledge, until now, this is the first MPT material that can be successfully exfoliated using an electrochemical technique without lithium ion intercalation. Due to fully exposed P and S atoms, the LSTL NiPS₃ flakes possess abundant active sites on the basal planes. By combining the experimental results with density functional theory (DFT) calculations, it is interesting to find that the S and P atoms on the basal planes of LSTL NiPS₃ are the active sites for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), respectively.

2. Results

2.1. Mechanism of electrochemical cathodic exfoliation

The layered NiPS₃ crystallizes in the space group C2/m (No. 12) with a triclinic unit cell of a = 5.812 Å, b = 10.070 Å, c = 6.632 Å, and V = 371.2 Å³. The model representing a lamella in both the normal direction and along the NiPS₃ layer stacking direction is illustrated in Figure S1(Supporting Information). To acquire LSTL NiPS₃, bulk NiPS₃ materials with a large crystalline size is a prerequisite. Our prepared bulk NiPS₃ crystals by chemical vapor transport (CVT) method were highly crystalline with a closely stacked lamellar architecture with a
maximum length of up to approximately 1 cm (Figure 1a and Figure S2-S3, Supporting Information). The X-ray diffraction (XRD) pattern of the bulk NiPS₃ crystals exhibited an intense grain orientation along the c axis, and the peak positions matched well with the planes of the standard XRD data (JCPDS no. 01-78-0499) (Figure S4, Supporting Information), manifesting the layered crystal structure along the c axis and the pure phase of the NiPS₃ crystals.

Electrochemical exfoliation of bulk NiPS₃ crystals was performed in a two-electrode system (Figure 1b). An in-house electrochemical cell combined with optical microscopy (Figure S5, Supporting Information) was established to in situ monitor the intercalation and expansion process by implementing a constant voltage via chronoamperometry. The morphology changes in the NiPS₃ crystals were also monitored by ex situ scanning electron microscopy (SEM) (Figure 1f) and optical photographs (Figure S6, Supporting Information), and the corresponding mechanism are described in Figure 1e. First, bulk NiPS₃ crystals displayed tightly stratified architectures (Figure 1f and Figure S6a, Supporting Information). Then, tetra-n-butylammonium salts, which possess larger ionic diameters and could be used for exfoliating 2D materials, such as graphene, black phosphorus and phase-pure semiconducting nanosheets (MoS₂, WSe₂, Bi₂Se₃, NbSe₂, In₂Se₃, Sb₂Te₃)¹⁰, was selected as the salts for intercalation. When applying a constant negative bias (-3 V) to the working electrode for few seconds, the tetra-n-butylammonium tetrafluoroborate were intercalated into the interlamination of the bulk NiPS₃ crystals. These salts significantly weakened the van der Waals interactions between the layers and expanded the lattice to a greater extent (Figure 1f). Second, after applying a voltage for more time, the intercalated tetra-n-butylammonium salts were electrochemically decomposed into gaseous species, generating the driving force for gigantic and ultrafast volume expansion of the tightly stratified bulk NiPS₃ crystals together with edge wrinkling and roughening (Figure 1f and Movie S1, Supporting Information), followed by dissociation and dispersion into N, N-dimethylformamide (DMF) (Figure S6b-h, Supporting Information). The
observed massive gas bubbles around the working electrode proved the decomposition of the intercalants. Finally, exfoliated NiPS$_3$ with unprecedentedly sizes and quality (Figure S7, Supporting Information) was detached from bulk NiPS$_3$ crystals by slight manual shaking, which supplied very weak hand-driven forces, forming LSTL NiPS$_3$ with preserved in-plane structural integrity. The *in situ* CV measurement related to the intercalation and deintercalation of tetra-n-butylammonium salt was shown in Figure S8 (Supporting Information). DMF was selected as the nonaqueous electrolyte because of its low boiling point, high dispersion capability for the generated LSTL NiPS$_3$, much better than other commonly used solvent, such as propylene carbonate, dimethyl sulfoxide and acetonitrile (Figure S9-11, Supporting Information). After removal of the unexfoliated NiPS$_3$, the dispersion was filtered under vacuum and washed with a copious amount of DMF. The collected LSTL NiPS$_3$, after being redispersed in DMF exhibited the conspicuous Tyndall effect (Figure 1c). A high yield of ~80 % was determined by calculating the mass ratio of dried LSTL NiPS$_3$ and the starting bulk specimens. After electrochemical exfoliation, only the (001), (002) and (004) reflections of LSTL NiPS$_3$ was observed in XRD pattern, and the intensity was significantly smaller than that of bulk NiPS$_3$ crystals (Figure 1d). In addition, the peaks of the (130), (131), (221), (-133), (060) and (005) reflections disappeared for the exfoliated LSTL NiPS$_3$ (Figure S12, Supporting Information). These results pinpoint the successfully exfoliation of bulk NiPS$_3$ crystals into atomically thin NiPS$_3$ flakes.

