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Lithium-assisted Exfoliation and Photoelectrocatalytic Water Splitting of 2D Palladium Thiophosphate

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Abstract

Efficient photoelectrocatalytic (PEC) water splitting could be the solution for environmental and energy problems on planet Earth. Here, we explore 2D palladium thiophosphate $\text{Pd}_3(\text{PS}_4)_2$, which is a promising photocatalyst absorbing light in the visible range. We obtain a few-layer $\text{Pd}_3(\text{PS}_4)_2$ through lithium-assisted exfoliation from the bulk phase and characterize it employing Raman spectroscopy, XPS, AFM, and STM combined with DFT calculations. The measured band gap for as-obtained few-layer $\text{Pd}_3(\text{PS}_4)_2$ is 2.57 eV (indirect) and its band edges span the electrochemical potentials of the hydrogen and oxygen evolution reactions. The performance in the water-splitting reaction is studied under acidic, neutral, and alkaline conditions under

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4 violet irradiation at 420 nm. 2D palladium phosphochalcogenides semiconductor with
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6 bifunctional electrocatalytic and photoelectrocatalytic properties. Our results show
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8 competitive performance compared with industrial Pt/C catalysts for solar-driven water
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10 splitting under acidic and alkaline conditions.
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13 **Introduction**

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16 Two-dimensional (2D) semiconductor photocatalysts are promising materials for the
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18 water-splitting reaction to generate hydrogen and oxygen – a sustainable supply of
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20 clean and renewable energy.¹⁻⁴ Compared with their three-dimensional (3D) bulk
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22 counterparts, the corresponding 2D nanosheets provide a high specific surface area and
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24 a low diffusion distance between the surface and the photogenerated electrons and holes,
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26 making them promising for the next generation of photocatalysts.⁵⁻⁶ A material for
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28 photoelectrocatalytic (PEC) water splitting should satisfy the following requirements:
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35 (i) The band gap should be larger than the potential difference of 1.23 eV to split water,
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37 but smaller than 3.00 eV to harvest visible light properly; (ii) the conductive and valence
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39 bands must span the redox potential of water; (iii) the potential difference between the
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41 conduction band maximum (valence band minimum) and reduction (oxidation)
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43 potential ensures substantial reducing (oxidizing) power, but low overpotentials.⁷⁻¹⁰
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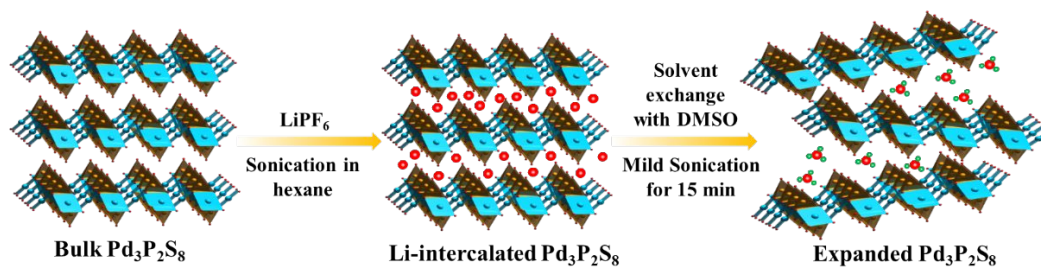
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48 Several 2D semiconductor materials show excellent performance for PEC, which can
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50 further be boosted by chemical modifications. These include transition-metal
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52 chalcogenides, graphene-based materials, platinum-group layered materials etc.¹¹⁻¹⁹
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56 The compound Pd₃(PS₄)₂, a palladium thiophosphate with a layered, interdigitated
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58 structure, was first fabricated by chemical vapor transport (CVT) method in 1971.²⁰
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4 This study noted unsuitable photocatalytic properties of bulk $\text{Pd}_3(\text{PS}_4)_2$. On the other
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6 hand, first-principle calculations suggested that mono- and bilayer $\text{Pd}_3(\text{PS}_4)_2$ are
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8 promising photocatalysts.²¹ In 2018, Zhang et al. reported an amorphous ultrasmall
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10 lithium-incorporated $\text{Pd}_3(\text{PS}_4)_2$.²² Such an amorphous ultrasmall structure could
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12 enhance the electrocatalytic activity towards the hydrogen evolution reaction (HER).
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14 First-principles calculations predicted the stability of mono-, bi-, and trilayer $\text{Pd}_3(\text{PS}_4)_2$,
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16 with a layer-number dependent band gap between 2.5 - 3.0 eV and the band edges
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18 spanning the redox potential of water, which makes it a promising photocatalyst for the
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20 water splitting reaction.^{21, 23-24} To date, the successful exfoliation of few-layer $\text{Pd}_3(\text{PS}_4)_2$
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22 has not been reported.
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30 Here, we report the exfoliation of few-layer palladium thiophosphate $\text{Pd}_3(\text{PS}_4)_2$ in
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32 solution from its bulk crystal via lithium intercalation and mild ultrasonication as shown
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34 in Scheme 1.²⁵ Firstly, the Li-ions were intercalated into the layers of bulk crystal in
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36 nonpolar hexane by continuous sonication, followed by solvation in highly polar
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38 DMSO to form a big solvated Li@DMSO group, which could effectively weaken the
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40 van der Waals forces between the 2D $\text{Pd}_3(\text{PS}_4)_2$ layers. Thus, exfoliated few-layer
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42 palladium thiophosphate sample could be achieved under further mild sonication. The
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44 red-purple bulk crystals (**Fig. S1a**) were grown by CVT.²⁰ We measured the valence
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46 band position and an indirect band gap of 2.57 eV, indicating the suitability of the
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48 material for photoelectrocatalytic water splitting, which is confirmed by DFT
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50 calculations. We further studied the electrochemical performance of HER and OER
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52 (oxygen evolution reaction) at pH=0, pH=7 and pH=14 under violet irradiation at 420
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nm.



