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Syntheses, characterizationsna and water-electrolysis properties of 2D α and β -PdSeO₃ bulk and nanosheet semiconductors^{*}



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ABSTRACT

In contrast to alkaline water electrolysis, water electrolysis in an acidic environment has higher energy efficiency, more compact cell design, higher gas purity, and less sensitivity to environmental impurity. Herein, the syntheses of the known 2D α - and β -PdSeO₃ were improved. The bulk materials were exfoliated into nanosheets using an ultrasonic-assisted liquid-phase exfoliation similar to that of preparing graphene nanosheets. Their band-gaps, valence band maximums (VBMs) and conduction band minimums (CBMs) were determined using Mott-Schottky plots and the linear potential scan method in acidic aqueous solution, 0.2 M Na₂SO₄ aqueous solution and non-aqueous solution. Their transient photocurrent properties were also examined, along with their Electrochemical Impedance Spectra (EIS). The bulk materials are stable in pH = 0–14 value water solution for at least 48 h. α - and β -PdSeO₃ nanosheets exhibit moderate catalytic activities for hydrogen evolution reactions in 0.5 M H₂SO₄ (η_{10} (overpotential at 10 mA cm⁻²: 185 and 209 mV, respectively; catalyst loading: 0.28 mg cm⁻²), much better than the performances of the bulk materials. In addition, β -PdSeO₃ bulk and nanosheets materials show good and similar OER catalytic activities in 0.5 M H₂SO₄ (η_{10} : 381 and 405 mV, respectively; catalyst loading: 0.28 mg cm⁻²). Thus, β -PdSeO₃ nanosheets were found to be a good overall water splitting catalyst in acidic solution. The above catalysts all show long-term stability. In contrast, α -PdSeO₃ does not have OER catalytic property. To our knowledge, Pd-based acidic overall water splitting catalysts are very rare.

1. Introduction

Exploring clean sustainable energy is an extremely urgent need in the modern society, owing to the fast depletion of remaining fossil fuel reservoirs and numerous environmental issues [1–3]. These issues could be mitigated by converting renewable energy sources such as waste heat, wind, and solar power into electricity, which is then converted to H_2 by water electrolysis. Hydrogen is clean and has high energy density. It is also a staple of chemical industry [4]. Compared to the present major hydrogen production method of steam reformation of fossil fuels, water

electrolysis with electricity generated by the above mentioned renewable energy sources is widely considered as a sustainable and cost-effective technology for producing high purity hydrogen on a large scale in the future and huge efforts have been investigated into electrocatalytic water splitting [5–13]. However, at present, only a small quantity of hydrogen (<5% of global hydrogen production) is produced by industrial water electrolysis, due to the poor efficiency or stability of both the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) electrocatalysts [14,15].

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The water-splitting process involves two half reactions: the HER and the **2. Experimental**

2.1. Materials and general methods

OER. The key challenge of this technology is to reduce the large overpotentials for both cathodic HER and anodic OER. Up to now, it is still difficult to find two such electrocatalysts that can couple in an integrated electrolyzer for overall water splitting, because their best working conditions often mismatch [16]. On the other hand, coupling the two catalysts in two differing conditions, in which they work best, complicates their integration into a single water splitting device, because they require different accessories, and preparation and optimization procedures [16]. So, developing efficient bifunctional electrocatalysts that can work well for both HER and OER under the same condition may address these issues, and may make it feasible to easily integrate them into a single working electrolyzer [16].

In contrast to alkaline water electrolysis, proton exchange membrane (PEM) water electrolysis in an acidic environment has higher energy efficiency, more compact cell design, higher gas purity, and less sensitivity to environmental impurity [17–19]. However, only handful bifunctional electrocatalysts were discovered, which can be applied in acidic electrolyte because of instability and corrosion during OER electrocatalysis under such harsh conditions [20–23].

Recently, two-dimensional (2D) layered materials have drawn enormous attention due to their unique layered structures and intriguing electrical characteristics, which brings the unprecedented broad applications in the fields ranging from electronic [24-27], spintronic [24,28, 29], optical [29–33], optoelectronic [34–40], thermal [41–43], magnetic [44], quantum devices [45–51] to energy storage [52–54] and catalysis [55-59], including water electrolysis [60-64]. Zhang et al. obtained amorphous lithium-incorporated 2D palladium phosphosulfide nanodots [65], which exhibit excellent electrocatalytic activity towards the hydrogen evolution reaction with an overpotential of 91 mV at 10 mA cm⁻², a Tafel slope of 29 mV dec⁻¹ in 0.5 M H₂SO₄, and outstanding long-term stability. To our knowledge, no other 2D Pd-containing compounds have been applied in water electrolysis. α - and β -PdSeO₃ are 2D layered materials that were synthesized in 2007 [66,67]. In 2018, Li et al. predicted that the α -PdSeO₃ monolayer is a promising photocatalyst which can split water without using sacrificial agent based on density functional theory (DFT) computations [68]. The calculations also predict that the exfoliation of the bulk 2D material should be easy, and require similar energy as that required for the exfoliation of graphene. In 2020, Liu and Zhang et al. did obtained 2D α-PdSeO₃ nanosheets (NNs) by using the quaternary ammonium intercalation-assisted electrochemical exfoliation method and obtained good activity and stability towards photocatalytic H₂ evolution from water [69]. Since photocatalysts can often be used also as electrocatalysts, and Pd-based materials have been used as water-splitting electrocatalysts [70-73], whether PdSeO₃ can also be a water-splitting electrocatalyst; and if it is, how the structural differences and the layer thickness of α - and β -PdSeO₃ affect the electrocatalytic water-splitting properties are worth investigations.

Herein, we improved the syntheses of α - and β -PdSeO₃ bulk materials, and obtained their NNs based on the ultrasonic-assisted liquid-phase exfoliation similar to that of making graphene NNs. The bulk materials are stable in pH = 0-14 value aqueous solution for at least 48 h. The water electrolytic properties of the above four materials were investigated. α - and β -PdSeO₃ NNs exhibit moderate catalytic activities for hydrogen evolution reactions in 0.5 M H₂SO₄, much better than the activities of the bulk materials; and α -PdSeO₃ NNs have better performance than that of $\beta\mbox{-}PdSeO_3$ NNs. In addition, $\beta\mbox{-}PdSeO_3$ NNs and bulk material show good and similar OER catalytic properties in 0.5 M H₂SO₄. Thus, β -PdSeO₃ NNs were found to be a good overall water splitting catalyst in 0.5 M H₂SO₄ solution at a catalyst loading of 0.28 mg cm⁻² (η_{10} : 209 mV (HER) and 405 mV (OER)). To our knowledge, only a handful overall water-splitting electrocatalysts can operate in acidic solutions [21-23, 74-80]; most of them are Ir- or Ru-based; and there is only one Pd-based compound (Sr₂PdO₃) [80], which has worse catalytic activity than that of β-PdSeO3 NNs. The above catalysts all show long-term stability. In contrast, α-PdSeO₃ does not show OER catalytic properties.

All chemicals and reagents were obtained from commercial sources and used without further purification. Pd(NO3)2·2H2O (99.8%, Alfa-Aesar), selenic acid H₂SeO₄ aqueous solution (40 wt% in H₂O, 1.407 g/mL, Aldrich), selenious acid H₂SeO₃ (97%, Alfa-Aesar) and potassium nitrate (99.994%, Alfa-Aesar). Nafion D-520 dispersion (5% w/w in water and 1-propanol) were purchased from Alfa Aesar (Lot# Z31E033, CAS: 31175-20-9). Ultrapure water obtained from a Millipore water purification system (≥18.23 MΩ cm, Millipore) was used in electrochemical experiments. Commercial Pt/C (20 wt%) was provided by Alfa Aesar Chemical Co., Ltd. All other chemicals and reagents were of analytical grade from commercial sources and used without further purification. The room-temperature powder X-ray diffraction (PXRD) spectra were recorded on a Rigaku D/Max 2500/PC diffractometer at 40 kV and 100 mA with a Cu-target tube ($\lambda = 1.54178$ Å) and a graphite monochromator. The XRD diffraction patterns were recorded in the 2θ range between 4 and 48° with a step size (2 θ) of 0.02° and at a scanning rate of 10° min⁻¹. Thermogravimetry analysis (TGA) experiments were carried out using a SDT 2980 thermal analyzer under Ar flow of 15 mL min⁻¹ over the temperature range from 25 to 800 °C at a heating rate of 10 °C min⁻¹, UV-Vis-IR diffuse reflectance spectral measurements were taken using a Varian Cary 5000 UV-Vis-NIR spectrophotometer using barium sulphate (BaSO₄) as a reference. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker tensor 27 Fourier transform infrared spectrometer. The spectra were measured using KBr plates in the wavenumber range of 4000–400 cm⁻¹. Raman spectra were recorded on a JY LabRam HR Evolution instrument at a laser excitation wavelength of 633 nm at room temperature.

