Doctoral (Ph.D.) Thesis

Photoelectrochemistry of layered metal chalcogenide electrodes

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1. Introduction and aims

One of the main challenges in the 21st century is to increase the consumption of sustainable energy to reduce our dependence on conventional fossil fuels. Solar energy is regarded as a clean and abundant source, comprising over 99% of available renewable energy. However, its intermittent nature necessitates efficient storage methods. Solar energy can be converted directly into electricity by photovoltaic solar cells, or into chemical energy by using photoelectrochemical (PEC) cells. The simplest PEC reaction is the hydrogen evolution reaction (HER), tracing back to when Honda and Fujishima first achieved photoelectrochemical water splitting in 1972.

The main element of a PEC HER cell is the semiconductor, which absorbs incident photons to generate electron-hole pairs. There are several requirements that a photoelectrode semiconductor must meet, such as the narrow bandgap to harvest UV-Vis light, high absorption coefficient, stable and insoluble in the test medium, and efficient charge transport. Despite significant advancements in PEC HER, the overall efficiency and long-term stability of semiconductor materials remain critical limitations. In this regard, the development of highly efficient and durable photoelectrodes has become the key research topic in the field of PEC HER.

Among various semiconductors, layered metal chalcogenides have attracted great attention as photoelectrode materials for PEC HER application due to their beneficial electronic and optical properties, such as the tunable bandgap by changing the flake thickness, and suitable conduction band position for proton reduction process. High PEC performance has been achieved only on single crystal metal dichalcogenides or in microelectrochemical cells, implying a limitation in the scalability of this solar energy conversion approach. There is a clear need to study macroelectrodes prepared from polycrystalline semiconductors and identify the opportunities and barriers for their applications. Moreover, many layered metal chalcogenides have not been widely studied in the field of PEC HER, therefore, the exploration of their PEC property is a very interesting research topic. We planned to prepare the electrodes using such layered materials and investigate their PEC HER behavior, aiming to expand the semiconductor family with high solar energy conversion efficiency.

During my doctoral research, I chose tin(II) selenide (SnSe) as macroelectrode material, which has not been widely studied in the field of PEC HER, especially in the form of flakes. First, we would like to find a suitable solvent for the liquid phase exfoliation (LPE) process of SnSe for achieving the highest PEC HER activity. Then we wanted to study the effect of flake edge density and Pt co-catalyst on the PEC performance of SnSe. We also aimed to examine the PEC HER performance of SnSe flakes synthesized by the hydrothermal method, and make a comparison with LPE prepared SnSe flakes.

My other goal was to study the PEC HER performance of gallium telluride (GaTe). Since the PEC HER activity of GaTe microelectrodes has not been studied, we would like to fabricate GaTe microelectrodes using mechanically exfoliated GaTe flakes, and investigate their thickness-dependent PEC activity. Moreover, from a practical point of view, it is desired to prepare GaTe macroelectrodes to scale up the PEC HER application of GaTe material.

We also would like to review the reported studies that employed two-dimensional (2D) and layered materials as photocathode materials for the PEC HER application, and summarize their PEC activity by a statistical analysis to reveal any specific trends. Importantly, we wanted to find out the reasons for limiting their PEC HER activity, and the corresponding strategies for their enhanced PEC activity.

2. Experimental techniques

The preparation methods of semiconductors and nanoflakes investigated during my PhD studies are listed in **Table 1**. SnSe and GaTe were employed as representative examples to show how the nanoflakes and electrodes were prepared.

Table 1. The preparation methods of semiconductors (bulk and nanoflakes) that we used for PEC HER.