Scheme 1. Reaction scheme for the fabrication of exfoliated few-layer $\text{Pd}_3(\text{PS}_4)_2$.

Experimental Section

Chemicals

Palladium powder (99.99%) and red phosphorus (99.999%) were obtained from Mateck. Sulfur (99.999%) was obtained from Strem, Germany. LiPF_6 (99.9%) was obtained from Sigma-Aldrich, Czech Republic. Hexane, dimethylsulfoxide, sulfuric acid (96%), potassium hydroxide (KOH), sodium sulfate (Na_2SO_4), ammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) were obtained from Penta (Czech Republic) as analytical grade reagents. Phosphate buffer solution (PBS) was made by $(\text{NH}_4)_2\text{HPO}_4$ and $\text{NH}_4\text{H}_2\text{PO}_4$.

Synthesis of $\text{Pd}_3(\text{PS}_4)_2$ crystals

Palladium, phosphorus and sulfur corresponding to 5g of the stoichiometric mixture were placed in quartz glass ampoule (20x100mm) and sealed under high vacuum (1×10^{-5} mbar) by oxygen-hydrogen torch. The ampoule was heated in muffle furnace on 750 °C for 14 days. Formed dark red crystals were mechanically separated from ampoule in glovebox.

Exfoliation of $\text{Pd}_3(\text{PS}_4)_2$ crystals

Firstly, 30 mg of $\text{Pd}_3(\text{PS}_4)_2$ bulk powder was dispersed in hexane solution (20 mL)

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4 containing an anhydrous LiPF_6 at 1:1.2 molar ratio. The mixture was sonicated using
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6 an ultrasonic bath with a duration of 2 h to get Li-intercalated materials. The resulting
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8 dispersion was centrifuged at 1000 rpm to remove hexane and unreacted LiPF_6 . Wet
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10 precipitate was dispersed into polar solvent DMSO to have the lithium ion which was
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12 intercalated into the layer of material solvated, followed by centrifugation and
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14 repeatedly washing for three times using DMSO. Finally, the sediments were put into
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16 DMSO and followed by mild sonication for 15 min to get the exfoliated $\text{Pd}_3(\text{PS}_4)_2$. The
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18 claybank color dispersion of exfoliated $\text{Pd}_3(\text{PS}_4)_2$ (**Fig. S1b**) was centrifuged at 5000
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20 rpm for 30 min, then collecting exfoliated sample in supernatant liquid for further
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22 characterization.
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30 **Characterization of materials**

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32 The crystal pattern and structure were characterized using X-ray diffractometer (XRD,
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34 Bruker D8 with $\text{Cu K}\alpha$ radiation, Germany) and transmission electron microscopy
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36 (TEM, EFTEM Jeol 2200 FS microscope, Japan). The XRD curve was fitted using
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38 Rietveld method by GSAS software.²⁶⁻²⁷ Scanning electron microscopy (SEM, Tescan
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40 MAIA 3, Czech Republic), scanning transmission electron microscopy (STEM, Tescan
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42 MAIA 3, Czech Republic), and atomic force microscopy (AFM, Ntegra Spectra, NT-
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44 MDT, Russia) were conducted to characterize the morphology of the materials. The
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46 analysis of chemical composition and valence were done by energy dispersive
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48 spectroscopy (EDX, Oxford Instrument, England) and X-ray photoelectron
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50 spectrometer (XPS, SPECS, Germany). Raman spectra were measured using inVia
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52 Raman Microscope (Renishaw, England) in a backscattering geometry with a CCD
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4 camera detector and DPSS laser (532 nm, 50 mW) with 5% laser power and 20×
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6 objectives. The particles size distribution was collected by Zetasizer ZSP (Malvern
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8 Panalytical, England). Visible light absorption spectra were recorded in solution by
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10 BLACK-Comet UV-Vis Spectrometer (StellarNet, United States).
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13 14 **Electrochemical analysis**