**2.2. Morphological and structural characterization of LSTL NiPS$_3$**

To study the morphology and structure of LSTL NiPS$_3$, optical microscopy, transmission electron microscopy (TEM) and atomic force microscope (AFM) were performed. Figure 2a depicts the optical microscope image of high-coverage LSTL NiPS$_3$. The low-magnification optical microscope and TEM images showed that ample intertangling and crinkles were on the surface of LSTL NiPS$_3$ (Figure 2b,c). Subsequently, the atomic lattice of LSTL NiPS$_3$ was analyzed via high resolution TEM (HRTEM). The distance between adjacent lattice fringes was
measured to be 2.87 Å, which exactly matched the theoretical value (Figure 2d). High-angle annular dark field-scan TEM (HAADF-STEM) of the (131) plane was further conducted, and the results are shown in Figure 2e. A homogeneous and almost defect-free structure was verified across the entire single crystal domain. In addition, the pattern was consistent with the image simulation along the c axis. The pattern revealed three sets of lattice fringes with spacings of 1.62 Å, 1.68 Å, and 1.62 Å, which corresponds well to the (330), (060), (330) planes of LSTL NiPS₃, respectively. All the consequences highlighted the atomic structure of LSTL NiPS₃ with intact phase structure and excellent crystalline quality. Furthermore, the TEM-electron energy loss spectrometer (EELS) mapping revealed a uniform distribution of Ni, P, and S elements over the entire exfoliated flake (Figure S13, Supporting Information). To ascertain the accurate thickness of LSTL NiPS₃, representative AFM images of LSTL NiPS₃ were exhibited in Figure 2f. The topographic height was approximately 0.92 nm, which can be assigned to a monolayer of NiPS₃. The statistical analysis based on large-area AFM measurements (Figure 2g) indicated that the monolayer ratio of LSTL NiPS₃ was approximately 70 % (Figure 2h and Figure S14, Supporting Information). The parameter comparison of LSTL NiPS₃ and other reported NiPS₃ specimens is provided in Figure 2i and Table S1 in Supporting Information. To the best of our knowledge, the electrochemical exfoliation reported here is the highest efficiency pathway for the preparation of large quantities of high-quality NiPS₃ with a large area and atomical thickness.[2, 4-6, 9]

Subsequently, a structural comparison between bulk NiPS₃ and LSTL NiPS₃ was implemented. An X-ray photoelectron spectroscopy (XPS) spectrum revealed distinct signals of Ni, P and S in LSTL NiPS₃ (Figure S15, Supporting Information). The atomic percentages of Ni (15.8 at%), P (25.1 at%) and S (59.1 at%) were estimated. The resolved Ni 2p spectrum illuminated the spin-orbit doublets for the 2p₃/2 (854.43 eV) levels of the typical Ni²⁺ species along with three satellite peaks at 856.5, 859.5 and 864.4 eV (Figure 3a).[2b] In the P 2p spectrum (Figure 3b), two peaks at 131.95 and 132.79 eV of covalent P-S in the PS₃ units were
ascribed to P 2p\(_{3/2}\) and P 2p\(_{1/2}\), respectively.\[^5\] The S 2p spectrum also displayed double peaks at 162.46 and 163.64 eV, attributed to Ni-S and P-S, respectively (Figure 3c).\[^5\] Notably the XPS results revealed that LSTL NiPS\(_3\) obtained by electrochemically cathodic exfoliation only exhibited characteristic peaks of P 2p\(_{3/2}\), P 2p\(_{1/2}\), S 2p\(_{3/2}\) and S 2p\(_{1/2}\). The peaks centered at ~134.5 eV and ~167.8 eV associated with oxidized P and S were not observed,\[^{11-12}\] suggesting the negligible oxidation degree of LSTL NiPS\(_3\). In contrast, traditional exfoliation methods always suffered from the production of 2D materials with an unwanted high oxidation degree.\[^{11-12}\] The Ni 2p, P 2p and S 2p peaks also display a slight redshift in the binding energy compared to those of the bulk crystals (Figure S16, Supporting Information), probably originating from the thickness change in NiPS\(_3\) during electrochemical exfoliation (Figure S17, Supporting Information).

