



Electrochemistry of Layered Semiconducting A^{III}B^{VI} Chalcogenides: Indium Monochalcogenides (InS, InSe, InTe)

Yong Wang,^[a] Katerina Szökölová,^[b] Muhammad Zafir Mohamad Nasir,^[a] Zdenek Sofer,^[b] and Martin Pumera^{*[c, d]}

Layered $A^{III}B^{VI}$ chalcogenides represent an interesting class semiconductors, where most of adopting 2D structures. Unlike the typical sandwiched structure of transition metal dichalcogenides (TMDs), layered $A^{III}B^{VI}$ chalcogenides like InSe and GaSe are composed of X–M–M–X motif where M is gallium/indium and X is sulfur/selenium/tellurium. The exception is InS, which adopt an orthorhombic 3D structure. Herein, we studied and compared the inherent electrochemical properties as well as the electrocatalytic performances towards hydrogen evolution (HER), oxygen evolution (OER) and oxygen reduction reaction (ORR) of indium monochalcogenides (InS, InSe and InTe). Inherent electrochemistry studies in phosphate buffered saline electrolyte showed that InS did not exhibit any inherent electrochemical signals when compared to bare glassy carbon electrode. However, InSe showed a reduction peak at -1.6 V

Introduction

The exploration and discovery of new two-dimensional (2D) materials have actively driven scientific research in the fields of materials research ever since the discovery of graphene in 2004.^[1] Transition metal dichalcogenides (TMDs) have been extensively studied attributing to their unique properties in single or few layers structures.^[2–5] These studies are herein extended to post transition metal chalcogenides which are often overlooked. The class of A^{III}B^{VI} chalcogenides represents a family of layered semiconductors which have attracted immense attention due to their unique electronic structures and

[a]	Y. Wang, Dr. M. Z. M. Nasir Division of Chemistry and Biological Chemistry School of Physical and Mathematical Sciences Nanyang Technological University
[h]	Singapore 03/3/1 (Singapore) K. Szökölová, Prof. 7. Sofer
[0]	Department of Inoraanic Chemistry
	University of Chemistry and Technology Prague
	Technická 5, 166 28 Prague 6 (Czech Republic)
[c]	Prof. M. Pumera
	Future Energy and Innovation Laboratory
	Central European Institute of Technology
	Brno University of Technology
	Purkyňova 656/123, Brno, CZ-616 00, Czech Republic
	E-mail: martin.pumera@ceitec.vutbr.cz
[d]	Prof. M. Pumera
	Department of Chemical and Biomolecular Engineering
	Yonsei University
	50 Yonsei-ro, Seodaemun-gu, Seoul 03722 (Republic of Korea) F-mail: pumera research@amail.com
	Connecting information for this article is available on the WWW under
	https://doi.org/10.1002/cctc.201900449

while InTe had an oxidation peak at 0.2 V. The heterogeneous electron transfer (HET) rates of indium monochalcogenides were measured with $[Fe(CN)_6]^{3-/4-}$ redox probe using cyclic voltammetry (vs. Ag/AgCl) at the scan rate of 100 mV s⁻¹. It was found that InTe exhibited the best electrochemical performance with the fastest HET rate with highest k_{obs}^0 obtained ($3.7 \times 10^{-3} \text{ cm s}^{-1}$). InS showed the best electrocatalytic performance for HER with the lowest overpotential value of 0.92 V at current density of -10 mA cm^{-2} . However, the performances of indium monochalcogenides were almost comparable to that of bare glassy carbon electrode and do not exhibit any improvements in electrocatalytic capabilities. This study provides insights into the electrochemical properties and electrocatalytic performances of layered A^{III}B^{VI} indium monochalcogenides which would influence potential applications.

optoelectronic properties.^[6-8] These layered materials have a general chemical formula of MX (M=Ga or In, X=S, Se or Te) unlike TMDs. Other forms, such as M₂X and M₂X₃, do not display layered structures.^[9,10] Indium monochalcogenides (InS, InSe, InTe) are an upcoming class of A^{III}B^{VI} chalcogenides which have been attracting interest due to their intriguing electronic properties. InS displays an orthorhombic structure belonging to the Pnnm space group with their ethane-like S₃InInS₃ motifs. These S₃InInS₃ motifs are mutually linked by sharing S atoms to form a three dimensional network structure. InS has an indirect band gap of about 1.90 eV at room temperature.^[11] Layered InSe shows a rhombohedral structure belonging to P6₃/mmc space group with an energy gap of 1.24 eV at room temperature. Each layer comprises of two metal and two chalcogen atoms in a X–M–M–X sequence. These layers are predominantly stacked with weak interlayer Van der Waals forces and covalent intra-layer bonds. However, InTe is a mixed-valence compound belonging to tetragonal 14/mcm space group which can be represented by the chemical formula of In⁺In³⁺Te₂²⁻. In³⁺ and In⁺ cations occupy two different crystallographic positions with different chemical bonding environments. Each In³⁺ cation is tetrahedrally coordinated to four Te²⁻ anions thus exhibiting a $In^{3+}Te_4^{2-}$ substructure. However, In^+ cations display distorted square anti-prismatic coordination with eight surrounding Te²⁻ ions. These In⁺ cation chains are linked to the In³⁺Te₄²⁻ substructure by weak electrostatic interactions.^[12]

A^{III}B^{VI} chalcogenides hold great potentials in various applications in electronics, optoelectronics and catalysis due to their moderate bandgaps, high carrier mobility and defined charge carrier properties.^[13] For example, InSe field effect transistors



Figure 1. Scanning electron micrographs (left) and corresponding elemental mappings of (a) InS, (b) InSe, and (c) InTe obtained by energy-dispersive X-ray spectroscopy (EDS).