The morphology of the samples was observed using a HITACHI H7650 transmission electron microscope (TEM) and a LEO1530VP field emission scanning electron microscope (SEM). Thickness test measurements were performed by a Pico Scan 5500 atomic force microscopy (AFM) with a Molecular Imaging Pico Scan 5500 AFM in an AC mode. AFM samples were prepared by dropping a diluted NNs/isopropanol dispersion on a freshly cleaved mica substrate and sucking the redundant dispersion with a piece of filter paper and then drying at ambient temperature. The surface elemental analysis of samples was performed by X-ray photoelectron spectroscopy (XPS) using a Thermo ESCALAB Xi+ with Al K α radiation. All binding energies were corrected based on the C 1s peak (284.8 eV).

2.2. Synthesis of α -PdSeO₃ bulk material

The experiment was carried out in a 50 mL open single-necked spherical flask. 5.0 mL selenic acid aqueous solution (19 mmol) was heated at 200 °C for 35–40 min using an oil bath and cooled down naturally to 25–60 °C. The final liquid was colourless, transparent and slightly viscous and the condensed liquid is about 1.0 mL of its original volume.

In a typical synthesis, Pd(NO₃)₂·2H₂O (90 mg, 0.34 mmol), KNO₃ (88.6 mg, 0.876 mmol), concentrated H₂SeO₄ (0.200 mL, about 3.9 mmol assuming it does not change to H₂SeO₃) and deionized water (0.50 mL, 28 mmol) were added in a glass vial (height 4 cm and diameter 1.1 cm) and stirred for 30 min. Since Pd(NO₃)₂·2H₂O, KNO₃ would absorb water, their weighing process was carried out in a glove box under argon atmosphere (H₂O < 10 ppm). The overall molar ratio of Pd(NO₃)₂: H₂SeO₄: KNO₃: H₂O is 1 : 11: 2.6 : 84. The vial containing the reaction mixture was transferred to a 20 mL PTFE-lined steel autoclave, put into an air circulation oven at room temperature, and heated at 200 °C for 2 d. The oven was then allowed to cool down naturally. Collected products were washed several times with methanol and water, then dried overnight in vacuum oven at 60 °C for 8 h, obtaining crystalline α-PdSeO₃ bulk material (50.3 mg, 0.216 mmol) of 64% yield. Plastic spatulas should be used instead of metal ones during the synthetic process.

2.3. Synthesis of β -PdSeO₃ bulk material

Solution 1 was made in glove box by mixing H_2SeO_3 (2.00 g, 15.4 mmol), H_2SeO_4 aqueous solution (1.00 mL, 3.86 mmol), and 3.0 mL H_2O (molar ratio: H_2SeO_3 : $H_2SeO_4 = 4.0$: 1); and stirred for 15 min. In a typical synthesis, $Pd(NO_3)_2 \cdot 2H_2O$ (100.0 mg, 0.375 mmol), KNO_3 (88.3 mg, 0.873 mmol), 0.25 mL solution 1 and deionized water (0.25 mL, 13.9 mmol) were added in a glass vial and stirred for 30 min. $Pd(NO_3)_2 \cdot 2H_2O$, KNO_3, and solution 1 were added in the glove box. Plastic spatulas should be used instead of metal ones during the synthetic process. The overall molar ratio of $Pd(NO_3)_2$: H_2SeO_3 : H_2SeO_4 : KNO_3: H_2O is 1 : 2.6: 0.64 : 2.3: 72. The vial was transferred to a 20-mL PTFE-lined steel autoclave, put into an air circulation oven at room temperature, and heated at 220 °C for 4 d. The oven was then allowed to cool down naturally. Other procedures are the same as that of the synthesis of α -PdSeO_3, obtaining crystalline β -PdSeO_3 bulk material (64.7 mg, 0.277 mmol) of 73.6% yield, which was used for preparation for β -PdSeO_3 NNs.

β-PdSeO₃ could also be prepared using only H₂SeO₃. Solution 2 was made in glove box by mixing H₂SeO₃ (1.00 g, 7.70 mmol) and 2.00 mL H₂O, and stirred for 15 min. In a typical synthesis, Pd(NO₃)₂·2H₂O (113.1 mg, 0.424 mmol), KNO₃ (88.6 mg, 0.877 mmol), 0.300 mL solution 2 and deionized water (0.400 mL, 22.2 mmol) were added in a glass vial and stirred for 30 min. Pd(NO₃)₂·2H₂O, KNO₃, and solution 2 were added in the glove box. The overall molar ratio of Pd(NO₃)₂: H₂SeO₃: KNO₃: H₂O is 1 : 2.7: 2.1 : 95. The vial was transferred to a 20mL PTFE-lined steel autoclave, put into an air circulation oven at room temperature, and heated at 200 °C for 4d. The oven was then allowed to cool down naturally. Other procedures are the same as that of the synthesis of α-PdSeO₃, obtaining crystalline β-PdSeO₃ bulk material (72.9 mg, 0.310 mmol) of 73.3% yield.

2.4. Synthesis of PdSeO₃ nanosheets (NNs)

The exfoliation NNs were prepared by a ultrasonic homogenizer (SCIENTZ-IID). These NNs were prepared according to a published method for the preparation of graphene [81]. Typically, a PdSeO₃ powder (20 mg) was dispersed in 40 mL isopropanol solvent. The mixture was placed in a centrifugation tube (50 mL). It was ultra-sonicated for 4s at 300 W, stopped for 2s, and continued for 1 h, the crusher was then shut off for 20–40 min; the above process was repeated 4 times at room temperature. Liquid supernatant was obtained after centrifuged at 3000 rpm for 5.0 min, followed by centrifuged at 12000 rpm for 20 min and removal of the supernatant. The NNs were collected after washing with water and ethanol several times, and then freezing dried, obtaining about 1.8 mg product.

2.5. Electrochemical characterization

All measurements in aqueous solution were carried out using threeelectrode systems with a saturated Ag/AgCl electrode as the reference electrode. Experiments for linear sweep voltammetry (LSV) in aqueous solution and photocurrent measurements were carried out using a Pt wire as the counter electrode and the working electrode is the PdSeO₃ modified ITO glass (sheet resistance 20–25 Ω /square). Electrochemical impedance spectroscopy (EIS) analyses were carried out using a graphite rod as the counter electrode, and sample modified glassy carbon as the working electrode. A 0.382 V amplitude AC signal over a frequency range from 100 kHz to 1 Hz were performed on an electrochemical workstation (CHI 760E). Photocurrent measurements were performed with a Zahner PEC workstation (Zahner, Germany). Detail procedures, Mott-Schottky plot measurements, LSV in nonaqueous solutions and methods of making modified electrodes are given in Supporting Information.