The variations in the coordination environment for Ni atoms were probed by X-ray absorption fine structure (XAFS) analysis. The Ni K-edge X-ray absorption near edge structure (XANES) (Figure 3d) and Fourier transformed (FT) \(k^3\chi(k)\) function extended X-ray absorption fine structure (EXAFS) spectra (Figure 3e) and also their corresponding \(k^3\chi(k)\) oscillation curves (Figure S18, Supporting Information) of the obtained LSTL NiPS\(_3\) exhibited similar but different features compared with bulk NiPS\(_3\) crystals. The Ni K-edge XANES spectra presented a Ni oxidation state (Figure 3d). The results for the energy of the absorption edge combined with the intensity of the white line demonstrated that the valence of Ni in LSTL NiPS\(_3\) was higher than that in bulk structure, which indicated a more abundant coordinate environment for LSTL NiPS\(_3\).\[^{13}\] The peak positions that corresponds to the Ni-S coordination for NiPS\(_3\) exhibited the same radial distance (2.00 Å) as that of bulk structure (Figure 3e). Moreover, the second coordination shell peak intensity of LSTL NiPS\(_3\) decreased significantly (11 \%) compared to that of bulk crystals, demonstrating the obvious structural distortion and the dimension reduction of NiPS\(_3\) crystals.\[^7\] A curve fitting was also conducted to obtain the detailed structure parameters (Table S2, Supporting Information). The Ni-S bond in LSTL
NiPS$_3$ showed supersaturated coordination, giving a higher coordination number (CN) of 5.6 (Ni-S) than that of the bulk crystals (CN = 5.4 for the Ni-S). Moreover, the fitted bond length results suggested that there was an obvious structural distortion in LSTL NiPS$_3$ because of the increasing Ni-S bond length. The supersaturated coordination and structural distortion of LSTL NiPS$_3$ likely resulted from the highly exposed supersaturated-coordinated edge sites,$^{[14]}$ further clarifying the atomic thin 2D character for LSTL NiPS$_3$.

Raman spectroscopy measurements of bulk NiPS$_3$ crystals and LSTL NiPS$_3$ excited by 532 nm laser on a SiO$_2$/Si substrate were also systematically performed. As displayed in Figure 3f, the three in-plane E$_g$ modes, three out-of-plane A$_g$ modes, and two second-order A$_g$ modes were detected. A$_{ig}^{(1)}$ was dominated by the in-plane motions of the sulfur planes, while A$_{ig}^{(2)}$ and A$_{ig}^{(3)}$ were assigned to the vertical components of their sulfur plane vibrations. E$_{ig}^{(1)}$ was attributed to Ni$^{2+}$ metal ions, and the 434 cm$^{-1}$ peak was attributed to the P-P bond vibrational mode.$^{[4,5b,6]}$ For LSTL NiPS$_3$, only E$_{ig}^{(1)}$ and E$_{ig}^{(2)}$ were detected, which was ascribed to a weakening of the interlayer interaction with a reduction in flake thickness.$^{[4]}$ Moreover, compared with bulk NiPS$_3$, the Raman modes of LSTL NiPS$_3$ revealed a distinct shift toward lower wavenumbers (inset of Figure 3f), which was attributed to the phonon confinement effect because of the ultrathin thickness.$^{[5c,6]}

### 2.3. Electrochemical performance of LSTL NiPS$_3$

Recently, numerous outstanding 2D electrocatalysts have been established for the half reaction of water splitting. For example, transition metal sulfides (e.g. NiS$_x$, MoS$_2$) and phosphides (e.g. Ni$_2$P) have shown promising HER and OER performance, whereas S-atoms and P-atoms are often suggested as the active sites for HER and OER, respectively.$^{[15-18]}$ However, most 2D catalytic materials have only a single-functional activity site that can only be used for a single half reaction. Thus, it remains an enormous challenge to exploit brand-new 2D materials with multifunctional activity sites to realize overall water splitting. Herein, LSTL NiPS$_3$ with high crystallinity and pure phase structure produced by electrochemical exfoliation...
perfectly combine the fully exposed S and P atoms in one 2D material, which offers an ideal model to exploit their inherent reactivity for overall water splitting.