(FETs) show high electron mobility exceeding 10³ cm² (Vs)⁻¹, outperforming their TMD counterparts.^[8,14] Besides that, fewlayers InSe photodetector displayed great performance from visible to near-infrared light region with fast response time and long-term stability in photoswitching. $^{[7]}$ Single-layer $A^{III}B^{VI}$ monochalcogenides were computationally calculated to be potential photocatalysts for water splitting,^[6,15] whereby InSe coupled with TiO₂ was reported as excellent photocatalyst for visible light H₂ production.^[16] Most research on InS and InTe were synthesis, focused on their optical and electrical properties.[11,17-21]

ChemPubSoc

Recently, numerous studies have investigated the possible applications of layered A^{III}B^{VI} chalcogenides with some reports on their electrocatalytic properties.[22-24] In addition, fundamental electrochemical properties and behaviors of indium monochalcogenides remain predominately unexplored. Therefore, it is essential and imperative to investigate the electrochemical as well as electrocatalytic performances towards hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) of indium monochalcogenides. The differences in performances of chalcogen atoms will also be compared between the indium monochalcogenides. Herein, we synthesized, characterized and investigated the fundamental electrochemical properties of indium monochalcogenides (InS, InSe, InTe). They were also characterized by scanning electron microscopy (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), Raman spectroscopy, photoluminescence spectra and X-ray photoelectron spectroscopy (XPS).

Results and Discussion

Characterization studies were first performed to understand the morphological features of the synthesized indium monochalcogenides. Scanning electron microscopy (SEM) was performed in order to reveal their surface morphologies. Figure 1 shows SEM images of InS, InSe and InTe where their layered structures were observed. The layers are stacked together indicating the bulk state of these materials. Elemental mappings by energy-dispersive X-ray spectroscopy (EDS) in Figure 1 showcased the homogeneous distribution of elements In, S, Se and Te for the respective materials. The chalcogen to metal ratios of InS, InSe and InTe obtained from EDS were 1.11, 0.77 and 0.91 respectively. These values are close to the theoretical chemical ratio of 1 which suggests the successful synthesis of the respective indium monochalcogenides.

CHEMCATCHEM

The morphology of indium monochalcogenides was further investigated by transmission electron microscope (TEM). Figure 2 shows the layered flakes of indium monochalcogenides with a high degree of crystallinity. The detail image of SAED with indexing of diffraction pattern is shown on Figure S1. The elemental mappings obtained from the TEM in Figure S2 indicate the homogeneous distribution of elements of In, S, Se and Te. X-Ray diffraction (XRD) was then conducted to study the crystallinity and phase composition of indium monochalcogenides shown in Figure S3. Diffractograms revealed the single phase of InS, InSe and InTe. InSe and InTe with layered structure exhibited preferential orientation due to its high anisotropy.





Figure 2. Transmission electron micrographs (left and center), and high-resolution TEM images (right) of (a) InS, (b) InSe and (c) InTe. The inset images in the left are the SAED of corresponding indium monochalcogenides. Scale bars for the HR-TEM images represent 5 nm.



Figure 3. Raman spectra of (a) InS, (b) InSe and (c) InTe.

Raman spectroscopy was subsequently performed to understand the structural features of indium monochalcogenides. Figure 3 shows the Raman spectra of InS, InSe and InTe obtained using green laser with wavelength of 532 nm. From the Raman spectrum of InS in Figure 3a, characteristic peaks with frequency values of 59.8 (A_g^{-3}) , 150.7 (A_g^{-1}) , 224.8 (A_g^{-4}) , and 318.2 cm⁻¹ (A_g^{-3}) were identified. These Raman peaks are consistent with the reported Raman spectrum of InS.^[25] A_g^{-1} and A_g^{-2} modes are due to the intra-layer stretching vibrations while A_g^{-3} and A_g^{-4} modes corresponding to the intra-layer bending



vibrations.^[25] In the case of InSe (Figure 3b), the spectrum displayed prominent peaks at frequency values of 117.5 (A'₁), 179.5 (E'',), 201.7 (E'(TO)) and 228.6 (A'₁) cm⁻¹, which were determined to originate from the InSe.^[26] As for InTe, the Raman spectrum reveals two peaks located at 122.0 and 138.8 cm⁻¹ (Figure 3c), which corresponds to A_{1g} and E_g vibrational modes respectively.^[27,28]

