

Supporting Information

Atomically-thin PdSeO₃ Nanosheets: Promising 2D Photocatalyst Produced by Quaternary Ammonium Intercalation and Exfoliation

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S1. Experimental Section

Chemicals and materials. Palladium nitrate dihydrate ($\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Pd} \geq 39\%$), Tetraethylammonium bromide (TEAB, 98%), Polyvinylpyrrolidone (PVP $M_w=58000$) were purchased from Aladdin Reagent. Acetonitrile (AN) and N, N-dimethyl formamide (DMF) were purchased from Tianjin ZhiYuan Reagent Co., Ltd. Selenic acid (H_2SeO_4 , 40%) solution was purchased from Alfa Aesar. Potassium nitrate (KNO_3 , 99%) was purchased from XiYa Reagent.

Synthesis of PdSeO_3 bulk crystals. PdSeO_3 bulk crystals were prepared according to the procedure described in earlier publication. Typically, 116.7 mg of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, 88.6 mg of KNO_3 , 0.5 mL of H_2SeO_4 and 0.2 mL of water were added in a 25-mL PTFE-lined autoclave. The autoclave was sealed and heated at 200 °C in an oven. After four days of reaction, the products were collected by centrifugation, and were washed several times with water and methanol.

Synthesis of PdSeO_3 nanosheets. A two-electrode electrochemical cell was used to conduct the intercalation reaction. The CHI760E electrochemical workstation (Chenhua, Shanghai, China) was used as the power source. PdSeO_3 bulk crystals (20 mg) closely wrapped within carbon cloth were placed as the cathode and graphite rod was used as the anode. Specifically, the carbon cloth was cut into small piece with the size of 2 cm \times 2 cm. After placing the PdSeO_3 bulk crystals in the center, the carbon cloth was folded three times. Then, it was clamped with an alligator clip and the part in contact with the PdSeO_3 samples was immersed in the electrolyte. The electrolyte solution was made by dissolving tetraethylammonium bromide (TEAB) in acetonitrile

(40 mL; 5 mg mL⁻¹). The applied voltage was set at 8 V and the intercalation process was allowed to proceed for 2 h. After completion of the reaction, the as-intercalated PdSeO₃ were washed several times with ethanol, followed by mild sonication in a solution containing polyvinylpyrrolidone (PVP, M_w = 58000) and N, N-dimethyl formamide (40 mL; 0.2 M). The dispersion was subsequently centrifuged and washed several times with isopropanol to eliminate the PVP residuals. Finally, to remove the large aggregates, the dispersion was centrifuged at 1000 rpm for 4 min and the precipitates were discarded.

Photocatalytic reaction. Photocatalytic hydrogen evolution was carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system (Beijing Perfectlight Technology, Labsolar 6A). The sample (4 mg of PdSeO₃ bulk crystals or PdSeO₃ nanosheets) was dispersed in 100 mL of aqueous solution containing 0.5 M Na₂S and 0.5 M Na₂SO₃ as the sacrificial agents. A 300 W Xe lamp was used to simulate the full spectrum of solar light. A Pyrex glass vessel with a cooling water-circulating jacket acted as the reactor and the temperature of the reaction solution was maintained at 20 °C by a flow of cooling water. The amount of evolved hydrogen was determined with online gas chromatography (Agilent; GC-7890B, MS-5A column, TCD, Ar Carrier). The photocatalytic water splitting or water oxidation reaction was performed under the same conditions except the pure water or 20 mM NaIO₃ (or 2 mM FeCl₃) aqueous solution was used as the reaction solvent.

Photoelectrochemical (PEC) measurements. The PEC measurements were performed using a standard three-electrode potentiostat system with a Pt counter

electrode and a saturated calomel electrode. The working electrode was prepared by depositing samples (PdSeO₃ bulk crystals or PdSeO₃ nanosheets) onto the ITO substrate (1 cm × 2 cm) that has been previously cleaned with ethanol and water. The surface area of the sample exposed to the electrolyte was fixed at 1 cm². An aqueous solution containing 0.5 M Na₂S and 0.5 M Na₂SO₃ was used as the electrolyte. The working electrode was illuminated from the front side with an optical fiber source (FX300, Beijing Perfectlight Technology Co. Ltd.). The EIS Nyquist plots were collected with the frequency ranging from 100 kHz to 0.1 Hz and the modulation amplitude of 5 mV.