2.6. HER or OER measurements

All polarization curves were iR-corrected in this work unless noted

otherwise. Measurements were performed on an electrochemical workstation (CHI 760E, CH Instruments Inc., Shanghai) using a typical threeelectrode setup with an electrolyte solution of 0.5 M H₂SO₄, a platinum wire (OER) or a graphite rod (HER) as the counter electrode, an Ag/AgCl electrode (saturated KCl) as the reference electrode, and the modified glassy carbon electrode with the diameter of 3.0 mm (GCE, geometric area: 0.071 cm^2) as the working electrode in a N₂- (HER) or O₂- (OER) saturated solution. To prepare the working electrode, 2.5 mg of catalyst powders and 10 µL of Nafion D-520 dispersion were ultrasonically dispersed in 1.0 mL of a mixed water-alcohol (1: 1 v/v) solution to form a homogeneous ink. 8.0 µL aliquot of the catalyst ink was drop-cast onto the glassy carbon electrode in three portions (3.0, 3.0 and 2.0 μ L) for the electrochemical measurements. After each dropping, the electrode was dried in a 60 °C oven for 10 min. Before each experiment, we scanned each electrocatalyst by CVs in the range of -0.5-0 V (HER) or 1.0-1.5 V (OER) for 40 cycles at a rate of 0.1 V s⁻¹ for activity activation. The HER and OER activities of the catalysts were evaluated using LSV at a scan rate of 5 mV s⁻¹. HER and OER potentials were converted to the reversible hydrogen electrode (RHE) based on the following formula: $E_{RHE} = E_{Ag/}$ $_{AgCl} + 0.197 + 0.059 \text{ pH}.$

2.7. Photoelectrocatalytic (PEC) HER experiments

Experiments were carried out in an outer irradiation type photoreactor (50 mL quartz glass) in a N2 environment. Working electrode in a typical HER measurement was replaced with sample-modified ITO glass. The ITO glass (1.0 x 5.0 cm², only one side is conductive) are pretreated by ultrasonically washing with acetone, ethanol and water for 20 min, respectively. 2.83 mg catalyst was dispersed in a 1.0 mL aqueous solution containing 500 µL deionized water, 500 µL ethanol and 10 µL Nafion D-520 dispersion under ultra-sonication for 2.0 h under 400 W. Afterwards, 50 µL x 2 of the slurry was dropped onto the pretreated ITO electrode (the bottom 1.0 x 1.0 cm² area out of the 1.0 x 5.0 cm² and the rest area was pasted with insulating paper), and dried at 60 °C for 20 min after each dropping (twice in total). The irradiation light source used was a 300 W Xe lamp without light filter. The intensity of light reached the ITO electrode was kept as 100 mW·cm⁻² to simulate the full spectra of solar light. Before irradiation, the system was thoroughly degassed to remove air by bubbling N2 for 30 min.

3. Results and discussion

3.1. Syntheses

Syntheses of α-PdSeO₃ Ling and Albrecht-Schmitt first synthesized α -PdSeO₃ and obtained its structure based on single-cyrstal X-ray diffraction [66]. We made α -PdSeO₃ as shown in Fig. 1 based on their method with some modifications. We concentrated the selenic acid aqueous solution (40%) using an oil bath instead of a heating plate and the reaction time was reduced from 4 d to 2 d. Without concentrating the selenic acid aqueous solution, α -PdSeO₃ could not be obtained. If the heating period is too long (>40 min), some white precipitate would form when the concentrated solution was cooled down to room temperature. Addition of such slurry would result in PdSe₂O₅ [66] and other unidentified product (Fig. S1). While too short concentration time (<35 min) will lead to the appearance of β -PdSeO₃ [67] alongside α -PdSeO₃, suggesting that a higher water content favour the formation of β -PdSeO₃. Although it is reported that selenic acid decomposes above 200 °C according to eq. (1) [82], we made α -PdSeO₃ at 200 °C for 2 d. Thus, we propose that under prolonged heating, eq. (1) does occur, producing H₂SeO₃, which then react with Pd(NO₃)₂ to produce PdSeO₃ or PdSe₂O₅ (when H_2SeO_3 is in large excess) according to eq. (2) or (3).

$$2H_2SeO_4 \rightarrow 2H_2SeO_3 + O_2 \tag{1}$$

$$H_2SeO_3 + Pd(NO_3)_2 \rightarrow PdSeO_3 + 2HNO_3$$
(2)



Fig. 1. PXRD patterns of α and β -phase PdSeO₃ bulk materials and the exfoliated α and β -phase PdSeO₃ NNs compared to the simulated patterns based on the cif files of single-crystal structures.

$$2H_2SeO_3 + Pd(NO_3)_2 \rightarrow PdSe_2O_5 + 2HNO_3 + H_2O$$
(3)



Fig. 2. Morphology of α -PdSeO₃ and β -PdSeO₃. (a)–(b) SEM images of bulk α -PdSeO₃ (a) and bulk β -PdSeO₃ crystals (b), (c) and (e)TEM images of α -PdSeO₃ NNs (NNs), (d) and (f) TEM images of β -PdSeO₃ NNs.

3.2. Syntheses of β -PdSeO₃

Arndt and Wickleder synthesized β -PdSeO₃ by reacting palladium powder and 1 mL of H₂SeO₄ in a glass ampoule at 350 °C for 3 d followed by cooling down slowly at a rate of 3 °C/h. Here, we reported a much simpler method to prepare β -PdSeO₃. It was obtained using a mixture with the overall molar ratio of Pd(NO₃)₂: H₂SeO₄: H₂SeO₃: KNO₃: H₂O is 1 : 2.6: 0.64 : 2.3: 72 at 220 °C for 4 d. Its PXRD pattern are consistent with the simulated PXRD pattern based on the single-crystal structure, indicating pure bulk β -PdSeO₃ crystals have been obtained (Fig. 1). It can be synthesized using H₂SeO₃ alone (Table S1 No. 2 and Fig. S2(i)), can be synthesized at 180 °C with lower yield (Table S1 No. 13 and Fig. S2(o)), and can be obtained within 2 d (Table S1 No. 6 and Fig. S2(f)).

The effect of various factors on the synthesis of β -PdSeO₃ were investigated (Table S1 and Fig. S2). Without adding H₂SeO₃, no PdSeO₃ was synthesized. Adding KNO₃ is beneficial to increase the yield of PdSeO₃ (Table S1 No 3). Excess water would reduce crystallinity (Table S1 No. 4 versus No. 9, Fig. S2(c) versus Fig. S2(k)). Without adding KNO₃, pure β -PdSeO₃ can also be prepared (Table S1 and Fig. S2(b)).

3.3. Syntheses of PdSeO₃ NNs

Since Li et al. predict that the cleavage of α -PdSeO₃ is only 4.2 J/m², which is close to that of graphene (0.37 J/m²) [68]. The van der Waals interactions between layers in β -PdSeO₃ are similar to those in α -PdSeO₃ since the nearest atom-atom distances are similar (see the structure section). We therefore made α - and β -PdSeO₃ NNs following the method of making graphene [81]. SEM images (Fig. 2(a)-(b)) indicate that the bulk materials have layered structures. TEM images (Fig. 2(c)-2(f)) indicate that PdSeO₃ NNs were obtained. Several NNs overlapping with each other (darker places in Fig. 2(c)–(d)) and wrinkled sheets (Fig. 2(e)–(f) and Fig. S5) were also observed. The thickness of the bulk materials is greater than 1 μ m (Fig. 2(a)–(b)). The thickness of α -PdSeO₃ is about 15–20 nm; the thickness of β -PdSeO₃ is about 13 nm and some place can be as thin as 4 nm as shown in Fig. 3.

The energy-dispersive X-ray spectroscopy (EDX) elemental analyses of the bulk materials are given in Fig. S14, showing an expected Pd to Se ratio of 1:1.