Specimen	Conductivity type	Nanoflakes preparation method	Solvent for LPE	Electrode preparation method	Substrate
SnSe	p	LPE, hydrothermal	IPA/H_2O, IPA	m-LB, SP	GC
GaTe	p	ME, LPE	IPA	ME, SP	SiO_2/Si, GC
ZnSe (ZnTe)	n (p)	LPE	IPA, EtOH, EtOH/H_2O, NMP	m-LB	GC
Cu_2S (Cu_2Se, Cu_2Te)	p	LPE hydrothermal	IPA, EtOH	m-LB, SP	GC
GeS	p	LPE	EtOH, EtOH/H_2O, IPA, IPA/H_2O, DCB, NMP, DMF	m-LB	GC
As_2S_3	p	LPE	IPA, EtOH/H_2O	m-LB	FTO, ITO, GC

Liquid phase exfoliation (LPE): The as-received semiconductor crystals were dispersed in liquid solvents with an initial concentration of 5 mg mL^{-1}, using a 250 mL of round-bottom flask. Then the dispersion was purged with argon for 10 minutes to remove the dissolved oxygen and sealed with parafilm, subsequently performed sonication for 12 h with an ultrasonic cleaner (Elmasonic P70H), operating at 37 kHz and 100% power, while keeping the bath temperature below 30 ºC with a recirculating cooler system (J. P. Selecta, Dig-iterm TFT). Then the suspension was centrifuged at 100 g (Z366K, Hermle centrifuge) for 15 min at 15 °C. 90% of the supernatant was gently taken out with a pipette, leaving the sediment as obtained nanoflakes. The concentration of the obtained sediment from centrifuge was measured via the gravimetric analysis method.

A sieving system (Blau-Metall, Inc., with 200 mm in diameter sieves of woven wire mesh) was only used to separate as-received SnSe crystals into large-, medium- and small-sized crystals before the exfoliation process. This step led to three different fractions of SnSe crystals with 0.16–0.4 mm, 0.69–1.6 mm and 1.6–12 mm, named as S-, M- and L-SnSe, respectively. SnSe nanoflakes were obtained by exfoliating above different-sized crystals in pure isopropanol (IPA) solvent, and the resulting fractions were denoted as S-, M- and L-SnSe-IPA, respectively.

Mechanical exfoliation (ME): SiO_2/Si wafer (Graphene Supermarket) was used as the substrate for GaTe microelectrodes. It was ultrasonically cleaned in acetone and IPA for 5-5 min, respectively, before using. A scotch-tape was used to cleave layered GaTe crystals into nanoflakes, then the resultant nanoflakes were transferred onto SiO_2/Si substrate using a thermal release tape (Graphene Supermarket) at 105 °C on a hotplate (MCS78, CAT Scientific).

Hydrothermal method: The hydrothermal method was employed to synthesize SnSe and Cu_2X (X=S, Se and Te) materials. The as-obtained products were separated from their suspensions by centrifugation, then washed three times with deionized water and ethanol successively, dried by argon flow, and then stored in a glass vial.

Modified Langmuir-Blodgett (m-LB) method: A beaker filled with ultrapure deionized water was used as a trough, and the flake sediment suspension was slowly dropped onto the surface of the water until a continuous film formed. Then, the substrate was inserted into the water and slowly fished up by a tweezer. Subsequently, the electrodes were dried on a pre-heated hotplate for a few minutes to remove the solvent traces and enhance the adhesion between the nanoflakes and substrates.

Spray coating (SP) method: The concentration of the obtained nanoflake suspension was adjusted to 2 mg mL^{-1}, then the suspension was spray-coated on a preheated substrate with an Alder AD320 type airbrush. The precise loading of the catalyst was monitored using a Mettler Toledo XPE-26 type analytical microbalance in all cases. Before the spray-coating process, the electrodes were masked with PTFE sealing tape (thickness: 0,1 mm, temperature resistant from −200 to +250 °C, VWR) to have an exposed surface area of 1 cm^2.

Co-catalyst deposition: Pt co-catalyst was photodeposited on the surface of SnSe photoelectrodes from an aqueous solution containing 5 mM H_2PtCl_6, 5 vol% methanol, and 0.25 mM H_2SO_4. The solution was purged with Ar for 1 h to remove the dissolved O_2 before deposition. The Pt photodeposition recipe was optimized by using different H_2PtCl_6 concentrations (1, 5, 10 mM), illumination times (30, 60, 90 s), and illumination intensities (30, 44, 100 mW cm^{-2}). After Pt deposition process, the SnSe electrodes were washed three times using ultrapure deionized water and then dried by Ar gas flow.