Measurements and instruments. Low-resolution transmission electron microscopy (TEM) images were obtained by HITACHI H-7650 (accelerating voltage of 80 kV) electron microscopy. High-resolution transmission electron microscopy (HRTEM) characterization and energy dispersive X-ray spectroscopy (EDS) analysis were performed using transmission electron microscopy (FEI Tecnai G2 F20 S-Twin, acceleration voltage of 200 kV) equipped with X-ray energy-dispersive spectroscopy detector. The XRD patterns were obtained using a Bruker D8 multiply crystals X-ray diffractometer (5° min⁻¹). UV-Vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer at RT. The XPS spectra were obtained with a PerkinElmer Physics PHI 5300 spectrometer using mono-chromatic Al K α radiation (1486.7 eV). All binding energies were corrected based on the C 1s peak (284.8 eV). The TEM and XPS characterizations were supported by Beijing Zhongke-baice Technology Service Co., Ltd.

S2. Supplementary Data

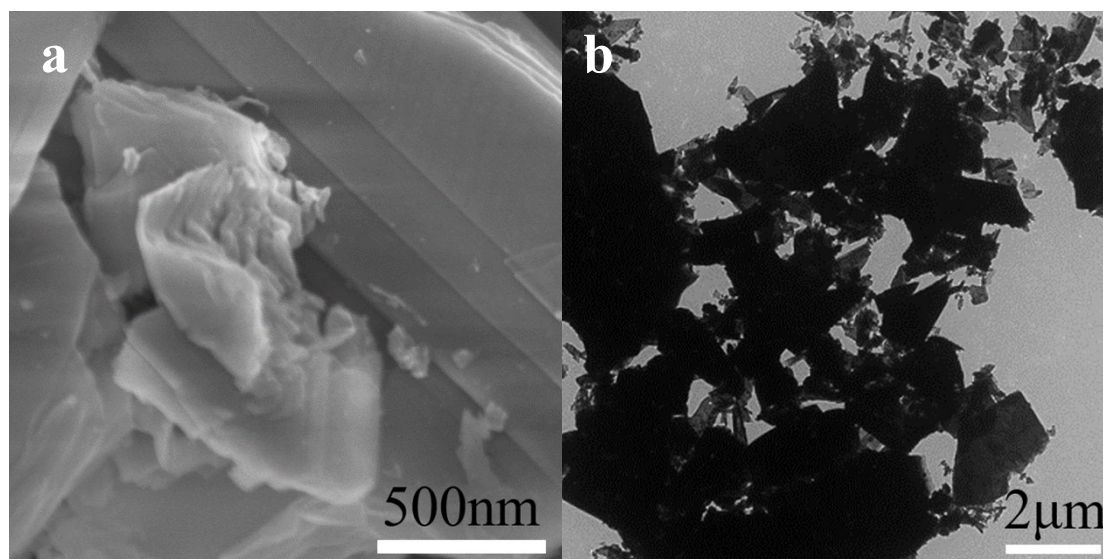


Figure S1 (a) SEM image and (b) TEM image of the PdSeO₃ bulk crystals.