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16 The electrochemical measurements were conducted on Autolab PGSTAT204 (Eco
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18 Chemie, Utrecht, The Netherlands) controlled by NOVA 2.1 software (Eco Chemie)
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20 consisting of a three-electrode system. In Mott-Schottky (MS) experiments, 6 μL
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22 sample mixture (0.2 mg mL^{-1}) was drop-casted onto the surface (0.3 cm diameter) of
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24 precleaned glassy carbon (GC) electrode and was vacuum-dried as working electrode.
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26 A saturated Ag/AgCl electrode (SSCE) and a platinum plate respectively were used as
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28 reference and counter electrodes. The supporting electrolyte was 0.5 M Na_2SO_4
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30 aqueous solution (pH 7.0). The MS plot was constructed at a fixed frequency of range
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32 from 100 to 200 Hz as a function of potential around open-circuit potential (OCP). The
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34 electrochemical impedance spectroscopy (EIS) measurements were implemented at the
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36 frequency range of 0.01 to 1000000 Hz with 0.1 V sinusoidal perturbations. A 4 series-
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38 connected 420 nm Ultraviolet LEDs with 2500 mW @ 500 mA was used for irradiation.
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48 **Evaluation of pH-dependent photoelectrocatalytic water-splitting activity**

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50 An 80 mL supporting electrolyte, at different pH values of 0.5 M H_2SO_4 , 1 M PBS (pH
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52 7.0, prepared by $(\text{NH}_4)_2\text{HPO}_4$ and $\text{NH}_4\text{H}_2\text{PO}_4$) and 1 M KOH aqueous solution,
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54 containing 1.2 μg of materials were placed to a 100 mL reactor with a temperature-
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56 controlled water bath at 25 °C. A 4 series-connected 420 nm violet LEDs with 2500
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4 mW @ 500 mA were used for irradiation. The onset overpotential is defined at the
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6 current density of 10.0 mA cm⁻² for HER or OER. All applied potentials were converted
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8 to a reversible hydrogen electrode (RHE) by adding a value of (0.2224 + 0.059 × pH).
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10 11 **Computational Methods**

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14 Full structural optimization (relaxation of lattice vectors and atomic positions) were
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16 performed in FHI-AIMS²⁸ employing the PBE functional²⁹ on *light* tier 2 numeric
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18 atom-centered orbitals, including the many-body dispersion correction (MBD)³⁰ and
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20 scalar relativistic corrections (ZORA) on a 8x8(x6) Γ -centered *k*-grid. Band structures
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22 and densities of states were calculated including spin-orbit coupling (SOC) employing
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24 the HSE06 functional³¹ on *tight* tier 1 numeric atom-centered orbitals with added
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26 auxiliary diffuse basis functions. Raman spectra were predicted employing a Coupled
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28 Perturbed Kohn-Sham approach³² in Crystal17³³ including corrections for experimental
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30 conditions of 532 nm and 295 K.
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37 **Results and discussion**