In the atomic structure of NiPS$_3$, Ni atoms on the basal planes immobilized the [P$_2$S$_6$]$^{4-}$ framework and were sandwiched by the S layers; thus, they could not be exposed and serve as active sites, which is similar to MoS$_2$.[16, 18, 19] To accurately clarify the effect of P and S atoms on the OER and HER, DFT was utilized to calculate the chemisorption free energies of hydrogen ($\Delta G_H$) and hydroxide ($\Delta G_{OH}$). Figure 4a-c,4j show that $\Delta G_H$ value was 1.03 eV for the P sites and 0.51 eV for the S site, respectively. Distinctly, the adsorption of H atoms on the S sites was much more favorable, namely, the S atoms on the basal planes of LSTL NiPS$_3$ were the active sites of HER. Considering water dissociation process in alkaline solution, we further performed DFT computations related to the atomic configurations of water dissociation step on the surface of 2D NiPS$_3$. The energy barrier in-between was located via searching for transition states by climbing image-nudged-elastic band method. As shown in Figure S19 (Supporting Information), when the kinetics of water dissociation from the Volmer step was considered, the S sites in 2D NiPS$_3$ exhibited a significant water dissociation barrier ($E_a = 1.48$ eV), substantively lower than that on P sites in 2D NiPS$_3$ ($E_b = 3.41$ eV). Therefore, from the kinetic viewpoint, the S atoms on the basal planes of LSTL NiPS$_3$ were the active sites of HER, which was consistent with the result in Figure 4j. Figure 4d-i,4k also display the calculated free energy along the OER pathway for the P and S sites. The adsorption of OH$^-$ onto the S atom needs an energy of 0.59 eV, which is energy unfavorable and prohibits continuing the OER. Furthermore, the conversion of $O^*$ to OOH$, which needs the largest uphill energy, is the rate-determining step for both P ($1.06$ eV, $O^* \rightarrow$ OOH$^+$) and S ($1.97$ eV, $O^* \rightarrow$ OOH$^+$). Obviously, P atoms on the basal planes possess the lower reaction energy barrier than S atoms, indicating its great potential as active sites for OER.

Due to abundant fully exposed multifunctional active sites on the basal planes (Figure S21, Supporting Information), a superhigh electrochemically active surface area (Figure S22,
Supporting Information), and improved mass/electron transport (Figure S23, Supporting Information), LSTL NiPS$_3$ could be employed as bifunctional electrocatalysts for water splitting. Thus, LSTL NiPS$_3$ immobilized on commercial nickel foam served as the working electrode to catalyze the HER and OER (Figure S24, Supporting Information). Bulk NiPS$_3$ crystals, commercial Pt/C and RuO$_2$ catalysts were also investigated for comparison. As illustrated in the left panel of Figure 5a, LSTL NiPS$_3$ displayed high activity for the HER, and the onset potential was approximately 100 mV, much lower than that of bulk NiPS$_3$ (200 mV). To realize a current density of 10 mA cm$^{-2}$, an overpotential of only 158 mV was required for LSTL NiPS$_3$, but 250 mV was required for bulk NiPS$_3$ crystals. In addition, when the overpotential exceeded 290 mV, the HER activity of LSTL NiPS$_3$ was observably superior to commercial Pt/C. Such performance transcended many of the previously reported nonprecious metal HER electrocatalysts (Table S3, Supporting Information). Furthermore, the catalytic kinetics were assessed from the Tafel plots.$^{[20-22]}$ The Tafel slope value of LSTL NiPS$_3$ was approximately 95 mV dec$^{-1}$, which was lower than the bulk NiPS$_3$ crystals (159 mV dec$^{-1}$) (Figure S25, Supporting Information), signifying its superior HER rate.

Subsequently, the OER performance of these materials were studied. As revealed in the linear sweep voltammetry (LSV) curves in the right panel of Figure 5a, the oxidation peak associated with the transition from Ni$^{2+}$ to Ni$^{3+}$ occurred between 1.35 and 1.45 V.$^{[13]}$ Therefore, a backward cyclic voltammograms (CV) scan was employed to estimate the OER performance of LSTL NiPS$_3$. As displayed in Figure S26 (Supporting Information), LSTL NiPS$_3$ exhibited an extraordinarily low onset potential (1.45 V), which was significantly lower than the bulk NiPS$_3$ crystals (1.60 V) and even superior to commercial RuO$_2$ (1.48 V). To realize a current density of 10 mA cm$^{-2}$, LSTL NiPS$_3$ required an overpotential of only 300 mV, outperforming bulk NiPS$_3$ crystals and commercial RuO$_2$. The Tafel slope of LSTL NiPS$_3$ was 88 mV dec$^{-1}$, which was also obviously lower than that of the bulk NiPS$_3$ crystal (152 mV dec$^{-1}$, Figure S25, Supporting Information). This excellent OER performance of LSTL NiPS$_3$ was superior to that
of many transition metals and even some noble-metal electrocatalysts (Table S4, Supporting Information).