PEC HER measurement on microelectrodes: GaTe crystals were mechanically exfoliated to flakes, then transferred onto SiO_2/Si substrate. The selected nanoflakes were electrically contacted by carbon paste and a copper wire, and used as microelectrodes for PEC HER application. All electrochemical measurements of GaTe microelectrodes were recorded by a PGSTAT302N potentiostat (Metrohm-Autolab) in a three-electrode configuration. GaTe microelectrode was the working electrode, while Pt wire, and Ag/AgCl were used as counter and reference electrodes, respectively. The linear sweep photovoltammetry was collected with 1 M HCl/6 M LiCl and 6 M LiCl electrolytes, respectively, under chopped white illumination (Fiber-Lite DC950 Illuminator, 200 mW cm^{-2}).

PEC HER measurement on macroelectrodes: The PEC HER measurements of macroelectrodes were performed with electrochemical workstation (Bio-logic SAS VMP-300) in a three-electrode configuration. Nanoflakes-coated substrates were used as the working electrodes, while GC plate, and Ag/AgCl were used as counter and reference electrodes, respectively. LSV was recorded in argon-saturated 0.5 M H_2SO_4 under chopped illumination (Newport LCS-100 solar simulator, 100 mW cm^{-2}). Chronoamperometry was performed for 1 h in argon-saturated 0.5 M H_2SO_4 solution under chopped illumination at −0.54 V vs. RHE and −0.79 V vs. RHE for SnSe and GaTe, respectively.

Another 1 h chronoamperometry was performed for GaTe macroelectrodes under chopped 10 sun illumination to collect the gas product and analyze the Faraday efficiency (FE). The hydrogen generated was measured using a Shimadzu GC-2010 Plus instrument fitted with a barrier discharge ionization detector. A Restek ShinCarbon ST column was used for the separation with 6.0 grade Helium carrier gas. Samples were taken at regular intervals using an automated 6-port valve. A Nafion membrane was used to separate the anode and cathode compartments. A peristaltic pump (Ismatec, ISM831C) was employed to homogenize the hydrogen within the gas-phase before each injection. FE values of the product were calculated from the amount of charge passed to produce the product divided by the total charge passed.

Incident photon-to-electron conversion efficiency (IPCE)/External quantum efficiency (EQE) measurement: IPCE/EQE measurements were carried out on a Newport Quantum Efficiency Measurement System (QEPVSI-B) in the same cell configurations as in the case of LSV. The resolution was kept at $\Delta\lambda = 20$ nm for macroelectrodes and $\Delta\lambda = 50$ nm for microelectrodes. Measurements were carried out in 0.5 M H_2SO_4 solution for macroelectrodes, and 1 M HCl/6 M LiCl droplets for microelectrodes. All IPCE data were recorded after argon-purging the electrolyte solution for 1 h to remove O_2 from the solution. Then IPCE value can be calculated via the following equation:

$$\mathrm{IPCE} = \mathrm{EQE} = \frac{number\ of\ electrons}{number\ of\ photons} = \frac{j * 1239.8}{P * \lambda}$$

where j, P, and λ represent the measured photocurrent density (mA cm^{-2}), monochromated illumination power intensity (mW cm^{-2}), and wavelength (nm), respectively.

Intensity modulated photocurrent spectroscopy (IMPS) measurement: IMPS was recorded using an AUTOLAB PGSTAT302N potentiostat. Spectra were recorded from 20 kHz to 0.1 Hz, employing sinusoidal light intensity modulation and bias illumination via a white LED in a 0.5 M H_2SO_4 solution.