Photoluminescence spectra of indium monochalcogenides were obtained using laser with a wavelength of 532 nm to study their band structure (Figure 4). InS showed two photo-



Figure 4. Photoluminescence spectra of InS, InSe and InTe obtained using a laser (532 nm) with 0.5 mW excitation power.

luminescence peaks. The peak located at about 650 nm (1.98 eV) can be attributed to the band-edge transition and the second peak at lower energy centered at 870 nm (1.51 eV) originated from deep level transitions (associated with defect and impurities) to the defect and deep levels within the band-gap. These results are in good agreement with reported literature.^[29] For InSe, the photoluminescence peak centered at 995 nm (1.25 eV) associated with band-edge transition can be clearly observed.^[24,26] InTe did not show any photoluminescence peak in the measured range, since its bandgap is reported to be 1.44 eV.^[30]

X-ray photoelectron spectroscopy (XPS) was then conducted to examine the surface elemental composition and bonding information of the indium monochalcogenides. From the survey scans obtained (Figure S4), characteristic peaks of C 1s at 284.5 eV, O 1s at 531.1 eV, In 3d at 444.4 eV, S 2p at 162.1 eV, Se 3d at 54.9 eV and Te 3d at around 575.4 eV were identified. Due to the limited information from the survey scan, high resolution XPS core-level spectra of In 3d, S 2p, Se 3d and Te 3d were investigated in Figure 5. These spectra were calibrated to the adventitious C 1s at 284.5 eV. For InS (Figure 5a), the deconvolution of In 3d revealed spin-orbit split doublets located at 443.9, 451.5 eV and 444.3, 451.9 eV ($\Delta E = 7.6$ eV), which originate from In (0) and In–S.^[31] The S 2p spectrum is well fitted to one spectral component, with binding energy of

161.2 and 162.3 eV corresponding to sulfide (Figure 5b). In the case of InSe, two pairs of peaks at 444.1, 451.7 eV and 444.8, 452.4 eV ($\Delta E = 7.6$ eV) were obtained by deconvolution (Figure 5c) and assigned to In-Se and In-O.^[32] In addition, the deconvolution of the Se 3d indicated metal selenide centered at binding energies of 55.7 and 54.9 eV (Figure 5d).^[32] As for InTe, Figure 5e shows two distinct pairs of peaks at 443.8, 451.39 eV and 444.8, 452.4 eV ($\Delta E = 7.6$ eV). These peaks were in agreement with reported binding energies assigned to In (0) and In-Te.^[33] Te 3d spectrum was deconvoluted into two pairs of peaks located at 572.3, 582.7 eV and 576.4, 586.7 eV which lie close to the reported values of In–Te and TeO₂ (Figure 5f).^[33] From the XPS spectra obtained, it affirms the synthesis of indium monochalcogenides with the small presence of the oxidized counterparts which were inherently formed during the synthesis procedures.

Having analyzed the structural morphologies and compositions of the indium monochalcogenides, we next proceed to analyze their electrochemical characteristics, namely their inherent electrochemical properties. The operating potential window of materials is limited by the inherent electrochemistry^[34,35] or solvent-related electrochemical reactions.^[36] Inherent electrochemistry refers to the redox behaviors of electrode materials stemmed from the surface electroactive components when an electrochemical potential is applied.^[5] Three consecutive cyclic voltammetry (CV) scans in both anodic and cathodic directions were performed to investigate their inherent electrochemical behaviors. CV measurements were performed over a potential range of -1.8 V to +1.8 V in phosphate buffered saline (PBS) of pH 7.2. Figure 6 shows the cyclic voltammogram of indium monochalcogenides. For the sake of clarity, the electrochemical potentials in this work were reported with reference to Ag/AgCl electrode unless otherwise indicated. As illustrated in Figure 6, all CV profiles in both anodic and cathodic scan directions show an inconspicuous reduction peak at about -0.6 V. Upon comparing with CVs obtained with bare glassy carbon (Figure S5), this signal was attributed to the intrinsic behavior of glassy carbon. Considering the CV scans for InS in both anodic and cathodic direction in Figure 6a and b, the absence of additional peaks would indicate that InS is electrochemically inert without any conspicuous redox properties. On the other hand, CVs with InSe displayed a sharp reduction signal at around $-1.6\,V$ in the cathodic scan. The signal was ascribed to the reduction of indium oxide (In₂O₃) as reported.^[24] This is consistent with the XPS study which showed the presence of In₂O₃ on the surface of InSe. However, this reduction peak was absent during the anodic scan which suggests the deactivation of this reducible moiety by positive potentials. In the anodic scan direction (Figure 6e), InTe exhibited an oxidative peak at about 0.3 V which shifted to a lower potential (0.2 V) at subsequent consecutive scans. However, no oxidation peak was observed in the first scan for cathodic direction (Figure 6f) but appeared in the subsequent two scans centered at 0.2 V. Comparison of the first scans for InTe in both anodic and cathodic directions, an initial oxidation scan is a prerequisite for the appearance of the oxidation peak. Since no similar oxidation peaks were spotted ChemPubSoc Europe