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40 Pd₃(PS₄)₂ crystals of red-purple color²⁰ (**Fig. S1a**) were fabricated using CVT (see
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42 Methods). Powder XRD and Rietveld analysis confirmed the phase of tripalladium-di-
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44 tetrathiophosphate in space group $P\bar{3}m1$ with the lattice parameters $a = b = 6.9079$
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46 (10) Å and $c = 7.2885(3)$ Å, which is in good agreement with the literature and the
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48 predictions from theory (see **Fig. S2a** and Table 1).²⁰ The chemical composition was
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50 identified via EDS-mapping. The EDS spectrum (**Fig. S2b-d**) shows an elemental
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52 composition of 2.8:2:7.9, close to the theoretical stoichiometry of 3: 2: 8 of Pd: P: S.
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58 SEM images of the as-prepared material indicate a lamellar stacking of exfoliated
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4 nanoflakes (**Fig. 1a**). The AFM images of the samples collected after the centrifugation
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6 at 5000 rpm for 30 min showed a thickness of 0.7 to 2 nm, (**Fig. 1b-c**). The exfoliated
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8 nanoflakes show a lateral size of about 100 nm based on AFM and STEM (**Fig. S3c**)
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10 analysis, which is close to the size (**Fig. S3a**) measured by dynamic light scattering
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12 method with an average distribution around 74.91 nm. The EDS spectrum of the
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14 exfoliated $\text{Pd}_3(\text{PS}_4)_2$ (**Fig. S3d**) indicates a stoichiometry of 3: 2: 8 of Pd: P: S,
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16 correspondingly.
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22 The EDX-mapping (**Fig. S3e**) shows the presence and uniform distribution of Pd, P and
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24 S in the $\text{Pd}_3(\text{PS}_4)_2$ nanosheets selected from TEM image (**Fig. 1d**). The corresponding
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26 high-resolution TEM (HRTEM) image of a typical $\text{Pd}_3(\text{PS}_4)_2$ sheet reveals the well-
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28 crystalline structure without visible defects. The distances between the miller planes
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30 (100) and (200) were measured to be 0.591 and 0.303 nm, respectively, agreeing with
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32 the literature. **Fig. 1e** depicts the crystal plane structures of a single layer of $\text{Pd}_3(\text{PS}_4)_2$
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34 with the (100) and (200) planes, where the distance between the (100) planes equals the
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36 sum of two (200) planes.
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43 As shown in the XRD in **Fig. S3b**, the (001) peak of $\text{Pd}_3(\text{PS}_4)_2$ shifts from 12.53° for
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45 the bulk to 11.87° for the exfoliated material, meanwhile only the (001) peak exists
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47 with a weaker intensity and other peaks disappear in the exfoliated $\text{Pd}_3(\text{PS}_4)_2$. This
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49 phenomenon occurs typically in the 2D materials after being exfoliated into few
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51 layers.³⁴⁻³⁵
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56 **Fig. 1f** shows the Raman spectra measured for the bulk and exfoliated material as well
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58 as the calculated spectra for different layer numbers. The E_g^1/A_{1g}^1 signals around
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200 cm^{-1} and the E_g^3 signal at 316 cm^{-1} are characteristic for this material. They correspond to vibration modes of the tetrathiophosphate units (see **Fig. 1g**), and are in good agreement with the literature³⁶ and theory. The A_{1g}^3 mode corresponds to the P-S-bond stretching and is visible at 720 cm^{-1} in the bulk sample, but disappears for fewer layers as predicted by the calculation. Furthermore, the E_g^3 mode shifts by 1.7 cm^{-1} to lower wavenumbers in the exfoliated sample compared to the bulk sample, which agrees with the prediction from theory for fewer layers. The Raman spectra revealed that the structure of $\text{Pd}_3(\text{PS}_4)_2$ is maintained after exfoliation.