Physical characterizations

The morphology and size of obtained nanoflakes were analyzed by scanning electron microscopy (SEM, Hitachi S-4700 Type II) equipped with energy dispersive X-ray spectroscopy (EDS) probe, and another SEM (Thermo Fisher Scientific Apreo C) equipped with Everhart−Thornley detector and a Bruker EDS probe. SEM images coupled with ImageJ software were employed to estimate the average size of nanoflakes.

Transmission electron microscopy (TEM) images were recorded on a FEI Tecnai G2 20 X-Twin type instrument, operating at 200 kV. The nanoflakes area and perimeter were analyzed by ImageJ software conducted from TEM images. The histogram distributions of nanoflake area and perimeter were conducted from over 100 nanoflakes in all cases.

The nanoflakes thickness was measured by using a NT-MDT Solver atomic force microscope (AFM) operated in the “tapping” mode with a silicon tip on a silicon nitride lever.

Raman spectra were recorded on a Senterra II Compact Raman microscope (Bruker) using a green laser ($\lambda = 532$ nm), operating at a power of ≤ 2.5 mW.

X-ray photoelectron spectroscopy (XPS) (Mg Kα) was carried out on a SPECS instrument equipped with a PHOIBOS 150 MCD 9 hemispherical analyzer. The binding energy scale was corrected by fixing the adventitious carbon peak to 284.8 eV. For XPS band deconvolution, CasaXPS commercial software package was used.

The band structure of GaTe microelectrode was analyzed by using Kelvin-Probe microscopy (KP Technology APS04). The bandgap, valence band position and the Fermi level of GaTe were determined by surface photovoltage spectroscopy (SPS), the ambient pressure photoemission spectroscopy (APS) and contact potential difference (CPD) measurements, respectively.

3. Summary of new scientific results

T1. The solvents used in liquid phase exfoliation affect the photoelectrochemical hydrogen evolution performance of SnSe flakes. Pure isopropanol is a more suitable solvent than the mixture of isopropanol and water to prepare SnSe flakes via liquid phase exfoliation, and for achieving improved PEC HER activity.

SnSe flakes were produced by exfoliating commercial SnSe crystals in different solvents, i.e., pure IPA and IPA/H_2O mixture with different IPA contents, using LPE method. The SnSe macroelectrodes were fabricated by depositing SnSe flakes on glassy carbon electrodes via m-LB method. The PEC HER performance was enhanced as the IPA content in the LPE solvents increased, and the pure IPA was found as the suitable solvent for SnSe, achieving the highest HER activity of 1.18 mA cm^{-2} photocurrent density at −0.69 V vs. RHE which was 10 times higher compared with IPA/H_2O case (1:3) (0.11 mA cm^{-2}).

T2. Varying the particle size of SnSe crystals before liquid phase exfoliation, the edge density of the obtained SnSe flakes can be tuned. While the photoelectrochemical test results indicate that the edge density has no significant effect on the PEC HER activity of SnSe flakes.

A sieving process was used to separate the as-received commercial SnSe crystals (diameter ≤ 12 mm) to three size fractions which were 12–1.6 mm, 1.6–0.69 mm and 0.4–0.16 mm size ranges named as L-, M- and S-SnSe, respectively, and then were exfoliated in pure IPA. The crystals after exfoliation are named as L-IPA-, M-IPA- and S-IPA-SnSe, respectively. These flakes had similar morphological characteristics, while the edge density values increased as the initial crystal size decreased. The photocathodes made from them by spray coating method showed the maximum photocurrent of ca. 2.3 mA cm^{-2}, which was higher than IPA-SnSe (1.18 mA cm^{-2}).

T3. Pt co-catalyst depositing on the SnSe surface can improve the PEC HER activity of SnSe flakes. This is caused by the enhanced charge transfer rate and suppressed charge carrier recombination at the electrode/electrolyte interface.

Pt nanoparticles were anchored on the surface of SnSe by the photodeposition method, and the effect of different deposition factors, such as illumination time, the concentration of Pt precursor, and illumination intensity, on the PEC activity was investigated. Under optimal conditions, Pt decorated SnSe photocathode gave higher PEC HER activity than bare SnSe (4.39 vs. 2.14 mA cm^{-2}). IMPS results demonstrated that the Pt co-catalyst improved charge transfer kinetics and suppressed charge carrier recombination at the electrode/electrolyte interface.