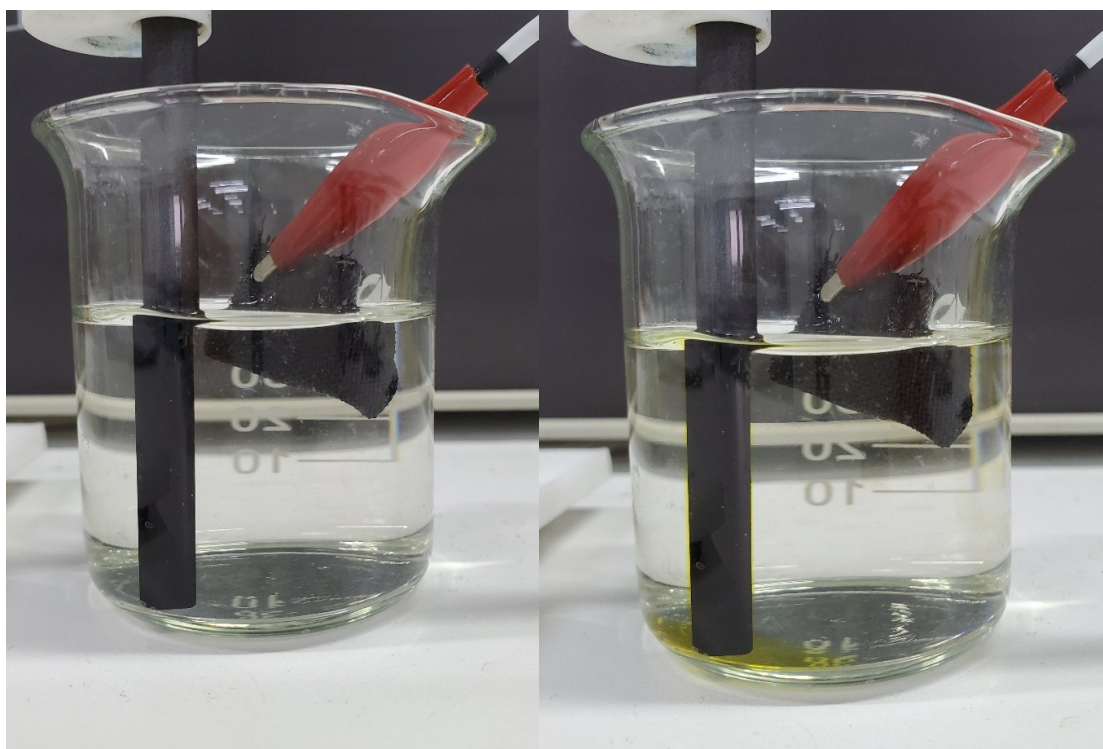


Figure S2 Photographs showing the color change near the graphite anode before (left) and during (right) the electrochemical exfoliation of the PdSeO₃ bulk crystals.

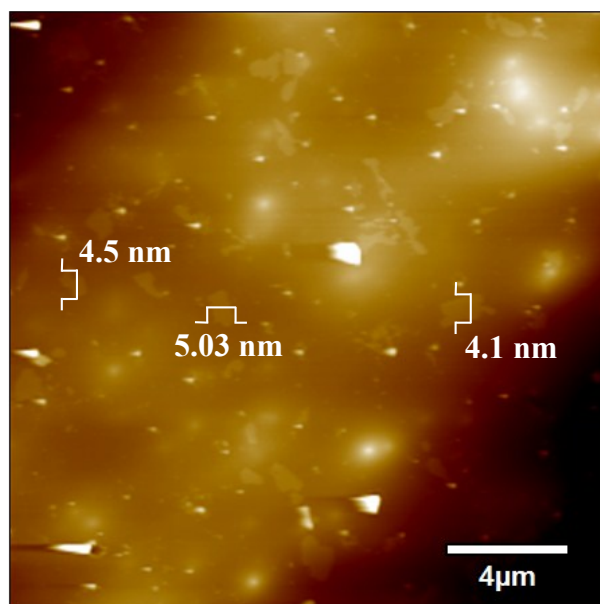


Figure S3 AFM image and the corresponding height profiles of the exfoliated PdSeO₃ nanosheets.