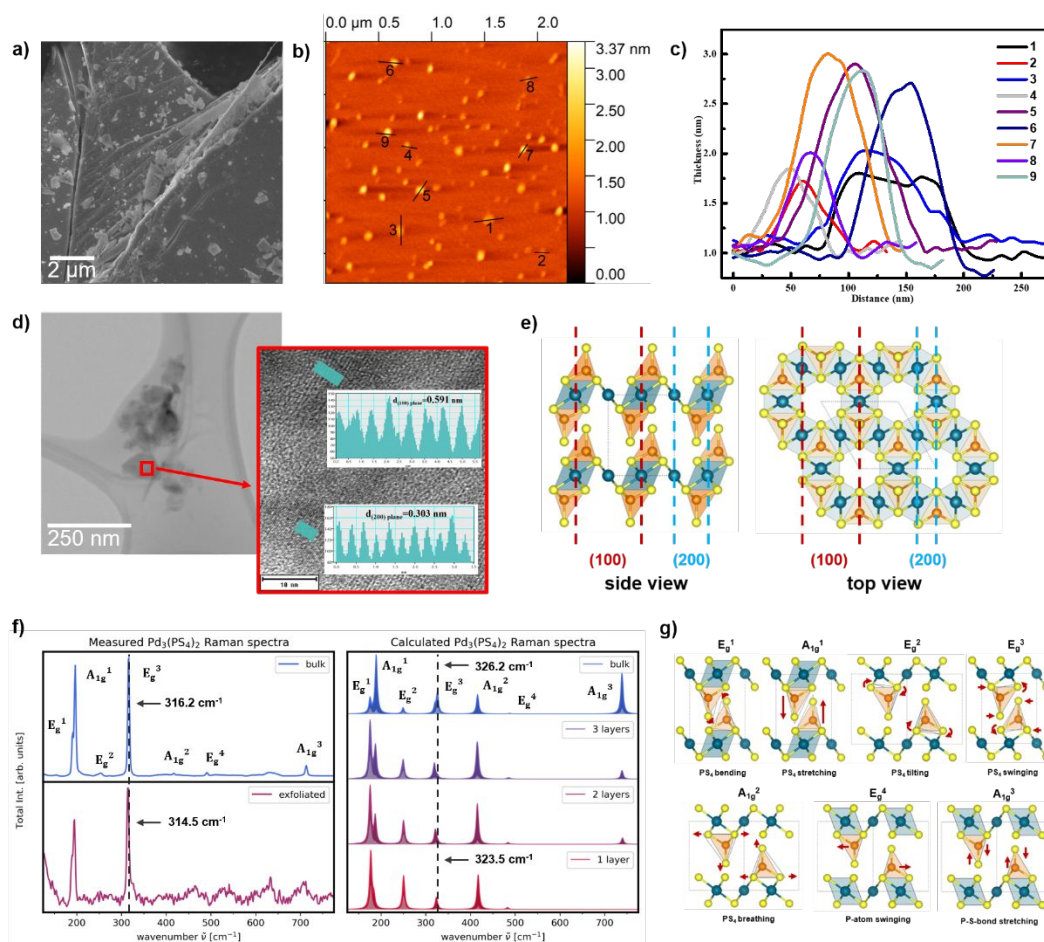


Figure 1 Morphology and structure characterization of bulk and exfoliated $\text{Pd}_3(\text{PS}_4)_2$: (a) SEM image of bulk $\text{Pd}_3(\text{PS}_4)_2$; (b) AFM image of exfoliated $\text{Pd}_3(\text{PS}_4)_2$ and (c) corresponding thickness of selected nanosheets; (d) TEM image and (e) visualization of the structure with given lattice planes; (f) Measured and calculated Raman spectra; (g) Raman modes.

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5 Additionally, we performed X-ray photoelectron spectroscopy (XPS) to investigate
6 surface oxidation. **Fig. S4** shows the XPS survey spectra of Pd, P, S O and C elements
7 of both bulk and exfoliated Pd₃(PS₄)₂ samples.²² For bulk material, the Pd 3d core-level
8 XPS spectra (**Fig. S4b**) demonstrates doublet peaks at around 337.1 and 342.2 eV,
9 corresponding to the Pd 3d_{5/2} and 3d_{3/2} levels, respectively, where the spin-orbit
10 components separated by about 5.1 eV are in a good agreement with previous reports.³⁷
11 Note that the decomposition of the peak located at about 341.5 and 336.3 eV in the Pd
12 3d XPS core spectrum of the bulk sample could be ascribed to the existence of surface
13 oxidation to PdO_y. The S 2p XPS core-level spectrum (**Fig. S4c**), spin-orbit doublet at
14 163.4 eV and 162.2 eV of S 2p_{1/2} and S 2p_{3/2} separated by 1.2 eV is in a good agreement
15 with the value reported for the chalcogenides.³⁸ As for the P 2p core-level XPS
16 spectrum (**Fig. S4d**), the peaks at about 132.2 eV and 131.1 eV correspond to the P
17 2p_{3/2} and P 2p_{1/2} spin-orbit. Moreover, the XPS spectrums for all elements of obtained
18 Pd₃(PS₄)₂ nanosheets show no apparent shift compared to the bulk sample.

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41 Strong visible light absorption is crucial for efficient photocatalysis. We performed
42 UV-Vis measurements to obtain diffuse reflectance spectra to study the absorption
43 properties of Pd₃(PS₄)₂. As seen in **Fig. 3a**, the exfoliated Pd₃(PS₄)₂ shows a significant
44 light absorption under 482.5 nm. Furthermore, the band gap (E_g) of as-prepared
45 Pd₃(PS₄)₂-based photocatalyst was calculated using the Eq. (1):

$$(ahv)^n = A(hv - E_g) \quad (1)$$

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where α , h , ν , A , E_g are the absorption coefficient, Planck's constant, light frequency,
proportionality constant and optical band gap energy, respectively. The n is a constant

determined by the type of optical transition. It is equal to 4 for an indirect transition and 1 for a direct transition.³⁹ As shown in **Fig. 3a**, the indirect band gap of exfoliated Pd₃(PS₄)₂ was measured to be 2.57 eV. Meanwhile, the calculated indirect band gap of the bulk sample (**Fig. 3b**) is 2.54 eV, which is above the values measured in reported literature of 2.12 eV³⁶ and 2.20 eV²⁰. Theory predicts an increase of the band gap by 460 meV from bulk to monolayer (**Fig. 3b**) that agrees with the increased band gap of the exfoliated material compared to the bulk material.^{21, 23-24}