T4. The different synthesis approaches (i.e., hydrothermal and liquid phase exfoliation methods) of SnSe flakes have no significant effect on the PEC HER activity of SnSe flakes.

SnSe flakes were also synthesized via the hydrothermal method, and spray-coated on GC substrates and used as photocathodes for PEC HER. The loading-dependent PEC HER activity indicated that 0.2 mg cm^{-2} was the optimal loading, achieving a maximum photocurrent of 3 mA cm^{-2}, which is in the same order of magnitude as LPE prepared SnSe flakes.

T5. The mechanically exfoliated GaTe flakes can be applied for the PEC HER application, and the larger flake thickness leads to higher PEC HER activity.

GaTe flakes were obtained by mechanically exfoliating as-received GaTe crystals, and immobilized on the SiO_2/Si substrate, and used as working electrode for PEC HER application. The PEC performance of GaTe microelectrode was conducted using our custom-developed PEC microscopy technique. It exhibited higher PEC activity with 6 M LiCl/1 M HCl than that of 6 M LiCl droplets. Meanwhile, GaTe has a thickness-dependent PEC HER performance, i.e., thicker flakes generally show higher PEC activity, achieving a maximum photocurrent of 6 mA cm^{-2} at −1.2 V vs. RHE with a thickness of 808±50 nm.

T6. GaTe macroelectrodes composed of liquid phase exfoliated flakes can be used for PEC HER application under concentrated illumination.

The LPE method was applied in pure IPA to prepare dispersions of GaTe flakes, and the GaTe macroelectrodes were prepared by spraying these flakes on glassy carbon electrode and employed as photocathodes for PEC HER. The loading dependent PEC activity indicated that the best performance was achieved with the mass loading of 0.3 mg cm^{-2}, showing 0.57 ±0.01 mA cm^{-2} photocurrent at −0.74 V vs. RHE. Besides, an illumination intensity dependent PEC HER performance was found under optimal loading, achieving a maximum photocurrent of 4 mA cm^{-2} at − 0.74 V vs. RHE under 10 sun illumination. Stability tests were performed by 60 min long chronoamperometry, and 92% and 80% of initial activity remained under 1 and 10 sun illumination, respectively.

T7. Higher photocurrent is achieved with GaTe microelectrode compared to the macroelectrode in PEC HER, caused by the abundant defects in the macroelectrode, which can be avoided in the microelectrode.

GaTe microelectrodes showed higher photocurrent than GaTe macroelectrodes (1.7 vs. 0.8 mA cm^{-2} at −0.76 V vs. RHE). This can be explained by that, in the case of macroelectrode, more defects are produced after liquid phased exfoliation process. In contrast, in the case of microelectrode, we can measure the PEC activity at less defective positions (basal plane). As reported, the defects can be the recombination centers for photogenerated charge carriers, resulting in high dark current and low PEC activity. Besides, the GaTe networks fabricated with solution-processed GaTe nanoflakes might have lower conductivity or carrier mobility compared to mechanically exfoliated GaTe microelectrodes, which can also result in lower PEC activity for GaTe macroelectrode.

T8. The PEC HER performance of various layered and 2D materials is typically limited to be below 10 mA cm^{-2}, which can be possibly explained by several reasons, including the abundant defects, the instability in the electrolyte media, and the low conductivity of the fabricated material networks.