Long-term stability is another significant parameter for both the electrocatalytic HER and OER. As depicted in Figure 5b-c, a current density of 50 mA cm$^{-2}$ for the HER (overpotential: 239 mV) and OER (overpotential: 350 mV) could be maintained for more than 24 h with a trivial current decline of 6.4 % and 2.8 %, respectively. However, both commercial Pt/C and RuO$_2$ catalysts with the same mass loading were unstable under the same test conditions, and the current densities of 50 mA cm$^{-2}$ showed a significant decrease of merely 54.6 % and 15.2 % maintaining, respectively. The decline in the stability of RuO$_2$ was probably because of the oxidation of RuO$_2$ to water-soluble RuO$_4^{2-}$ or other solvated Ru$^{VI}$ ions under alkaline conditions.$^{[23]}$ The decrease in Pt/C stability was mainly attributed to Pt particles largely peeling off the support, caused by the generated H$_2$ bubbles during long reaction times.$^{[24]}$ The morphology and chemical composition of the LSTL NiPS$_3$ after the HER and OER stability tests was displayed in Figure S27-28 (Supporting Information).

Inspired by the remarkable HER and OER performances, we assembled a water electrolyzer in 1.0 M KOH by applying LSTL NiPS$_3$ as both the anode and cathode electrode for overall water splitting. As indicated in Figure 5d, the overall water splitting performance of LSTL NiPS$_3$ was much better than the RuO$_2$-Pt/C couple. To deliver a current density of 10 mA cm$^{-2}$, approximately 1.56 V was required, that is, a combined overpotential of approximately 330 mV for electrochemical overall water splitting. The electrocatalytic overall water splitting activity at 30 mA cm$^{-2}$ was also monitored (Movie S2, Supporting Information). The results revealed that massive H$_2$ and O$_2$ bubbles were rapidly generated on both LSTL NiPS$_3$ electrodes. More importantly, LSTL NiPS$_3$ exhibited outstanding stability with an insignificant decline in a 24 h galvanostatic electrolysis at 30 mA cm$^{-2}$ (Figure 5e). The comparison of the overall water splitting performance in a 1.0 M KOH solution for LSTL NiPS$_3$ with other bifunctional
electrocatalysts is displayed in Table S5 (Supporting Information), which further highlights its robust catalytic performance.

3. Conclusion

In summary, we have successfully demonstrated that large-size and atomically thin NiPS$_3$ flakes with high crystallinity and pure phase structure can be prepared by a sonication-free and fast (in minutes) electrochemical cathodic exfoliation approach with a high yield. With the help of tetra-n-butylammonium salt with large ionic diameter and gas releasing nature, atomically thin monolayer or few-layer NiPS$_3$ can be obtained by slight manual shaking after the electrochemical intercalation. Due to the fully exposed P and S catalytic active site without contamination of oxygen groups, the exfoliated NiPS$_3$ flakes possess ultrahigh electrochemically active surface area and extremely low reaction resistance, which deliver a robust HER, OER and enable efficient overall water-splitting performance. The successful electrochemical cathodic exfoliation of NiPS$_3$ provides the possibility for the scalable preparation of other MPT and 2D materials and facilitates the development of 2D-based applications.
Experimental Section

Chemicals

Red phosphorus powder (99.999 %), tetra-n-butylammonium tetrafluoroborate (99 %), RuO$_2$ (99.95% metal basis) and Nafion (0.5 wt%) were purchased from Alfa Aesar. Sulfur powder (99.999 %) and nickel powders (99.99 %) was purchased from Adamas-beta. DMF (99 %) and KOH were purchased from Macklin. The commercial Pt/C (20 wt%) catalysts were obtained from Johnson Matttey (Shanghai, China). Water was purified through a Millipore system.