The band edge alignment with the electrochemical potentials of the water splitting reaction is another significant factor to overall PEC efficiency; the measurements were done by electrochemical Mott–Schottky analysis. As shown in **Fig. 3c**, exfoliated Pd₃(PS₄)₂ shows an n-type semiconducting character with a flat band position of -0.83 V (*vs.* SSCE) in 0.5 M Na₂SO₄ aqueous solution (pH=7.0) at the frequency range from 100 to 200 Hz, which correspond to the conduction band minimum (CB) of -0.59 eV *vs.* NHE (pH 7.0).³⁹ From the band gap, we can estimate the valence band maximum at 1.98 eV *vs.* NHE using the Eq. (2):⁴⁰

$$E_v = E_g + E_c \quad (2)$$

where E_v , E_g and E_c are the energies of VB, band gap and CB, respectively. The reduction and oxidation potentials of the HER and OER are at -0.41 V and 0.82 V *vs.* NHE at pH=7, respectively. Thus, the band edges of as-exfoliated Pd₃(PS₄)₂ span the electrochemical potentials of the water splitting reaction. This is confirmed by theory, as shown in **Fig. 3d** and summarized in **Table 3** (supporting information), which assigns the vacuum-energy corrected valence band maximum of the bulk material to

-0.13 eV relative to the absolute electrode potential of the hydrogen electrode, which matches the measured valence band maximum at -0.18 eV.

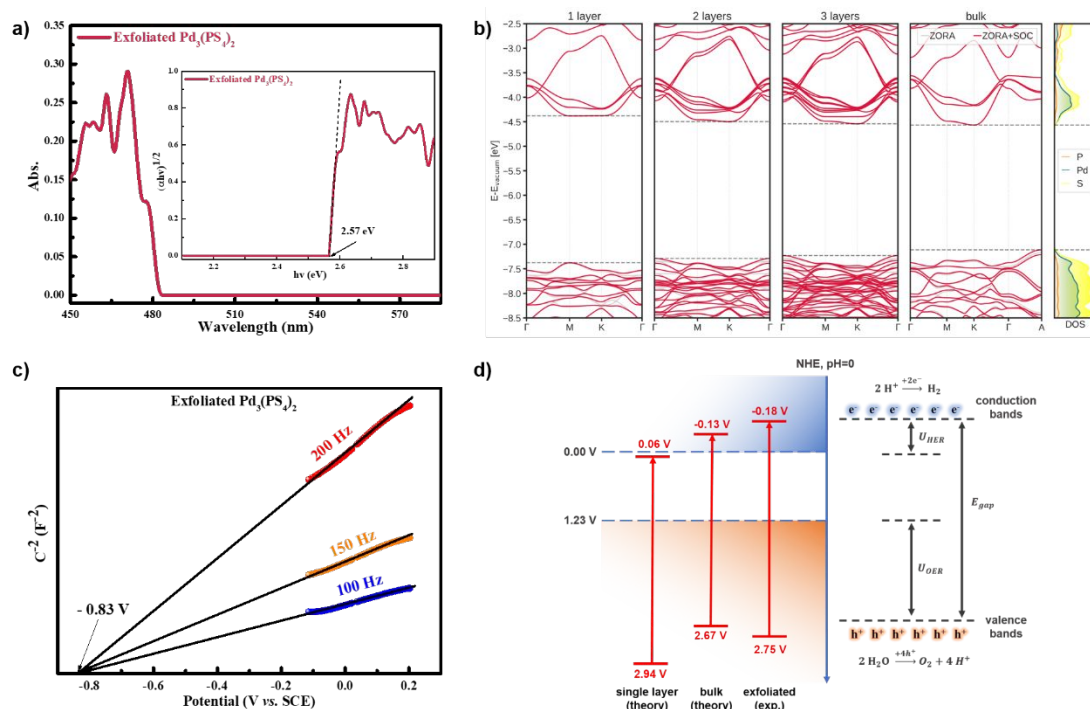


Figure 3 (a) UV-Vis absorption spectra and (b) vacuum-corrected band structures for different layer numbers of $\text{Pd}_3(\text{PS}_4)_2$ at the HSE06 level of theory including SOC. (c) Mott-Schottky plots of exfoliated $\text{Pd}_3(\text{PS}_4)_2$ under frequencies of 100 to 200 Hz at 0.5 M Na_2SO_4 (pH 7.0) aqueous solution. (d) schematic diagram of PEC water splitting of exfoliated $\text{Pd}_3(\text{PS}_4)_2$ photoelectrode based on Mott-Schottky and band edge. Note that the valence band energies are given with positive signs, such that the band gap is $E_g = E_v + E_c$.