CHEMCATCHEM Full Papers



Figure 5. High-resolution X-ray photoelectron spectra of InS, InSe and InTe. C 1s peak at ca. 284.5 eV is used as calibration reference.

in the CV profiles of InS and InSe, we can rationally assign these oxidation peaks to the inherent oxidation of tellurium. Similar oxidative peaks were also identified for GaTe,^[24] VTe_2 ,^[37,38] PdTe₂ and PtTe₂.^[39] The anodic signal at about 0.2 V is due to the oxidation of Te (0) to Te(II) while the signal at about 0.3 V may correspond to the oxidation of Te (0) to Te(IV).^[39–41] The inherent oxidation signals obtained could potentially hinder the performance of InTe as a sensing platform for the detection of analytes with low oxidation potentials. The electrochemical signals from the target analyte might get overlapped and masked.

Having understood the intrinsic electrochemical behaviors of these materials, we proceed to analyze their electrochemical efficiencies. Heterogeneous electron transfer (HET) rate is preliminarily measured to examine the suitability of materials for electrochemical sensing applications. The ideal electrode material for electrochemical sensing possesses innately rapid HET rate in order to lower the overpotential required for an examine the HET rates of indium monochalcogenides in the presence of $[Fe(CN)_6]^{3-/4-}$ redox probe using cyclic voltammetry. The peak-to-peak separation (ΔE) between the oxidation and reduction peaks correlates with the HET rate constant, k_{abs}^{0} obtained by Nicholson's method, where wider $\triangle E$ can be interpreted as slower HET and smaller k_{obs}^0 value.^[42] The electrochemical measurements of $[Fe(CN)_6]^{3-74-}$ redox probe were performed from -0.6 V to 1.0 V to minimize interference from the inherent electrochemical signals of indium monochalcogenides. Figure 7 shows the voltammetric profiles of indium monochalcogenide-modified electrodes and histogram of experimentally observed ΔE . From Figure 7a, both bare glassy carbon (GC) and indium monochalcogenides showed a pair of reversible redox peaks at about +0.15 V and +0.28 V. It is worth to note that the observed inherent oxidation peak for InSe at 0.6 V vs. Aq/AqCl did not totally overlap with the redox peak of $[Fe(CN)_6]^{3-/4-}$ probe and had no significant influence on

electrochemical reaction to take place. In this study, we





Figure 6. Cyclic voltammograms (vs. Ag/AgCl) of InS (a) anodic and (b) cathodic scan, InSe (c) anodic and (d) cathodic scan, InTe (e) anodic and (f) cathodic scan. Insets show (a–d) reduction, and (e–f) oxidation peaks observed. Arrows indicate the direction of scans starting at scan potential of 0 V. Conditions: 0.5 M PBS at pH 7.2 as electrolyte; scan rate of 100 mV s⁻¹.



Figure 7. (a) Cyclic voltammograms (vs. Ag/AgCl) of indium monochalcogenides with 5 mM $[Fe(CN)_6]^{3^{-/4-}}$. (b) Peak-to-peak separations of indium monochalcogenides along with their error bars. Conditions: 0.1 M KCl as electrolyte; scan rate of 100 mV s⁻¹.

the measurement of HET rate. The k_{obs}^0 of InS, InSe, InTe and GC were calculated to be 9.3×10^{-41} cm s⁻¹ ($\Delta E = 0.21$ V), 3.1×10^{-3} cm s⁻¹ ($\Delta E = 0.12$ V), 3.7×10^{-3} cm s⁻¹ ($\Delta E = 0.11$) and 3.8×10^{-3} cm s⁻¹ ($\Delta E = 0.11$), respectively. InS showed the poorest HET performance with an order of magnitude lower than that of InSe and InTe, while InTe displayed the best HET performance. However, the HET performance of InTe was very comparable to that of bare GC. Comparing the indium monochalcogenides, InSe and InTe would be preferred over InS for electrochemical sensing applications if required.

We subsequently studied the electrocatalytic performances of InS, InSe and InTe towards hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), which are of importance for energy harvesting applications^[43,44] and fuel cells.^[45] Previous literature reported the electrochemical properties of InSe for hydrogen evolution reaction.^[24] Therefore, it would be essential to extend and compare the research scope to InS and InTe.

The HER performances of InS, InSe and InTe were measured in 0.5 M H_2SO_4 at a scan rate of 2 mV s⁻¹. Figure 8a shows the HER polarization curves of indium monochalcogenides as well as bare GC for comparison. It was observed that all indium monochalcogenides exhibited an inherent reduction peaks in the acidic electrolyte used. The inherent reduction peaks of InS, InSe and InTe at -0.97 V vs. RHE during the first scan were due to the reduction of indium oxide in 0.5 M H₂SO₄.^[24] Furthermore, the additional reduction peak at -1.10 V vs. RHE for InTe was attributed to the reduction of Te as previously described. A consecutive second measurement was performed where the inherent peaks were observed to disappear as shown in Figure 8b. No conducting binders was used for the subsequent HER measurement. The respective overpotential and Tafel slope values were presented in Figure 8c and d. Comparing with the electrocatalytic performance of bare GC (0.95 V), InS, InSe and InTe showed negligible HER catalytic performance with overpotential of 0.92 V, 1.32 V and 1.31 V at the current density of





Figure 8. (a) Polarization curves (vs. RHE) for hydrogen evolution reaction (HER) of InS, InSe and InTe. (b) Polarization curves (vs. RHE) of the successive second scan of InS, InSe and InTe. (c) Overpotential values obtained at current density of -10 mA cm^{-2} from (b). (d) Tafel slope values of InS, InSe and InTe from (b). Conditions: 0.5 M sulfuric acid as electrolyte; scan rate of 2 mV s⁻¹.