Synthesis of bulk NiPS$_3$ crystals

Bulk NiPS$_3$ crystals were prepared by the CVT method. High-purity nickel, phosphorus and sulfur powders (total mass: ~ 2 g) with a stoichiometric mole ratio (1:1:3) were fully mixed and grinded in a glove box. Then, powders were sealed in an evacuated quartz tube (length: 25 cm; external diameter: 13 mm; wall thickness: 1 mm) under a vacuum of $10^{-5}$ Pa using an oxygen/hydrogen welding torch by Partulab device (MRVS-1002, Partulab Technologies, China). Next, the sealed tube was placed in a two-zone furnace. Then, the temperature in the reaction and growth zone were programmed to 700 °C and 650 °C with a heating rate of 1 °C min$^{-1}$, and the corresponding temperature was maintained for 7 days to generate a temperature gradient for the growth of the bulk crystals. Finally, the two-zone furnace was cooled naturally to ambient temperature, and the bulk NiPS$_3$ crystals were collected.

Electrochemical exfoliation of bulk NiPS$_3$ crystals

The electrochemical exfoliation of bulk NiPS$_3$ crystals was performed by using an electrochemical workstation (CHI 760E, Shanghai Chenhua Instrument Factory, China) consisting of a two-electrode system. The obtained bulk NiPS$_3$ crystals were clamped to a Pt clip and were employed as the working electrode. A Pt sheet (length: 10 mm; width:10 mm) electrode was utilized as the counter electrode and was installed approximately 1.5 cm away
from the bulk NiPS₃ crystals. A DMF solution (60 mL) consisting of 0.05 M tetra-n-butylammonium tetrafluoroborate was used as the electrolyte.

The electrochemical exfoliation of bulk NiPS₃ crystals to LSTL NiPS₃ was performed by executing a static bias of -3 V on the working electrode. After the exfoliation process was accomplished, the obtained suspension was manually shaken for approximately 20 s, and then the dispersion was centrifuged to precipitate unexfoliated NiPS₃. The top part of the dispersion was filtered through a nylon membrane filter (Agela Technologies, 47 mm, 0.45 µm) and washed with plenty of DMF by vacuum filtration to remove the residual tetra-n-butylammonium salts. Finally, the collected LSTL NiPS₃ was redispersed in DMF for characterization and application.

Electrode preparation
Nickel foam served as the three-dimensional scaffold, which was sonicated and washed in acetone, ethanol, 0.5 M HCl solution and water. Subsequently, the 2 mL LSTL NiPS₃ dispersion (2 mg mL⁻¹) containing a 200 µl Nafion (0.5 wt%) aqueous solution was uniformly dispersed onto the dried nickel foam (1 × 2 cm²) and then dried in a vacuum drying oven. Thus, the loading weight of LSTL NiPS₃ on the nickel foam was approximately 1.0 mg cm⁻². For comparison, commercial Pt/C and RuO₂ catalysts were loaded on nickel foam with the same loading (1.0 mg cm⁻²) and acted as both the cathode and anode electrode, respectively.

Electrochemical tests
The electrochemical HER and OER activities were investigated in a three-electrode system equipped with a proton exchange membrane (Nafon-117 membrane). A saturated Ag/AgCl electrode in 3.0 M KCl solution and a Pt sheet served as the reference and counter electrodes, respectively. All the potentials were converted to the reversible hydrogen electrode (RHE) scale via the Nernst equation (1):

\[ E_{\text{RHE}} = E_{\text{SHE}} + 0.0591 \times \text{pH} = E_{\text{APPL}} + \phi_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} \]  (1)
in which, $E_{SHE}$ is the potential versus standard hydrogen electrode (SHE) potential, $E_{Appl}$ is the applied potential vs. Ag/AgCl reference, and $\phi_{Ag/AgCl}$ is the electrode potential of the KCl-saturated Ag/AgCl reference electrode (0.198 V vs. SHE). Unless otherwise noted, all potentials used refer to the RHE via calibration. All current densities were normalized using the geometrical area of the nickel foam immersed in solution (2 cm$^2$).

The HER and OER performances were investigated in 1.0 M KOH by the LSV method within the range of $-0.5$–$0.5$ V and $1.0$–$1.8$ V, corrected by iR-compensation (80 %) for the ohmic potential drop losses. For the OER, a flow of O$_2$ was employed to ensure the O$_2$/H$_2$O equilibrium at 1.23 V. For the HER, a flow of Ar was used to purge the electrolyte. The overpotentials ($\eta$) at 10 mA cm$^{-2}$ were ascertained based on the equation (2), and the Tafel slope (b) was calculated according to Tafel equation (3):

$$\eta = E \text{ (vs. RHE)} - 1.23 \quad (2)$$

$$\eta = a + b \log |J| \quad (3)$$

Chronopotentiometry and chronoamperometry measurements were performed to evaluate the stability. Electrochemical impedance spectra (EIS) were recorded at 1.51 V from 100 kHz to 0.01 Hz with amplitude 5 mV in O$_2$-saturated 1.0 M KOH solution. The electrochemically active surface areas of bulk NiPS$_3$ and LSTL NiPS$_3$ were estimated by using CV in an O$_2$-saturated 1.0 M KOH solution at different scan rates (20, 40, 60, 80 and 100 mV s$^{-1}$).