As the interfacial electron transfer efficiency is essential for the PEC water splitting process, the electrochemical impedance spectra (EIS) are compared for the bulk and exfoliated $\text{Pd}_3(\text{PS}_4)_2$ at different pH values. Compared to bulk samples, the smaller arc radius in the Nyquist plots (**Fig. 4a-c**) of exfoliated $\text{Pd}_3(\text{PS}_4)_2$ nanosheets under irradiation means lower electron transfer resistance, revealing a faster electron transfer process under each pH condition of 0.5 M H_2SO_4 , 1 M PBS (pH 7.0) and 1 M KOH. Additionally, the arc radius is smallest under acidic conditions for each measured

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4 sample, indicating fast electron transfer, while the larger arc radius occurring in neutral
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6 conditions indicates slower electron transfer. The transient photocurrent responses of
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8 materials were recorded through multiple on/off light (420 nm violet light) irradiation
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10 cycles under different pH conditions at constant potentials of both -0.4 V (vs. RHE)
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12 (for HER) and +2 V (vs. RHE) (for OER). As shown in **Fig. 4d-e**, the photocurrent
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14 density of Pd₃(PS₄)₂ nanosheets electrodes are higher than bulk Pd₃(PS₄)₂ electrodes in
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16 our experimental conditions. As the photocurrent response within electrodes is bound
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18 to the separation efficiency of photogenerated electron-hole pairs,⁴¹ the higher
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20 photocurrent suggests low electron-hole pair recombination and a higher electron
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22 transfer efficiency for exfoliated Pd₃(PS₄)₂ nanosheets. Notably, the detected
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24 photocurrent density under neutral conditions is lower than under alkaline and acidic
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26 conditions for the measurements of both -0.4 V (vs. RHE) and +2 V (vs. RHE), and the
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28 photocurrent density is higher in an acidic environment compared to an alkaline
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30 environment in the -0.4 V (vs. RHE) measurement. We could conclude from the
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32 characterizations of EIS and transient photocurrent responses that exfoliated Pd₃(PS₄)₂
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34 nanosheets show a faster electron transfer process and higher photogenerated electron
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36 transfer efficiency than its bulk counterpart, and the most efficient reaction environment
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38 for PEC water splitting might be under acidic conditions.
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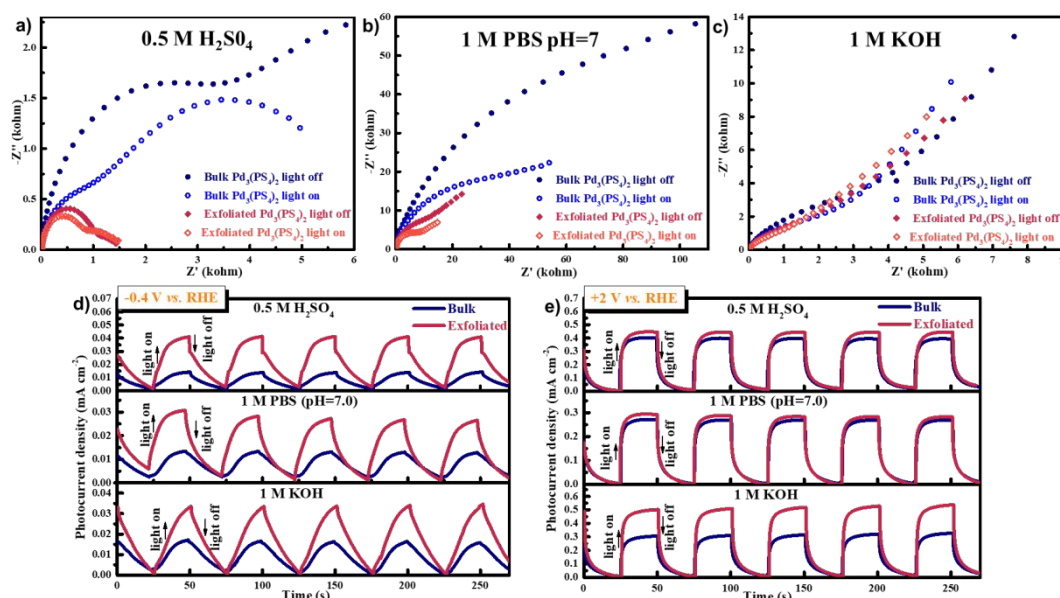


Figure 4 Electrochemical impedance Nyquist plots of bulk and exfoliated Pd₃(PS₄)₂ under 420 nm irradiation at different pH values of (a) 0.5 M H₂SO₄, (b) 1 M phosphate buffer solution (pH=7.0) and (c) 1M KOH aqueous solution; (d) and (e) transient photocurrent responses of materials under different pH range at -0.4 V and +2 V (vs. RHE), respectively. The collected photocurrent density is multiplied by -1 for the measurements at -0.4 V (vs. RHE).