3.4. Structures of α -PdSeO₃ and β -PdSeO₃

The single crystal X-ray structure of α -PdSeO₃ and β -PdSeO₃ have been reported [66,67]. They have layered structures as shown in Fig. 4. Although the atomic connectivities of these two phases are the same (Fig. 4(a) and (c)), the steric arrangements of atoms are different (Fig. 4(b) and (d)). Both structures contain planar [PdO₄] units. Pd–O distances are 2.008(2) and 2.021(2) Å in α-PdSeO₃, 2.014 and 2.012 Å in β -PdSeO₃. The O1–Pd–O2 are 88.96(7) and 85.14° in α - and β -PdSeO₃, respectively. Se-O1 and Se-O2 distances are 1.689(3) and 1.785(3) Å for α -PdSeO₃, 1.6911 and 1.7632 Å for β -PdSeO₃. The neutral layers are held together only by weak Van der Waals interactions with respect to the observed distances between the atoms of adjacent sheets (O-O distances of 2.929(3) Å (O–O), 3.008(3) Å (Se–O), and 3.9017(5) Å (Se–Se) for $\alpha\text{-PdSeO}_3\text{; }3.1390\text{-}3.1586$ Å (O–O), 3.1590 Å (Se–O), and 3.7021 Å(Se–Se) for β -PdSeO₃. The thicknesses of single layers of α -and β -PdSeO₃ are 5.1 and 5.5 Å, respectively; and the distances between the layers are less than 0.71 and 0.74 Å, respectively.

3.5. FT-Raman and FT-IR spectra of α -PdSeO₃ and β -PdSeO₃ materials

The FT-IR and FT-Raman spectra of bulk and NNs of α - and β -PdSeO₃ were obtained and are shown in Fig. 5. The IR spectra of the NNs are consistent with those of the bulk materials. The IR spectra shows that the samples contain adsorbed water and methanol. The adsorbed methanol has higher vibrational frequencies than those of gas phase methanol (Fig. 5(I)). Methanol does not give IR bands in the <800 cm⁻¹ region. The



Fig. 3. AFM images and the corresponding thickness (b) (d) of α -PdSeO₃ ((a)-(b)) and β -PdSeO₃ ((c)-(d) NNs.

IR and Raman bands of α - and β -PdSeO₃ are summarized in Table 1 and their assignments are straightforward by comparison with literature data. α - and β -PdSeO₃ consists of planar PdO₄, Pd–O–Se, and SeO₃ units. The bands due to PdO₄ were assigned by comparison with compounds containing also PdO₄ units [83–87]. In the PdO structure, the Pd atoms are planar coordinated with four O atoms, while O atoms are tetrahedral-coordinated with four Pd [86]. Pd–O bond length in PdO is 2.01 Å [87], which is slightly shorter than the P–O bond lengths in α - and β -PdSeO₃ (2.008-2.021 Å). McBride et al. assigned the Raman bands of PdO [86]. G. Kliche obtained and assigned the IR spectrum of PdO [83]. The sharp band observed at 652 cm⁻¹ in the Raman spectrum of PdO is assigned to the B1g stretching mode. Baran et al. obtained the IR spectrum of a PdO₄ unit containing compound Nd₂BaPdO₅ [84]. They observed the antisymmetric stretchings of the PdO₄ unit at 645 and 622 (vs).

The symmetry of the selenite ion is similar to that of sulfite, which is tetrahedral with one vacant orbital, thus giving C_{3V} symmetry. The selenite ion SeO₃²⁻ thus has four fundamentals: the ν_1 symmetric stretching vibration (approximately 790–806 or 760–855 cm⁻¹); the ν_2 symmetric bending vibration (approximately $430-461 \text{ cm}^{-1}$); the doubly degenerate ν_3 antisymmetric stretching vibration (approximately 714–769 or 680–775 cm⁻¹); the ν_4 doubly degenerate antisymmetric bending vibration (approximately 387-418 cm⁻¹). All vibrations are Raman and infrared active [88]. The symmetry of the SeO_3^{2-} ions is remarkably lower in PdSeO3 than in the free anions. Thus, the bands would not be degenerate and would split. We assigned the bands due to SeO_3^{2-} (Table 1) by comparing the spectra and assignments of similar selenite compounds, e.g. Pb₂Cu₅(UO₂)₂ (SeO₃)₆(OH)₆·2H₂O [88] (Se–O: 1.68-1.73 A) [89], Er2(SeO3)3 and Dy3(SeO3)4F (Se-O: 1.65-1.68 and 1.70-1.72 Å) [90] and others [91,92]. The Se–O distances in α - and β -PdSeO₃ are 1.69, 1.76 (β) and 1.79 (α) Å.

Since Se–O–Se symmetric stretching vibration were found at 540-577 cm⁻¹ in Se₂O₅^{2–} salts [92] and Pd has higher mass than Se, we assigned the peak at 510-521 cm⁻¹ to the symmetric stretching of Pd–O–Se unit.

3.6. XPS of α -PdSeO₃ and β -PdSeO₃ bulk materials

To verify the surface elemental composition and elemental oxidation

state of $\alpha\text{-}$ and $\beta\text{-PdSeO}_3$ bulk materials, X-ray photoelectron spectroscopy (XPS) spectra were obtained as shown in Fig. 6. C1s (248.1 eV) is used as a benchmark to calibrate the position of all element peaks. The high-resolution Pd 3d spectrum of α -PdSeO₃ shows that Pd 3d_{3/2} and Pd 3d_{5/2} bands are at 343.0 and 337.6 eV (Fig. 6(b)), respectively, which can be assigned to the Pd²⁺ state and nearly the same as those reported by Zhang et al. (343.1 and 337.7) [69] and those of β -PdSeO₃ (Fig. 6(b)). The bands associated with the Se $3d_{3/2}$ and Se $3d_{5/2}$ bands are at 59.9 and 58.4 eV (Fig. 6(c)), respectively, and are assigned to the Se⁴⁺ state, which disagree with the assignments of Zhang et al. [69] They assigned the broad peak at about 59 eV to only Se $3d_{5/2}$. Since Se⁰ $3d_{3/2}$ and $3d_{5/2}$ bands appears at 56.5 and 55.6 [93], we think the Se $3d_{3/2}$ in PdSeO₃ should appear at a position close to that of Se $3d_{5/2}$. And we successfully simulated the broad peak into two bands with an area ratio of 2:3 to be Se $3d_{3/2}$ and $3d_{5/2}$, respectively. The Se $3d_{3/2}$ and $3d_{5/2}$ band positions in β -PdSeO₃ are similar to those of α -PdSeO₃ (60.0 and 59.2 eV, respectively). The crystal structures show that both PdSeO₃ have two kinds of O, one is three-coordinated (O_a) and one is two-coordinated (O_b) and their molar ratio is 1:2. We successfully simulated the O1s spectra to three peaks, fixing the peak area ratio of O_a and O_b to be 1:2, the other peak is due to adsorbed water molecules. XPS spectra shows that α -PdSeO₃ adsorbed more water than that by β -PdSeO₃, consistent with the IR spectra shown in Fig. 5. The bands of O_a1s , O_b1s of α - and β -PdSeO₃ and O1s in H₂O and methanol bands appear at 534.6, 534.7 (α-PdSeO₃); 530.5 and 530.8 (β-PdSeO₃); and 532.5 and 532.7 (H₂O and methanol) eV. In summary, the XPS spectra indicate that the composition of the surfaces of α - and β -PdSeO₃ are consistent with the bulk materials.

3.7. Stability of α - and β -PdSeO₃ bulk materials

α- and β-PdSeO₃ bulk materials are stable in pH = 0–14 aqueous solutions for at least 48 h (Fig. 7). The IR spectra of selected samples after immersing in acidic or basic aqueous solutions for 48 h were also taken (Fig. S13), and shows the same patterns as those of as-synthesized samples, again indicating the high stability of PdSeO₃ materials. The thermogravimetric (TG) and the differential thermal analyses (DTA) were carried out with these materials (Fig. S3). Bulk α-PdSeO₃ bulk material



Fig. 4. Structures of α -PdSeO₃ ((a)–(b)) and β -PdSeO₃ ((c)–(d). Viewing along *a* and *b* axes and the structures of one layer ((b) and (d)). Unit cell edges are shown.

decomposes at 416 °C, and bulk β -PdSeO₃ bulk material decomposes drastically at 464 °C. Thus, β -PdSeO₃ bulk material was found to be more stable than α -PdSeO₃ bulk materials. β -PdSeO₃ bulk material was also found to be stable at 310 °C for at least 12h as indicated by PXRD results shown in Fgi. S4. Both materials decompose to PdO as indicated by PXRD pattern (Fig. S4). The weight loss after decomposition also fit very well as expected according to eq. (4). The theoretical weights of PdO left are 52.1% for α - and β -PdSeO₃, respectively, consistent with the observed weights in TG/DTA curves (52.9 and 52.0%, respectively) as shown in Fig. S3. When using 13.033 mg sample, the obtained TG curve of β -PdSeO₃ (Fig. S3b) are flat before the decomposition temperature, and gave excellent fit with the theoretical weight percentage of PdO. When measuring its TG curve with <5 mg sample, the TG curve gradually went



Fig. 5. FT-IR and Raman spectra of α - and β -phase $PdSeO_3$ bulk and NNs materials in the range of 3600-50 cm $^{-1}$ (I) and 1000-100 cm $^{-1}$ (II). IR spectra of gas phase methanol and net water were obtained from https://webbook.nist.gov/chemistry/.