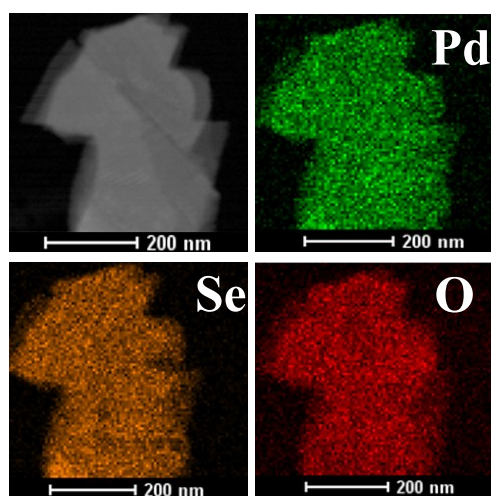


Figure S4 HAADF-STEM image and the corresponding EDX elemental maps for the PdSeO₃ nanosheets.

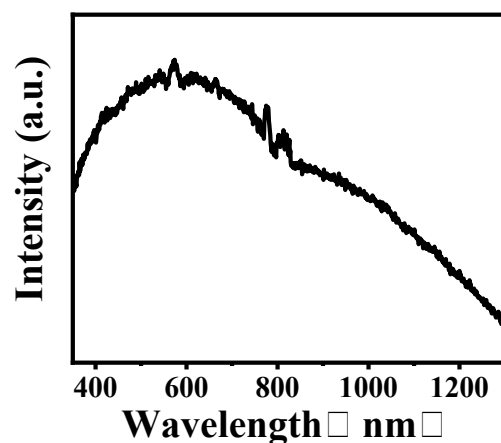


Figure S5 UV-Vis-NIR absorption spectrum of the PdSeO₃ bulk crystals.

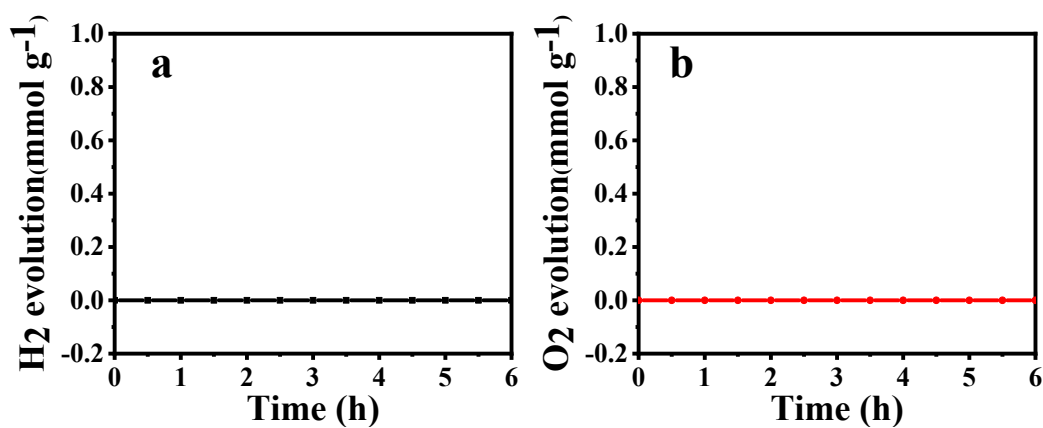


Figure S6 (a) Hydrogen and (b) Oxygen evolution curves for the exfoliated PdSeO₃ nanosheets in photocatalytic pure water splitting under UV-Vis light irradiation.