 -10 mA cm^{-2} . The reasons for the poor HER performances are mainly due to their semiconducting properties with lower conductivity and less active sites at bulk state. Tafel slope is another parameter to evaluate the HER performance that can be used to elucidate the HER electrochemical mechanism. In general, the HER pathway can be expressed as the following steps [Eqn. (1)–(3)]:

 $\label{eq:Adsorption step} \begin{array}{l} (Volmer): \ H_3O^+ + e^- \to H_{ads} + H_2O; \\ b \approx 120 \, mV \, dec^{-1} \end{array} \tag{(}$

Desorption step (Heyrovsky) :

$$\begin{split} H_{ads} + H_3 O^+ + e^- &\rightarrow H_2 + H_2 O; \\ b &\approx 40 \, \text{mV} \, \text{dec}^{-1} \end{split}$$

From Figure 8d, InS showed the smallest Tafel slope value of 75.7 mV dec⁻¹ and is inferred to undergo a fast Volmer step followed by the rate limiting step of Heyrovsky step. It is followed by InSe (115.7 mV dec⁻¹) with the rate limiting step of Volmer step. InTe presented the biggest Tafel slope value of 197.5 mV dec⁻¹. The HER limiting step of InTe is postulated to be Volmer adsorption step as the value is close to 120 mV dec⁻¹.

protons and four electrons for the production of each molecule O₂.^[46] From Figure S6a, InS, InSe and InTe are regarded as weak catalyst towards OER with high onset potentials of about 2 V vs. RHE which is very comparable to bare GC. The possible reasons for this negligible enhancement in performance may be due to (1) unfavorable free energies of OOH* and OH* intermediates and the instability of the materials at high anode potential.^[47] Subsequently, we studied the electrocatalytic performances of indium monochalcogenides towards ORR (Figure S6b). All materials displayed cathodic peaks at about -0.4 V vs. Aq/AqCl which was ascribed to the reduction of O₂. Onset potential is usually adopted as a parameter to evaluate the electrocatalytic activity for ORR. As observed in Figure S6b, InS and InTe displayed similar onset potentials of about -0.22 V vs. Aq/AqCl. However, the ORR performance of InSe interfered with the inherent electrochemical performance, making it difficult to obtain the onset potential. Overall, InS, InSe and InTe are not ideal electrocatalysts for ORR due to the low current response and relatively high onset potential.

We then examined the electrocatalytic performance of InS,

InSe and InTe towards oxygen evolution (OER) and oxygen

reduction reaction (ORR) in 1.0 M KOH solution as presented in

Figure S6. The mechanism of OER requires the extraction of four



Conclusion

We have synthesized and investigated the electrochemical properties of indium monochalcogenides. Indium monochalcogenides were characterized by SEM, TEM, XRD, Raman spectroscopy, photoluminescence spectroscopy and XPS. The results indicate that InSe and InTe exhibit inherent electrochemical activities while InS is electrochemically inert. InSe showed a reduction peak ascribed to indium oxide at -1.6 V and InTe got oxidized at 0.2 V due to the oxidation of tellurium. Further studies were made to reveal the electrochemical activities of indium monochalcogenides towards HER, OER and ORR. All indium monochalcogenides exhibit negligible HER, OER and ORR performances when compared to bare glassy carbon. This is attributed to their semiconducting properties with lower conductivity and less active sites at bulk state. These fundamental findings provide insights into the comprehensive electrochemical attributes of layered A^{III}B^{VI} indium chalcogenides which can be useful for future applications.

Experimental Section

Materials

Sulfur, selenium, tellurium and indium of 99.999% purity were obtained from Alfa Aesar. Potassium hydroxide, sulfuric acid, sodium phosphate monobasic, sodium chloride, potassium phosphate dibasic, potassium hexacyanoferrate(III), potassium chloride potassium hexacyanoferrate(III) trihydrate and platinum on carbon were purchased from Sigma-Aldrich, Singapore. Working glassy carbon (GC), counter platinum and reference Ag/AgCl electrodes were obtained from CH Instruments, Texas, USA. The glassy carbon electrode used has a diameter of 3 mm. Ultrapure water (Milli-Q) was utilized for the preparation of background electrolytes.