Table 1

IR and Raman bands of $\alpha\text{-}$ and $\beta\text{-}PdSeO_3$ and tentative assignments. ^

α- PdSeO ₃		β-PdSeO ₃						
IR	Raman	IR	Raman	Assign.				
806 m 728 s,br 672 vw	780 s	874 vw 828 m 745 s, br	794 w	$\nu_1(\text{SeO}_3^{})$ symmetric stretching $\nu_1(\text{SeO}_3^{})$ symmetric stretching $\nu_3(\text{SeO}_3^{})$ antisymmetric stretching				
620 s 589 m 568 w 436 w	637 m 607 m 578 m 521 s 417 s 283 s 211 w	638 s, br 531 m	636 m 620 m 510 s 405 w,br 312 w 281 m	PdO ₄ stretching mode PdO ₄ stretching mode PdO ₄ stretching mode Pd–O–Se symmetric stretching $\nu_2(\text{SeO}_3^2)$ symmetric bending $\nu_1(\text{SeO}_3^{2-})$ antisymmetric bending				
	176 m 141 s		202 s 128 w 95 m	A ₁ vibrational mode of of PdO ₄ [87]				

 $^{a}\,\,s=$ strong, m= medium, br= broad, w= weak, vw= very weak.

down even before decomposition temperature as also observed with α -PdSeO₃ (Fig. S3(a), 4.183 mg). Thus, if a TG curve gradually goes down, the sample might not be decomposing. Such phenomena are



Fig. 6. (a) Full spectrum survey and (b-d) high resolution XPS spectra of PdSeO₃ bulk materials.



Fig. 7. PXRD patterns of as-synthesized α - and β -PdSeO₃ bulk materials, and the patterns after immersed in pH = 0 and pH = 14 aqueous solutions for 48 h.

simply caused by instrumental factors, which can be detected by using large amounts of sample (13 mg in our case).

$$PdSeO_3 \rightarrow PdO + SeO_2$$
 (4)

3.8. UV–Vis diffuse reflectance spectra of bulk α - and β -PdSeO₃ materials

The ultraviolet–visible (UV–vis) diffuse reflectance spectra of α - and β -PdSeO₃ bulk materials in the form of absorbance are given in Fig. 8. Their adsorption of light is strong and nearly constant in the range of 250–500 nm and gradually decreases when the wavelength increases to



Fig. 8. UV–Vis absorption spectra of the α and β -phase PdSeO₃ bulk materials.

greater than 500 nm in the range of 500–800 nm. If they are direct bandgap semiconductor, the bandgaps of α - and β -PdSeO₃ bulk materials would be 2.05 and 2.11 eV, respectively, determined by plots of $(\alpha hv)^2$ vs hv where α is the absorbance of the light, and hv is the light energy derived based on the wavelength of the light (Fig. S8); if they are indirect band-gap semiconductors, the bandgaps would be 1.40 and 1.35 eV, respectively, determined by plots of $(\alpha hv)^{1/2}$ vs hv based on UV–vis reflectance spectra (Fig. S8) [94,95]. They are found to be direct band-gap semiconductors based on electrochemical studies (see below).

3.9. Determination of band-edge positions

The conduction band minimum (CBM) (LUMO) and valence band maximum (VBM) (HOMO) positions of materials were also determined by an EC method, the linear potential scan method [94,96–99]. In this method, the potential corresponding to the first onset oxidation current and the potential corresponding to the first onset potential of reduction

current can be observed by separate cathodic and anodic scans, respectively; and are regarded as the energy levels of the HOMO (CBM) and LUMO (VBM) of the material, respectively. The band gap (E_g) is the difference between the two on-set potentials. In our study, the linear potential scans were also carried out using ITO working electrodes without modifying with samples under the same condition as background curves to compare with those scans using the sample modified electrodes.

The CBM and VBM of α - and β -PdSeO₃ bulk materials and NNs were measured in pH = 0, 2, $4H_2SO_4$ aqueous solutions, and the results are given in Table 2 (also in Fig. 9 and Fig. S6). The band-edge positions remain constant in the pH range of 0–4. The CBM and VBM of α - and β-PdSeO₃ bulk materials were also measured in 0.2 M Na₂SO₄ aqueous solution as described by Wang et al. [97] and in non-aqueous solutions $(0.10 \text{ M Bu}_4\text{NPF}_6 \text{ in acetonitrile})$ according to the literature [100,101]; and the results are given in Table 2 and Fig. S7. However, in neutral 0.2 M Na₂SO₄ solution and non-aqueous solution the conduction band maximum was found to be considerably lower (-0.6- -0.7 eV) than the values obtained in the acidic aqueous solution (-0.08- 0.05 eV). The band gaps of α - and β -PdSeO₃ NNs were much greater than those of bulk materials, consistent with observations on other layered materials [102]. The CBMs of NNs have higher energies than those of bulk materials, while VBMs of NNs have lower energies than those of bulk materials. Li et al. reported that when the number of layers increase, the CBM values of α -PdSeO₃ increases [68], which is consistent with the above experimental results. The band-gap values determined by LSV method of α - and β-PdSeO3 bulk materials are consistent with the values determined based on UV-Vis reflectance spectra assuming they are direct band-gap semiconductors, but not with the values obtained (1.35-1.40 eV) assuming they are indirect band-gap semiconductors (Fig. S8). Thus, the experimental values suggest that both α - and β -PdSeO₃ bulk materials are direct band-gap materials.

Mott–Schottky plots of α - and β -PdSeO₃ bulk materials are obtained in 0.2 Na₂SO₄ aqueous solution as shown in Fig. 10. The negative slope of the C⁻² versus potential E indicate that they are n-type semiconductor [103]. By extrapolating the linear part of the Mott-Schottky plots to the X axis, the flat band potentials of α - and β -PdSeO₃ bulk materials were found to be -0.77 and -0.80 V versus.

Ag/AgCl. It is known that the conduction band potentials (E_{CB}) for ntype semiconductor is more negative about 0.1–0.3 eV than its flat band potential [104,105]. Thus, their E_{CB} were estimated as -0.9 V (vs NHE) using this method. Based on E_{VB} = E_{CB} + E_g and the E_g values obtained from the UV–Vis reflectance spectra (2.05 and 2.11 eV) (see above), the EVB values of α - and β -PdSeO₃ bulk materials were calculated to be 1.2 V (vs NHE). These values are consistent with values obtained from LSV carried out in 0.2 M Na₂SO₄ solution and non-aqueous solution. However, this likely is not the true values for their band-edge positions (see discussions in *Why the values of CBM and VBM determined by LSV are different when using different electrolyte*? section).