Material characterization

The NiPS$_3$ suspension prepared by electrochemical exfoliation was dispersed onto a superthin carbon-coated porous copper grid for TEM, a frosted glass for XRD, clean silicon substrates for SEM, optical microscopy and XPS, a clean SiO$_2$/Si substrate for Raman characterization, a mica substrate for AFM. XRD (Ultima IV, Rigaku Corporation, Japan) measurements were performed with Cu-K$\alpha$ radiation as the X-ray source ($\lambda = 1.5418$ Å). The TEM, HRTEM and
HAADF-STEM images were obtained by employing probe Cs-corrected TEM equipment (FEI Titan ChemiSTEM, USA). Energy dispersive X-ray spectroscopy was utilized to characterize the elemental mapping of LSTL NiPS₃. SEM images were acquired by employing a field emission SEM (Zeiss SUPRA® 55, Carl Zeiss, Germany). AFM images were acquired by employing a Bruker Dimension FastScan Atomic Force Microscope (Bruker L01F4C8, USA) in tapping mode in air. Optical imaging of bulk NiPS₃ and LSTL NiPS₃ on the SiO₂/Si and mica substrate was conducted using an optical microscope (Nikon ECLIPSE LV100ND, Japan). Raman spectra and mapping were recorded at room temperature using a WITec (Alpha 300R, Germany) Raman Microscope with laser excitation at 532 nm. XPS measurements were obtained using an ESCALAB 250Xi (Thermo Fisher, UK) X-ray photoelectron spectroscopy instrument. The sample analysis chamber pressure was ~5×10⁻¹⁰ mbar during the spectrum acquisition. X-ray absorption spectra were collected at Shanghai Synchrotron Radiation Facility (SSRF) on beamline BL14W1. The storage ring is operated at electron energy of 2.5 GeV with a beam current of 250 mA. A Si (111) double-crystal monochromatic was applied. The beam size used at the sample position was approximately 900 × 300 μm². All the data were collected at ambient temperature applied in the transmission mode. More details are shown in Supplementary Note 4.

Computational details and models

DFT calculations were carried out using the plane-wave technique with exchange-correlation interactions modeled by GGA-PBE functional,[25] as implemented in the Vienna ab initio simulation package (VASP).[26] The ion–electron interactions were described by the projector augmented plane wave approach and the cutoff energy was set to 500 eV.[27] Structural optimizations were performed by minimizing the forces on all the atoms to below 0.02 eV·Å⁻¹ and minimizing the energy to below 10⁻⁵ eV. The Monkhorst-Pack method was adopted to sample the k-space with an 8×4×8 mesh for the bulk and a 4×4×1 mesh for the surface of the
NiPS$_3$ system. To describe the strongly correlated d electrons of a Ni atom, the GGA+U (U = 4 eV) scheme introduced by Dudarev et al was employed.$^{[28, 29]}$ The van der Waals correction was included using Becke-Jonson damping with function parameters of the D3 method by Grimme et al.$^{[30]}$ To explore the catalytical performance of NiPS$_3$, a (2×1) slab of the (001) surface was constructed with a vacuum layer of 15 Å to avoid the interaction between neighboring images. Additionally, the dipole corrections were employed in all slabs calculations. All the atoms in the slab were relaxed during the geometrical optimization process. The free energy analyzing method developed by Nørskov et al was used to predict the reaction activity.$^{[31]}$ In the end, we adopted the equation (4) to evaluate the adsorption free energy of H on different sites of the NiPS$_3$ surface, where the $\Delta E_H^*$ is the adsorption energy of a H atom.