Synthesis of Materials

The materials were prepared by direct reaction of elements in quartz glass ampoules under high vacuum. Stoichiometric amount of indium and respective chalcogens corresponding to 10 g of respective monochalcogenides were placed in quartz glass ampoule and melt sealed under high vacuum $(1 \times 10^{-3} \text{ Pa})$ using oxygen-hydrogen torch. InS was prepared by heating of ampoule with In and S at 800 °C for 24 h using heating and cooling rates of 10 °C min⁻¹. Subsequently, the ampoule with InS was heated at 540 °C for 100 h. InSe was prepared by heating of ampoule with In and Se at 850 °C for 12 hours. The heating rate was 5 °C min⁻¹ and the cooling rate was 0.5 °C min⁻¹. InTe was prepared by heating of ampoule with In and Te at 800 °C for 12 h using heating rate of 5 °C min⁻¹ and cooling rate of 0.5 °C min⁻¹.

Apparatus

Scanning electron microscopy (SEM) was performed using a JEOL 7600F field-emission SEM (JEOL, Japan) at the voltage of 5 kV. Besides, Energy dispersive X-ray spectroscopy (EDS) was conducted at an acceleration voltage of 20 kV.

X-ray powder diffraction was conducted on Bruker D8 Discoverer (Bruker, Germany) powder diffractometer, and Bragg-Brentano

geometry was focused using CuK_a radiation ($\lambda = 0.15418$ nm, U = 40 kV, I = 40 mA) at room temperature. The data were scanned over an angular range of 10–80° (20) with a step size of 0.016° (20). Data evaluation was performed in the software package EVA.

Raman spectroscopy was collected using a Raman microscope (Renishaw, England) in a backscattering geometry with a CCD detector. Measurements were made using a DPSS laser (532 nm, 50 mW) with an applied power of 5 mW and a 50× magnification objective. Silicon wafer reference was used to calibrate the instrument which has a peak position at 520 cm⁻¹ and a resolution of less than 1 cm⁻¹. The sample was suspended in deionized water (1 mg ml⁻¹) and sonicated for 10 min prior to the deposition of the suspension on a small piece of silicon wafer.

The photoluminescence spectrum was obtained by using Nd-YAG laser (532 nm, 50 mW). Spectra were collected with a TE cooled CCD camera and a 50× objective lens. The samples were suspended in deionized water with the concentration of 1 mg ml⁻¹ and treated by sonication for 10 min. Then the suspensions were deposited on a small silicon wafer and dried before the measurements.

High resolution transmission electron microscopy (HR-TEM) was conducted by using an EFTEM Jeol 2200FS microscope (Jeol, Japan) at the accelerated voltage of 200 KeV. Element maps were obtained using the SDD detector X–MaxN 80 TS from Oxford Instruments (England). The samples were prepared by dropping suspension (1 mg mL⁻¹ aqueous solution) on a TEM grid (Cu; 200 mesh; Formvar / carbon) and drying at 60 °C for 12 h.

X-ray photoelectron spectroscopy (XPS) was performed by using monochromatic Mg K α source (SPECS, Germany) at 1253 eV and a multi-channel energy analyzer (SPECS Phoibos 100 MCD-5). Wide scan and high resolution core level spectra for analysis were collected and C 1s at 284.5 eV was used for calibration.

Electrochemical measurement of cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were conducted with a μ Autolab type III electrochemical analyzer (Eco Chemie, The Netherlands) using NOVA 1.10 software.

Electrochemical Procedure

5 mg mL⁻¹ of indium monochalcogenides suspensions were prepared in ultrapure water by sonication for 1 h to obtain the homogeneous suspensions. 4 μ L of the suspensions were dropcasted on glassy carbon and dried at room temperature. Glassy carbon was renewed by polishing with 0.05 mm alumina particles and rinsed with ultrapure water. Cyclic voltammetry was used to study the inherent electrochemical properties and heterogeneous electron transfer (HET) of indium chalcogenides in a three-electrode system where modified glassy carbon, Ag/ AgCl, and Pt electrode as working, reference, and counter electrode. 5 mL of phosphate buffer solution (PBS) (50 mM, pH = 7.2) electrolyte was used for inherent electrochemical studies and $\left[\text{Fe}(\text{CN})_6\right]^{3-/4-}$ redox probe in 0.1 M KCl for HET measurements. $[Fe(CN)_6]^{3-/4-}$ redox probe was prepared by mixing equal volumes of 2.5 mM Fe(CN) $_6^{3-}$ and 2.5 mM Fe(CN) $_6^{4-}$. The HET rate constants (k_{0bs}^{0}) were calculated using Nicholson's method, which correlates the peak-to-peak separation (ΔE_{p}) to a dimensionless parameter Ψ and in turn to $k_{\rm obs}^{\rm 0}$. The roughness factor was not taken into consideration. The diffusion coefficient used for calculation is $D = 7.26 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ in 0.1 M KCl. Electrocatalytic measurements towards hydrogen evolution, oxygen evolution and oxygen reduction reaction was performed in a threeelectrode system. 5 mL of 0.5 M H₂SO₄ was used for HER measurements and 1.0 M KOH was used for OER and ORR.