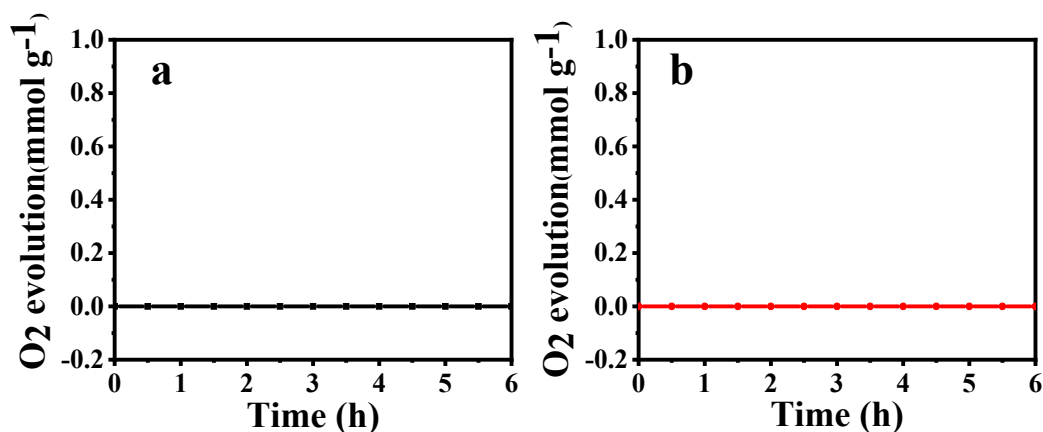


Figure S7 Photocatalytic oxygen evolution curves for the PdSeO₃ nanosheets using (a) NaIO₃ (20 mM) or (b) FeCl₃ aqueous solution (2 mM, pH=2) as the electron sacrificial agents under UV-Vis light irradiation.

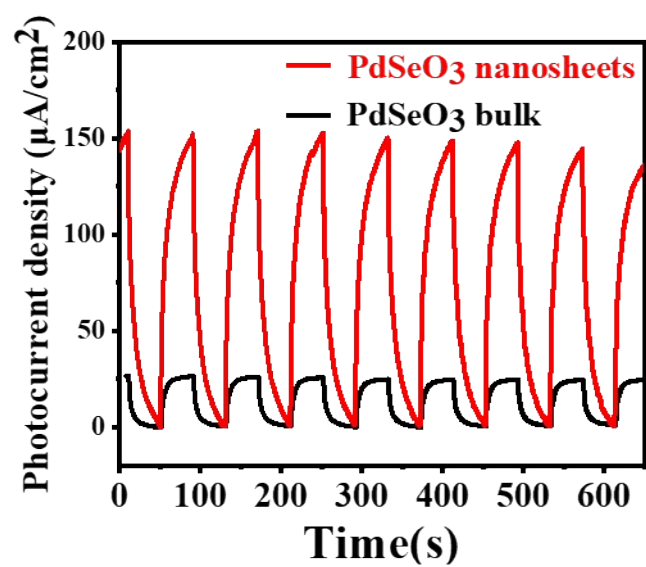


Figure S8 Photocurrent density–time curves for PdSeO₃ nanosheets and PdSeO₃ bulk crystals.

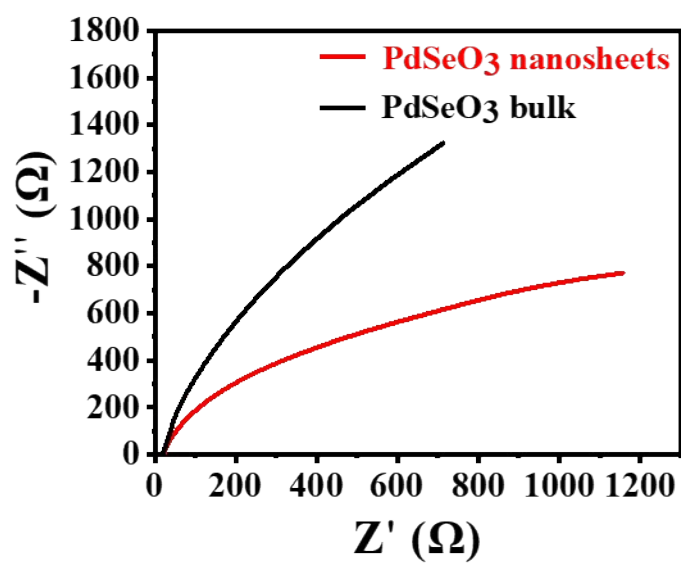


Figure S9 The EIS Nyquist plots for PdSeO₃ nanosheets and PdSeO₃ bulk crystals.

Table S1 Elemental composition of the PdSeO₃ nanosheets determined by EDX elemental analysis. The content of oxygen cannot be precisely determined considering its small atomic number (< 18).

Element	Atomic ratio (%)
O	41.97
Se	28.53
Pd	29.49