We further performed OER and HER measurements of both bulk and exfoliated Pd₃(PS₄)₂ at acidic, neutral and alkaline pH. As shown in **Fig. 5a-d**, the exfoliated Pd₃(PS₄)₂ nanosheets exhibit better electrocatalytic performance than their bulk counterparts. **Fig. 5a** shows that the irradiated Pd₃(PS₄)₂ nanosheets demonstrate excellent HER activity with an overpotential of 412 mV at 10 mA cm⁻² in 0.5 M H₂SO₄. In contrast, its OER activity is weakly expressed due to the slight decrease of the overpotential barrier from 955 to 914 mV. In **Fig. 5b**, the HER and OER with Pd₃(PS₄)₂ nanosheets under irradiation show overpotentials of 890 mV and 1029 mV in 1 M PBS (pH 7.0), respectively. In an alkaline environment with 1 M KOH, the HER is only weakly catalyzed by both bulk and exfoliated samples (**Fig. 5c**). To compare the PEC activity of Pd₃(PS₄)₂ catalysts, we analyzed the overpotential in various pH

environment at a current density of 10 mA cm^{-2} (**Fig. 5d**), where the PEC activity of commercial Pt/C under ambient conditions was used as reference (corresponding LSV curves shown in Fig. S6a). Both OER and HER activity of exfoliated $\text{Pd}_3(\text{PS}_4)_2$ nanosheets are superior to their bulk counterparts. Under irradiation at 420 nm, the HER overpotentials for as-prepared $\text{Pd}_3(\text{PS}_4)_2$ nanosheets are 0.41 V (pH 0), 0.89 V (pH 7.0) and 0.66 V (pH=14), respectively, which can nearly compete with the commercial Pt/C electrode with HER overpotentials of 0.38 mV, 0.87 mV and 0.64 mV.

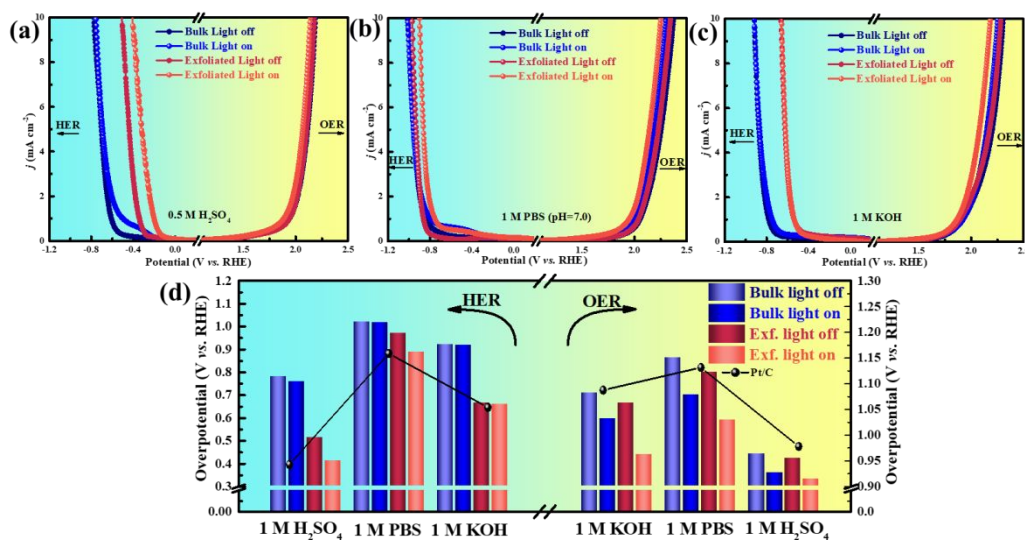


Figure 5 The PEC water splitting studies of bulk and exfoliated $\text{Pd}_3(\text{PS}_4)_2$: polarization curves of bulk and exfoliated samples for HER and OER at (a) 0.5 M H_2SO_4 , (b) 1 M phosphate buffer solution (pH 7.0) and (c) 1M KOH aqueous solution, respectively. (d) Comparison of the overpotential of PEC water splitting at 10 mA cm^{-2} . The collected current density (j) is multiplied by -1 for HER.

Conclusion

In summary, a novel two-dimensional semiconductor material $\text{Pd}_3(\text{PS}_4)_2$ was successfully exfoliated by lithium intercalation and ultrasonication from its bulk counterpart. The band gap of the as-exfoliated material was estimated at 2.57 eV; this indicates the ability of the material to absorb in the visible light and further use it in

photoelectrocatalysis. The as-exfoliated Pd₃(PS₄)₂ nanosheets demonstrate their dual photoelectrocatalytic activity as electrodes for HER and OER. The photo-induced water splitting of the Pd₃(PS₄)₂ nanosheets works best in an acidic environment. This new exfoliated 2D Pd₃(PS₄)₂ might enrich the database of materials applied in the field of photoelectrocatalysis.

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