Supporting Information

The Supporting Information is available free of charge on the publisher website. EDS obtained from TEM, XRD and XPS survey scan of indium monochalcogenides. Cyclic voltammograms of bare glassy carbon in anodic and cathodic scan direction. Linear sweep voltammograms for oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) of indium monochalcogenides.

Acknowledgements

M.P. acknowledges the financial support of Grant Agency of the Czech Republic (EXPRO: 19-26896X). K.S. was supported by Specific University Research (MSMT No. 20-SVV/2019). Z.S. was supported by Neuron Foundation for scientific support.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Indium monochalcogenides · layered materials · electrochemistry · electrocatalysts · hydrogen generation

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* 2004, *306*, 666-669.
- [2] a) M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, H. Zhang, Nat. Chem., 2013, 5, 263–275; b) X. Chia, M. Pumera, Nat. Cat. 2018, 1, 909.
- [3] a) C. Rao, H. Ramakrishna Matte, U. Maitra, Angew. Chem. Int. Ed. 2013, 52, 13162–13185; Angew. Chem. 2013, 125, 13400–13424; b) A. K. Singha, P. Kumar, D. J. Late, A. Kumar, S. Patel, J. Singh, Appl. Mater. Today 2018, 13, 242; c) T. S. Min, M. Pumera, ACS Nano 2019, 13, 2681.
- [4] a) V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano, J. N. Coleman, Science, 2013, 340, 1226419; b) P. K. Rastogi, S. Sarkar, D. Mandler, Appl. Mater. Today 2017, 8, 44; c) D. Escalera-López, R. Griffin, M. Isaacs, K. Wilson, R. E. Palmer, N. Rees, Appl. Mater. Today 2018, 11, 70.
- [5] a) X. Chia, A. Y. S. Eng, A. Ambrosi, S. M. Tan, M. Pumera, *Chem. Rev.* 2015, *115*, 11941–11966; b) M. Velicky, P. S. Toth, *Appl. Mater. Today* 2017, *8*, 68; c) M. Pumera, Z. Sofer, A. Ambrosi, *J. Mater. Chem. A* 2014, *2*, 8981; d) X. Chia, M. Pumera, *Chem. Soc. Rev.* 2018, *47*, 5602; e) X. Chia, A. Ambrosi, Z. Sofer, J. Luxa, M. Pumera, *ACS Nano* 2015, *9*, 5164; f) X. Chia, A. Ambrosi, P. Lazar, Z. Sofer, J. Luxa, M. Pumera, *Adv. Funct. Mater.* 2016, *26*, 4306418; g) X. Chia, Z. Sofer, J. Luxa, M. Pumera, *Chem. Eur. J.* 2017, *23*, 11719.
- [6] H. L. Zhuang, R. G. Hennig, Chem. Mater. 2013, 25, 3232–3238.
- [7] S. R. Tamalampudi, Y.-Y. Lu, R. Kumar U. R. Sankar, C.-D. Liao, K. Moorthy B. C.-H. Cheng, F. C. Chou, Y.-T. Chen, *Nano Lett.* **2014**, *14*, 2800–2806.
 [8] S. Sucharitakul, N. J. Goble, U. R. Kumar, R. Sankar, Z. A. Bogorad, F.-C.
- [8] S. Sucharitakui, N. J. Goble, U. K. Kumar, R. Sankar, Z. A. Bogorad, F.-C. Chou, Y.-T. Chen, X. P. Gao, *Nano Lett.* **2015**, *15*, 3815–3819.
- [9] B. Čelustka, S. Popović, J. Phys. Chem. Solids 1974, 35, 287–289.
- [10] J. Tabernor, P. Christian, P. O'Brien, J. Mater. Chem. 2006, 16, 2082–2087.
- [11] T. Nishino, Y. Hamakawa, Jpn. J. Appl. Phys. 1977, 16, 1291–1300.
- [12] M. K. Jana, K. Pal, U. V. Waghmare, K. Biswas, Angew. Chem. Int. Ed. 2016, 55, 7792–7796; Angew. Chem. 2016, 128, 7923–7927.
- [13] K. Xu, L. Yin, Y. Huang, T. A. Shifa, J. Chu, F. Wang, R. Cheng, Z. Wang, J. He, *Nanoscale* **2016**, *8*, 16802–16818.