$$\Delta G_{H^*} = \Delta E_{H^*} + 0.24 \text{ eV} \quad (4)$$

**Supporting Information**
Supporting Information is available from the Wiley Online Library or from the author.

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**Figure 1.** Mechanism of the electrochemical cathodic exfoliation. (a) Photographs of the single crystal bulk NiPS$_3$ specimens. (b) Schematic illustration of the experimental setup for electrochemical exfoliation. (c) Images of (left) expanded NiPS$_3$ in DMF after electrochemical charging at -3 V for ~ 20 min; (center) dispersion of expanded NiPS$_3$ via manual shaking; and (right) final LSTL NiPS$_3$ dispersion exhibiting the Tyndall effect. (d) XRD pattern of the bulk and LSTL NiPS$_3$ samples with a standard JCPDS pattern (01-78-0499). The wide peak approximately 20 - 30° was assigned to the silicon substrate. (e) Mechanism illustration of electrochemically exfoliating bulk NiPS$_3$ crystals in tetra-n-butylammonium salts solution. (f) **Ex situ** SEM images of NiPS$_3$ after applying a bias voltage of -3 V for 0, 30, and 60 s in tetra-n-butylammonium salts solution.
Figure 2. Morphological and structural characterization of LSTL NiPS$_3$. (a) Typical optical microscope image of high-coverage LSTL NiPS$_3$ on mica substrate. (b) Representative optical microscope image of single LSTL NiPS$_3$ on SiO$_2$/Si substrate. (c) TEM, (d) HRTEM, (e) HAADF-TEM images of LSTL NiPS$_3$. (f) AFM image of large-sized and monolayer NiPS$_3$ on SiO$_2$/Si substrate. (g) High-coverage AFM image of LSTL NiPS$_3$ on mica substrate. (h) Statistical analysis of length, width and thickness distribution of LSTL NiPS$_3$. The total number of LSTL NiPS$_3$ for statistics was about 200. (i) Parameter comparison of LSTL NiPS$_3$ and other previously reported NiPS$_3$. “1-11” stands for published paper.\textsuperscript{[2, 5, 6]}
Figure 3. Structure comparison between bulk NiPS$_3$ crystals and LSTL NiPS$_3$. High-resolution XPS spectra of the (a) Ni 2$p$, (b) P 2$p$, and (c) S 2$p$ regions of electrochemically exfoliated LSTL NiPS$_3$. Ni-K edge (d) XANES, (e) FT-EXAFS spectra of the bulk NiPS$_3$ crystals and LSTL NiPS$_3$. (f) Raman spectra of the bulk NiPS$_3$ crystals and LSTL NiPS$_3$ in the range from 100 to 1250 cm$^{-1}$. 
Figure 4. Chemisorption models and calculated free energy. (a-i) Chemisorption models of the H and OH intermediates on the P and S sites in NiPS₃ for the HER and OER respectively. The corresponding adsorbed configurations in the NiPS₃ (100) direction were shown in Figure S20 (Supporting Information). (i-k) Calculated free energy diagram on the NiPS₃ (001) surfaces for the HER and OER at equilibrium (applied potential $U = 0$) with the adsorbed configurations shown in a-i, and the proposed mechanisms of the dissociation of H₂O, OH on LSTL NiPS₃. The blue balls represent Ni atoms, red for P, yellow for S, white for H, and cyan for O.
**Figure 5.** HER, OER, and overall water-splitting performance of LSTL NiPS$_3$. (a) Steady-state LSV curves at a scan rate of 5 mV s$^{-1}$. (b-c) Chronoamperometry curves of these electrodes at a high current density of 50 mA cm$^{-2}$. (d) LSV curves of LSTL NiPS$_3$, and RuO$_2$(+)/Pt/C (-) for overall water splitting in a two-electrode configuration. Inset: Photograph of bubble overflow on LSTL NiPS$_3$ during overall water splitting. (e) Chronopotentiometry curves of LSTL NiPS$_3$ under a current density of 30 mA cm$^{-2}$. Inset: LSV curves of LSTL NiPS$_3$ before and after chronopotentiometry measurement.
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**Large-sized** (typically $\sim 150 \mu m^2$) and **thinly layered** ($\sim 70 \%$ monolayer) NiPS$_3$ flakes with **pure phase structure** is harvested (yield $\sim 80 \%$) from ultrafast (in minutes) electrochemical exfoliation of bulk NiPS$_3$ crystals. The obtained NiPS$_3$ exhibits remarkable performance for overall water splitting due to its fully exposed S and P atoms that are the active sites for HER and OER.

Keyword
electrochemical exfoliation, two-dimensional materials, NiPS$_3$, bifunctional, overall water splitting


**High-yield Electrochemical Production of Large-sized and Thinly layered NiPS$_3$ flakes for Overall Water Splitting**