3.10. Why the values of CBM and VBM determined by LSV are different when using different electrolyte?

The VBM and CBM of α-PdSeO3 NNs were determined as -0.71 and 1.98 eV, thus the bandgap is 2.69 eV, which is very close to the value determined using the ultraviolet-visible (UV-Vis) absorption spectrum of the exfoliated PdSeO3 NNs obtained by Liu and Zhang et al. [69]. This is also close to the value predicted for the PdSeO3 monolaver at 2.84 eV [68]. Liu and Zhang et al. [69] determined the CBM and VBM and Fermi Level at -3.99, -6.65 and (-6.65 + 1.93) eV with respect to vacuum. Since the NHE is -4.44 eV with respect to vacuum [68], these values are -0.45, 2.21 and 0.28 eV, respectively with respect to NHE. When we carried out the LSV experiments to determine the band-edge positions, sample-modified ITO electrodes were applied as the working electrode using three electrode system. It is helpful to draw energy level digrams to understand LSV results. The E_F (ITO) equals +0.40 V vs NHE [106,107]. The work function of ITO is -4.59 eV vs vacuum [108], thus its CBM is +0.19 vs NHE [109]. The band gap of ITO is in a range of 3.5–4.3, thus its VBM is in a range of 3.7–4.5 V vs NHE. Based on the above information, the important energy levels for a pH = 0 aqueous solution/PdSeO₃/ITO working electrode system were presented in Fig. 11.

Both ITO and PdSeO₃ are n-type semiconductors and they form a stepscheme heterojunctions [110]. Since the Fermi level of α-PdSeO₃ NNs is higher than that of ITO, when they are in contact, the electrons in α -PdSeO₃ NNs transfers to ITO across their interface until their Fermi levels are the same (Fig. 11(b)), resulting in band bending and internal electric field [110]. When a LSV experiment of negative scan is carried out, a negative bias potential ($-\Delta \varphi$) is applied to ITO, the *E*_F of ITO would raise, the band-bending would decrease as shown in Fig. 11(c), the electrons can flow from ITO to α -PdSeO₃ NNs to form a current [111]. However, to form a continuous current also requires that the crossover electrons can reduce a species (e.g. H⁺) in the electrolyte. At the beginning, the energy of electrons on ITO is still too low to do the reduction as shown in Fig. 11(c) and no current flow can be observed [112]. To form a current, a species in the electrolyte should be oxidized on the surface of the counter electrode. This is usually not a problem since the counter electrode in a three electrode system will often swing to extreme potentials at the edges of the solvent window, where it oxidizes or reduces the solvent or supporting electrolyte [113]. When the bias potential continuously reaches to more negative potential, the bands of ITO and α -PdSeO₃ NNs would become flat, and then bend to the reversed directions [103]. When the E_F of ITO becomes higher than the CBM of α-PdSeO₃ NNs, electrons would transfer from ITO to the conduction bands (CBs) of PdSeO₃, and then to reduce H⁺ in the solution to form current. Thus, the on-set potential of this current would be the CBM of the PdSeO_{3.} For other cases, if there is lacking of a readily reducible species in the electrolyte, the current would not form immediately, the value would be measured higher than its real values. Thus, our reasoning suggest that CBM values measured in neutral or non-aqueous solution for

Table 2

Theoretical and experimental determined band gaps (E_g in eV) and band positions (eV).

	pH	0		2		4		Na ₂ SO ₄ aq. ^a		Non-aqueous ^b		UV–Vis ^c
		NHE ^d (eV)	BG (eV)	NHE (eV)	BG (eV)	NHE (eV)	BG (eV)	NHE (eV)	BG (eV)	NHE (eV)	BG (eV)	BG (eV)
α bulk	CBM	-0.09	1.83	-0.03	1.82	-0.03	1.83	-0.68	2.47	-0.77	2.36	2.05
	VBM	1.74		1.79		1.80		1.79		1.59		
β bulk	CBM	-0.10	-	-0.09	1.90	-0.10	1.94	-0.60	2.38	-0.58	2.12	2.11
	VBM	-		1.83		1.86		1.78		1.54		
A NNs	CBM	-0.72	2.74	-0.71	2.67	-0.71	2.61					
	VBM	2.02		1.96		1.95						
B NNs	CBM	-0.73	2.74	-0.73	2.60	-0.73	2.64					
	VBM	2.01		1.87		1.91						

^a 0.2 M Na₂SO₄ was used as electrolyte.

^b using an Ag/Ag^+ (0.01 M $AgNO_{3}$, 0.09 M Bu_4NPF_6 in acetonitrile) electrode as the reference electrode, 0.10 M acetonitrile solution of Bu_4NPF_6 as electrolyte. c. Derived based on UV–Vis diffuse reflectance spectra (Fig. S8) assuming to be direct-band semiconductors. d Potentials obtained versus Ag/AgCl and Ag/Ag + electrode (nonaqeous) were added 0.197 and 0.54 V [101], respectively. e.Single layer as reported in Ref. [68].



Fig. 9. Cathodic and anodic linear potential scans for searching the positions of the CB and VB edges of α and β -PdSeO₃ bulk materials as well as NNs at pH = 0 ((a)–(b)); β -PdSeO₃ bulk material in 0.2 M Na₂SO₄ aqueous solution ((c)–(d)).



Fig. 10. Mott-Schottcky plots of (a) $\alpha\text{-PdSeO}_3$ and (b) $\beta\text{-PdSeO}_3$ bulk materials in 0.2 M Na_2SO_4 aqueous solution.

 $PdSeO_3$ bulk materials are quite negative, which might likely be due to the very low concentration of H^+ . Thus, using a high concentration acidic solution would be beneficial to avoid such situations.

Similarly, if a LSV scan of positive bias potential is carried out, the E_F of ITO would decrease, however, this would not result in current flow from α -PdSeO₃ NNs to ITO since the E_F of α -PdSeO₃ NNs is still higher than the oxidation potential of water (Fig. 11(c)). When the E_F of ITO would continuously decrease to an energy level below the VBM of α -PdSeO₃ NNs, the electrons would flow from the valence bands (VBs) of to the ITO, and H₂O would transfer electron to the VBs of α-PdSeO₃ NNs. In some other cases, if there is lacking of a readily oxidizable species in the electrolytes, current would not form until the VBM of α-PdSeO₃ NNs were also brought to a much lower energy level during the scan, so that the species in the electrolyte can be oxidized. This would result in higher VBM values than its true value. The E_F of the sample would always try to reach equilibrium with the ITO electrode. Thus, it would decrease as the E_F of ITO decreases. To reduce the phenomenon (since this will change the band-edge values), a fast scan rate would help. Moreover, if the interested area on the ITO surface is not completely covered with the sample or some of ITO surface was exposed to the solution, when the CBM of ITO is below 1.23 V, not 2.21. H₂O would transfer electron to the CBM of ITO to form current, and one would thought it is due to VBs of the sample, and obtained a CBM value much smaller than its true value. Thus electrode preparation need to be meticulous and no immersion of ITO parts should be in the electrolyte.

The above analysis suggests that values obtained in neutral Na_2SO_4 solution and non-aqueous solution may not be reliable, and to do such experiments, a readily reducible (for CBM measurements) or oxidizable species (for VBM measurements) might need to be added into the electrolyte. How to accurately measure the CBM and VBM of a semiconductor material using LSV is still need further investigations.

3.11. Photoelectric responses

The photoelectrical properties of the exfoliated α - and β -PdSeO₃ NNs and bulk materials were studied using a three-electrode setup under 365 nm and 470 nm light illumination at -0.5, -0.1, -0.25, 0.1, 0.25 and 0.5 V. Photocurrents were observed only when applying 0.5 V bias potential versus Ag/AgCl (saturated KCl) as shown in Fig. 12. Under illumination, the photocurrent increases with anodic potential as commonly observed



Fig. 11. (a) The energy levels of ITO and α -PdSeO₃ NNs before contact. (b) The band-edge bending at the interface after contact. The CBM and VBM values determined by Liu and Zhang et al. was used [69].

in a n-type semiconductor [114–117]. Thus, α - and β -PdSeO₃ were found to be n-type semiconductors. This is consistent with the negative slopes of the Mott-Schottky plots of these materials (Fig. 10), which also suggests that they are n-type semiconductors.