- [14] W. Feng, W. Zheng, W. Cao, P. Hu, Adv. Mater. 2014, 26, 6587–6593.
 - [15] Q. Peng, R. Xiong, B. Sa, J. Zhou, C. Wen, B. Wu, M. Anpo, Z. Sun, Catal. Sci. Technol. 2017, 7, 2744–2752.
 - [16] D. Wei, L. Yao, S. Yang, J. Hu, M. Cao, C. Hu, Inorg. Chem. Front. 2015, 2, 657–661.
 - [17] S. Pal, D. Bose, Solid State Commun. 1996, 97, 725–729.
 - [18] R. Mane, C. Lokhande, Mater. Chem. Phys. 2003, 78, 15-17.
 - [19] M. Calixto-Rodriguez, A. Tiburcio-Silver, A. Ortiz, A. Sanchez-Juarez, *Thin Solid Films* 2005, 480, 133–137.
 - [20] A. Zahab, M. Abd-Lefdil, M. Cadene, Phys. Status Solidi 1990, 117, K103– K106.
 - [21] S. Hussein, Cryst. Res. Technol. 1989, 24, 635-638.
 - [22] A. Harvey, C. Backes, Z. Gholamvand, D. Hanlon, D. McAteer, H. C. Nerl, E. McGuire, A. Seral-Ascaso, Q. M. Ramasse, N. McEvoy, *Chem. Mater.* 2015, 27, 3483–3493.
 - [23] S. M. Tan, C. K. Chua, D. Sedmidubský, Z. Sofer, M. Pumera, Phys. Chem. Chem. Phys. 2016, 18, 1699–1711.
 - [24] J. Luxa, Y. Wang, Z. Sofer, M. Pumera, Chem. Eur. J. 2016, 22, 18810– 18816.
 - [25] N. Gasanly, H. Özkan, A. Aydinli, I. Yilmaz, Solid State Commun. 1999, 110, 231–236.
 - [26] D. Pozo-Zamudio, S. Schwarz, J. Klein, R. Schofield, E. Chekhovich, O. Ceylan, E. Margapoti, A. Dmitriev, G. Lashkarev, D. Borisenko, arXiv preprint arXiv:1506.05619, 2015.
 - [27] M. Zapata-Torres, J. Peña, Y. Mascarenhas, R. Castro-Rodríguez, M. Meléndez-Lira, O. Calzadilla, *Superficies y vací* 2001, 13, 69–71
 - [28] M. Nizametdinova, *Phys. Status Solidi* **1980**, *97*, K9–K12.
- [29] N. Gasanly, A. Aydinli, Solid State Commun. 1997, 101, 797–799.
- [30] J. Jalilian, M. Safari, Phys. Lett. A 2017, 381, 1313-1320.
- [31] A. N. MacInnes, W. M. Cleaver, A. R. Barron, M. B. Power, A. F. Hepp, Adv. Funct. Mater. 1992, 1, 229–233.
- [32] J. Lauth, F. E. Gorris, M. Samadi Khoshkhoo, T. Chassé, W. Friedrich, V. Lebedeva, A. Meyer, C. Klinke, A. Kornowski, M. Scheele, *Chem. Mater.* 2016, 28, 1728–1736.
- [33] O. Balitskii, W. Jaegermann, Mater. Chem. Phys. 2006, 97, 98–101.
- [34] M. Z. M. Nasir, Z. Sofer, A. Ambrosi, M. Pumera, Nanoscale 2015, 7, 3126–3129.
- [35] H. S. Toh, A. Ambrosi, C. K. Chua, M. Pumera, J. Phys. Chem. C 2011, 115, 17647–17650.
- [36] M. Zafir Mohamad Nasir, Z. Sofer, M. Pumera, ChemElectroChem 2015, 2, 1713–1718.
- [37] Y. Wang, Z. Sofer, J. Luxa, M. Pumera, Adv. Mater. Interfaces 2016, 3, 1600433.
- [38] X. Chia, A. Ambrosi, P. Lazar, Z. Sofer, M. Pumera, J. Mater. Chem. A 2016, 4, 14241–14253.
- [39] X. Chia, Z. k. Sofer, J. Luxa, M. Pumera, ACS Appl. Mater. Interfaces 2017, 9, 25587–25599.
- [40] Y. Liftman, M. Albeck, J. Goldschmidt, C. Yarnitsky, *Electrochim. Acta* 1984, 29, 1673–1678.
- [41] E. Mori, C. Baker, J. Reynolds, K. Rajeshwar, J. Electroanal. Chem. Interfacial Electrochem. 1988, 252, 441–451.
- [42] R. S. Nicholson, Anal. Chem. 1965, 37, 1351-1355.
- [43] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.* 2010, *110*, 6446–6473.
- [44] J. Barber, Chem. Soc. Rev. 2009, 38, 185–196.
- [45] J. S. Spendelow, A. Wieckowski, Phys. Chem. Chem. Phys. 2007, 9, 2654– 2675.
- [46] R. Eisenberg, H. B. Gray, Inorg. Chem. 2008, 47, 1697–1699.
- [47] Y. Jiao, Y. Zheng, M. Jaroniec, S. Z. Qiao, Chem. Soc. Rev. 2015, 44, 2060– 2086.

Manuscript received: March 12, 2019 Revised manuscript received: April 3, 2019 Version of record online:

CHEMCATCHEM Full Papers



FULL PAPERS

Hot property! We studied and compared the inherent electrochemical properties as well as the electrocatalytic performances towards hydrogen evolution, oxygen evolution and oxygen reduction reaction of indium monochalcogenides (InS, InSe and InTe).



Y. Wang, K. Szökölová, Dr. M. Z. M. Nasir, Prof. Z. Sofer, Prof. M. Pumera*

1 – 10

Electrochemistry of Layered Semiconducting A^{III}B^{VI} Chalcogenides: Indium Monochalcogenides (InS, InSe, InTe)