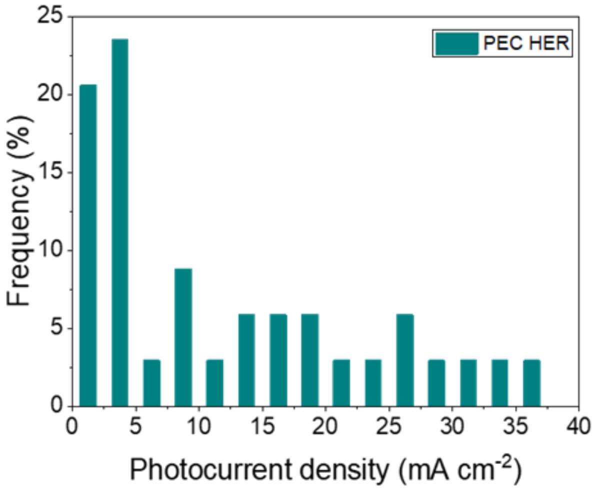

Fig.1. Statistical analysis of maximum photocurrent density distribution for PEC HER (under 1 sun illumination) using metal chalcogenide electrodes.

The PEC HER performance of various layered and 2D metal chalcogenide was reviewed and summarized by a statistical analysis, revealing that around 60% of photocurrent density is below 10 mA cm^{-2}, which can be possibly explained by several reasons: i) abundant defects are produced after exfoliation process, acting as recombination centers for photogenerated charge carriers. ii) the exfoliation process destroys the structure of crystals, leading the resultant nanoflakes not being stable in the electrolyte media. iii) the fabricated nanoflakes network possesses low conductivity. Moreover, some common strategies, such as heterojunctions, tunnelling, and co-catalysts, can be used to enhance PEC performance.

4. Scientific publications

Hungarian Scientific Bibliography (MTMT) identifier: 10069636

Publications related to the scientific topic of the dissertation:

1) **Qianqian Ba**, Péter S. Tóth, Cintia Hajdú, Csaba Janáky. Photoelectrochemical behavior of GaTe nanoflakes prepared by exfoliation. Electrochimica Acta 507 (2024): 145105.

   IF_{2025} = 5.5

2) **Qianqian Ba**, Péter S. Tóth, Ádám Vass, Krishnan Rajeshwar, Csaba Janáky. Photoelectrochemical hydrogen evolution on macroscopic electrodes of exfoliated SnSe flakes. Applied Catalysis A, General 661 (2023): 119233.

   IF_{2025} = 4.7

3) Péter S. Tóth, **Qianqian Ba**, Csaba Janáky. Photoelectrochemistry of two-dimensional and layered materials: a brief review. Journal of Solid State Electrochemistry 27 (2023): 1701–1715.

   IF_{2025} =2.6

∑IF = 12.8

Conferences

Oral presentation:

Qianqian Ba, Péter S. Tóth, Csaba Janáky: Application of SnSe-based macroscopic electrodes for photoelectrochemical hydrogen evolution reaction.

XLV. CHEMISTRY LECTURES, 25-27, October, 2022, Szeged, Hungary.

Poster presentations:

1) **Qianqian Ba**, Péter S. Tóth, Csaba Janáky: Study of the hydrogen evolution reaction on macroscopic SnSe-based photoelectrodes.

   244th ECS Meeting, 8-12, October, 2023, Gothenburg, Sweden.

2) **Qianqian Ba**, Péter S. Tóth, Csaba Janáky: Photoelectrochemical hydrogen evolution on macroscopic SnSe-based electrodes.

   Graphene2023 Conference, 27-30, June, 2023, Manchester, UK.

3) **Qianqian Ba**, Péter S. Tóth, Csaba Janáky: Study of the photoelectrochemical hydrogen evolution reaction on exfoliated SnSe electrodes.

   YOURHETCAT 2022 CONFERENCE, 11-13, July, 2022, Szeged, Hungary.

4) **Qianqian Ba**, Péter S. Tóth, Csaba Janáky: Investigation of photoelectrochemical hydrogen evolution reaction on exfoliated SnSe electrodes.

   E-MRS SPRING MEETING 2022, 30 May-3 June, 2022, Online.

5) **Qianqian Ba**, Péter S. Tóth, Csaba Janáky: Application of exfoliated SnSe photoelectrodes for hydrogen evolution reaction.

   XXV. SPRING WIND CONFERENCE, 6-8, May, 2022, Pécs, Hungary.