The photocurrent density increases upon irradiation at shorter wavelength (365 nm) for all materials except for α -PdSeO₃ bulk material (36–57 nA/cm²), indicating that the photogenerated electrons and holes usually combine faster when applying longer wavelength. This observation was also reported by others [114,118,119]. The photocurrent response was stable over the course of the experiment, meaning the sensitization process was regenerative/photocatalytic and not



Fig. 12. Photocurrent density–time curves for the exfoliated α - and β -PdSeO₃ NNs (a) and α and β -PdSeO₃ bulk materials (b) in a solution of 0.1 M Tris-HCl (pH = 7.4) with λ = 365 and 470 nm light at a bias voltage of 0.5 V versus Ag/AgCl (saturated KCl).

stoichiometric [119]. The current could not last for the entire light illumination time when a longer wavelength or bulk materials were applied, suggesting that the charge recombination rates were even greater than the rate of charge generation through light excitation in these cases.

The photocurrent (105 and 410 nA cm⁻²) generated using α - and β -PdSeO₃ NNs are significantly greater than those (36 and 202 nA/cm²) using of bulk materials under 365 nm light illumination. However, the photocurrent (26 nA cm⁻²) generated using α -PdSeO₃ NNs are smaller to that (36 nA/cm²) of α -PdSeO₃ bulk material under 470 nm light illumination. When the layer is thin, the light absorption would be poorer than the thicker material, such less electron and holes were generated in the α -PdSeO₃ NNs than those generated in the α -PdSeO₃ bulk material. Photocurrents of β -PdSeO₃ materials are greater than those of α -PdSeO₃ at 365 nm light irradiation except for the current generated under 470 nm light irradiation (same or smaller). This is consistent with the fact that

 β -PdSeO₃ bulk material absorbs more light than α -PdSeO₃ bulk material in the range of 250–550 nm as shown in Fig. 8 β -PdSeO₃ bulk materials did not show current at 470 nm illumination is due to its rather poor conductivity as shown in Fig. 13, which results in the localization of the light generated electrons and holes, leading to fast charge recombination.

However, the photogenerated electrons and holes in its NNs could go to surroundings to produce current. In contrast, the conductivity of α -PdSeO₃ bulk material is good enough to produce current.

3.12. Electrocatalytic hydrogen evolution

To measure the electrocatalytic activity of the NNs and bulk of α - and β -PdSeO₃ toward water splitting, the synthesized samples were drop-cast onto glassy carbon electrodes. The electrocatalytic HER performance of the NNs and bulk of α - and β -PdSeO₃ in acidic solutions were then tested using a standard three-electrode system. The NNs samples are found to be more active than the bulk materials, and α -PdSeO₃ is more active than β -PdSeO₃ (Fig. 13(a)). α -PdSeO₃ NNS shows the highest catalytic activity among all catalysts ($\eta_{10} = 185 \text{ mV}$), followed by the 209 mV of β -PdSeO₃. The α - and β -PdSeO₃ bulk materials have overpotentials of 283 and 477 mV at 10 mAcm⁻², respectively. The commercial Pt/C (20 wt%) gave a η_{10} of 24 mV and a Tafel slope of 29 mV·dec⁻¹ obtained under the same experimental conditions, which are consistent with the reported values (30 mV·dec⁻¹) [120,121]. We did this experiment to show that our experimental method is valid as we produced the literature result.

The above results are consistent with the Electrochemical impedance spectroscopy (EIS) results of these materials (Fig. 13(e)). The semicircle of NNs display a much smaller arc radius compared to the bulk materials, substantiating that the 2D structure of PdSeO₃ NNs can markedly promote the charge transfer through the solid/liquid interfaces. The α -PdSeO₃ NNs generate the smallest semicircle radius, thus achieving the lowest charge transfer resistance among all the samples. Thus, it may have the most efficient charge transport during the electrochemical HER process. Without iR drop compensation, η_{10} values are only slightly higher (less than 8 mV as shown in Fig. S9).

To understand the electrocatalytic HER kinetics, the Tafel slope was determined by fitting the linear regions of Tafel plots to the Tafel equation: $\eta = b \log j + a$, where η is the overpotential, j is the current density, and b is the Tafel slope. The Tafel slope (b) designates the potential difference necessary to increase or decrease the current density by 10fold, which indicates the mechanism of the HER process [122]. A smaller Tafel slope usually indicates that current density can increase faster with smaller overpotential change (i.e., faster reaction rate constant), which implies good electrocatalytic kinetics [123,124]. As shown in (Fig. 13(b)), the Tafel slope of α -PdSeO₃ NNs shows a Tafel slope of 88 mV dec⁻¹, this value is significantly smaller than those of β NNs (103 mV dec⁻¹), α bulk (108 mV dec⁻¹) and β bulk (172 mV dec⁻¹), highlighting the faster reaction kinetics of the α NNs. After 1000 cycle testing, the overpotential of α -PdSeO₃ NNs only increased 9 mV (Fig. 13(c)). As shown in Fig. 13(d), α -PdSeO₃ NNs can yield a stable overpotential at 10 mA cm⁻² for at least 6 h in 0.5 M H₂SO₄ solution, indicating the good long-term operating stability.

The Tafel plot slope of PdSeO₃ materials are much greater than the 29 and 39 mV·dec⁻¹, which are for the chemical-desorption (Tafel reaction as shown eq. (3)) rate limiting and the electrochemical-desorption (Heyrovsky reaction as shown in eq. (2)) rate limiting HER processes, respectively. If the rate limiting step is the first step-the hydrogen adsorption step (the Volmer reaction (eq. (1)), the Tafel slope would be about 120 mV dec⁻¹ [122,125]. The distinct HER Tafel slopes of these PdSeO₃ materials suggest their different HER kinetics and intrinsic catalytic activities [15,126].

$$H_3O^+ + M + e^- \rightleftharpoons M - H^* + H_2O$$
 (5)

$$\mathbf{H}^{+} + \mathbf{e}^{-} + \mathbf{M} - \mathbf{H}^{*} \rightleftharpoons \mathbf{H}_{2} + \mathbf{M}$$

$$\tag{6}$$

$$2\mathbf{M} - \mathbf{H}^* \rightleftharpoons \mathbf{H}_2 + 2\mathbf{M} \tag{7}$$

Where H* is the adsorbed hydrogen atom and M is the electrode material surface.

The performances of α - and β -PdSeO₃ NNs in acid media indicate that they are not the best HER electrocatalysts and their catalytic activities are moderate [122,125,127–130]. The performance of α -PdSeO₃ NNs ($\eta_{10} = 185 \text{ mV}$, Tafel slope = 88 mV dec⁻¹) are similar to that of a MoS₂/ultrathin graphene heterostructure ($\eta_{10} = 180 \text{ mV}$, Tafel slope = 79 mV dec⁻¹) made by Zhao, Lyu and Zhang et al. [131].

Most Pd-based HER electrocatalysts are Pd alloys or composites of Pd metal and other materials [71–73,126,132]. Few reports are on other Pd containing materials. In acidic media (0.5 M H₂SO₄), PdP₂@CB (carbon black) gave an η_{10} of 27.5 mV and a Tafel slope of 29.5 mV·dec⁻¹, which is an outstanding performance [133]; Pd₃P₂S₈ gave an η_{10} of 175 mV and a Tafel slope of 123 mV·dec⁻¹ with long-term stability [65]; Li–Pd₃P₂S₈ gave an η_{10} of 91 mV and a Tafel slope of 29 mv·dec⁻¹ [65], while palladium black gave an η_{10} of 92 mV and a Tafel slope of 107 mV·dec⁻¹ [65].

The HER performance of α -PdSeO₃ NNs in 1.0 M KOH and 1.0 M PBS (pH = 7.0) (Fig. S11) were also tested, showing overpotentials of 0.591 and 0.682 V, indicating it is poor HER electrocatalyst in alkaline [134, 135] and neutral solutions [136,137].

3.13. Photoelectrocatalytic hydrogen evolution reaction

Photoelectocatalytic HER experiments were carried out by replacing the glass carbon working electrode with a sample-modified ITO glass. The current density became much lower, and overpotentials were much higher than those obtained when using glassy carbon electrode. Upon light irradiation (Xe lamp, full spectra, 100 mW cm⁻²), the overpotential of α -PdSeO₃ NNs at 1.0 mA cm⁻² reduced significantly (from 212 mV to 13.6 mV) in contrast to a much smaller reduction using β -PdSeO₃ NNs (61–26 mV) (Fig. 14). These results consistent with the better conductivity of α -PdSeO₃ NNs which would facilitate the charge separation (Fig. 13). Without iR drop compensation, the overpotentials at 2 mA cm⁻² are only slightly higher (less than 6 mV) as shown in Fig. S10.

3.14. Electrocatalytic oxygen evolution reactions

The four PdSeO₃ materials were tested for OER electrocatalytic properties in acidic, neutral and basic solutions and the results are given in Fig. 15 and Fig. S12. α -PdSeO₃ bulk and NNs materials gave overpotentials over 1.0 V in all pH condition, which are poor performance. However, β -PdSeO₃ bulk and NNs materials gave overpotentials of 381 mV and 405 mV at 10 mA cm⁻², respectively; Tafel slopes of 342 and 369 mV·dec⁻¹, respectively in 0.5 M H₂SO₄ solution; stability at least for 6 h, which are good performances considering the high pH value and low catalyst-loading (0.28 mg cm⁻²). Surprisingly, the β -PdSeO₃ bulk materials outperformed the β -PdSeO₃ NNs. Under light irradiation using Xe lamp and light intensity of 100 mW·cm⁻² did not improve the performances (Fig. 15(a)–(b)), which is probably again due to their poor conductivities (see above).

The Tafel behavior, especially the Tafel-slope, is an important kinetic parameter to reveal changes in the apparent OER mechanism [138]. The value of the Tafel slope usually ranges from 30 to 120 mV dec⁻¹ and can help to determine whether the slowest step of the reaction is from the first or second electron transfer or the recombination step. In our case, much higher Tafel slope values are observed, indicating additional contributions related to the oxide-surface processes, which might be a potential drop in the anode charge layer, or a blockage of the electrode surface by the bubble accumulations [139–143]. The high Tafel slope values, 200–500 mV dec⁻¹, were also reported in literature [80,143].

Water oxidation catalysts (WOCs) are essential to electrochemical hydrogen production, but (electro)chemical instability remains a critical



Fig. 13. (a) iR compensated polarization curves obtained in 0.5 M H_2SO_4 solution at a scan rate of 5 mV s⁻¹ (b) Corresponding tafel slopes of α - and β -PdSeO₃ bulk materials and NNs. (c) Polarization curves of α -PdSeO₃ NNs before and after 1000 cycles. (d) Chronoamperometric test of α -PdSeO₃ NNs at 10 mA cm⁻² for 6h. (e)The EIS Nyquist plots for α - and β -PdSeO₃ bulk materials and NNs.



Fig. 14. iR-compensated J–V curves of α and β -phase PdSeO₃ NNs measured with or without light illumination of 100 mW/cm² in a solution of 0.5 M H₂SO₄.

issue for WOCs especially under acidic conditions [123,144,145]. In principle, water electrolysis in acidic media has several advantages over that in alkaline media, including favorable reaction kinetics, easy product separation, and low operating pressure [19]. However, acidic water electrolysis poses higher requirements for the catalysts, especially the ones for the oxygen evolution reaction. It is a grand challenge to develop highly active, durable, and cost-effective catalysts for acidic water oxidation [19]. The state-of-the-art catalysts for OER in acidic media are usually iridium-based metal or metal oxides [17-19,77,146]. To our knowledge, the best OER electrocatalyts in acidic solution in terms of overpotential and Tafel slope are a Mn-doped RuO2 prepared by Wang and Chen et al. ($\eta_{10} = 158 \text{ mV}$, Tafel slope = 43 mV·dec⁻¹ in 0.5 M H₂SO₄ solution) [147]. The best Pd-based acidic water oxidation electrocatalysts are $Ir_{44}Pd_{10}$ prepared by Xia et al. [148] ($\eta_{10} = 226$ mV, Tafel slope = 54-69 mV·dec⁻¹ in 0.1 M HClO₄ solution) and Pd-Ru nanoparticles prepared by Tilley et al. [149] ($\eta_{10} = 225 \text{ mV}$, Tafel slope = 61 mV·dec⁻¹ in 0.1 M HClO₄ solution). Besides Pd-metal-based acidic water oxidation electrocatalyst, few Pd compounds were reported as acidic water oxidation electrocatalyst. A strontium Palladium Perovskite

Sr₂PdO₃ gave a $\eta_{10} = 450-550$ mV, Tafel slope = 454 mV·dec⁻¹ in 0.1 M HClO₄ solution [80], which is less active than β -PdSeO₃.

4. Conclusions

The syntheses of 2D α - and β -PdSeO₃ bulk materials were greatly improved. They are found to be n-type direct band-gap semiconductors. Their transient photocurrent experiments suggest that they only weakly respond to light irradiation. Their photocurrent intensities depend on the conductivities and light absorbance properties of the materials. Stronger conductivity and light absorbance would increase the photocurrent. In addition, short wave-number light would produce stronger photocurrent, which might be due to higher mobility of the photo-generated charges produced by such light so that the charge recombination would be supressed. The band-gaps, valence band maximums (VBMs) and conduction band minimums (CBMs) of α - and β -PdSeO₃ bulk and NNs were determined using Mott-Schottky plots and the linear potential scan method in acidic solution, 0.2 M Na₂SO₄ and non-aqueous solution. We found the electrolyte would affect the results. Although using LSV method to determine CBM and VBM has been widely applied, our finding indicate that how to reliably determine the CBM and VBM positons using LSV method still need to be investigated.

α- and β-PdSeO₃ NNs exhibit moderate catalytic activities for hydrogen evolution reactions in 0.5 M H₂SO₄, much better than the bulk materials; and α-PdSeO₃ NNs have better performance than that of β-PdSeO₃ NNs. In addition, β-PdSeO₃ NNs and bulk material show good and similar OER catalytic properties in 0.5 M H₂SO₄. Thus, β-PdSeO₃ NNs were found to be an overall water splitting catalyst in 0.5 M H₂SO₄ solution. The above catalysts all show long-term stability. In contrast, α-PdSeO₃ does not show OER catalytic properties. Pd-based but not Pdmetal-based acidic overall water splitting catalysts are very rare. Only a strontium Palladium Perovskite Sr₂PdO₃ was applied in acidic OER process [80], showing worse activity than that of β-PdSeO₃. We also found that PEC HER can be improved if the catalyst is more conductive.

Usually, thin layer materials were found to have better performance than the thicker materials due to better charge transfer properties. However, the β -PdSeO₃ bulk material were found to have slightly better performance than β -PdSeO₃ NNs in the acidic OER reactions, which is a surprising result deserving further investigations. This result might be related with the slow kinetics of OER reactions.

Again, we found that a photocatalyst can be used as an electcatalyst (α -PdSeO₃). We think this is because that the energy provided by light



Fig. 15. (a)-(b) iR compensated OER polarization curves of β-PdSeO₃ bulk (a) and NNs (b) obtained in 0.5 M H₂SO₄ solution at a scan rate of 5 mV s⁻¹ (c) Corresponding tafel slopes. (d)–(e) Chronoamperometric test of β -PdSeO₃ bulk material (d)and β -PdSeO₃ nns (e)at 9.2 mA cm⁻² for 6h.

can be provided by battery. The CBM and VBM position can also be adjusted by control of the electrode potentials.

CRediT authorship contribution statement

Yusheng Wu: Investigation, Data curation, Writing - original draft. Lin Wang: Investigation. Hongyan Zhang: Investigation. Jie Ding: Investigation. Min Han: Methodology. Min Fang: Conceptualization, Methodology, Supervision, Writing - review & editing. Jianchun Bao: Conceptualization, Methodology, Supervision. Yong Wu: Conceptualization, Methodology, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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