Modulation of the Electronic Structure of IrSe$_2$ by Filling the Bi Atom as a Bifunctional Electrocatalyst for pH Universal Water Splitting

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1. Introduction

Owing to the depletion of fossil fuels, their excessive consumption and the severe environmental problems are becoming a challenge to search for affordable sustainable energy. Hydrogen appears to be a promising candidate and eco-friendly energy source in future, which can be potentially and ideally produced from the electrochemical dissociation of water. In general, the overall reaction of water splitting consists of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). However, HER and OER are intrinsically efficiency-limited, requiring the efficient electrocatalysts to accelerate the reaction rate and reduce the energy consumption. This irreconcilable contradiction has been unmet mainly because the state-of-the-art electrocatalysts hardly have the best performance in the same electrolyte for both HER and OER. For example, Pt-based materials remain the most efficient metal-based electrocatalysts, while Ir- or Ru-based electrocatalysts are still the benchmark for OER. However, Ir-based homologues are unsatisfactory during the HER process. Therefore, the development of bifunctional electrocatalysts for various electrolyte systems is an urgent issue in this field.

Transition metal dichalcogenides (TMDs) with open structure appears to be a promising candidate and eco-friendly energy source in future, which can be potentially and ideally produced from the electrochemical dissociation of water. In general, the overall reaction of water splitting consists of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). However, HER and OER are intrinsically efficiency-limited, requiring the efficient electrocatalysts to accelerate the reaction rate and reduce the energy consumption. This irreconcilable contradiction has been unmet mainly because the state-of-the-art electrocatalysts hardly have the best performance in the same electrolyte for both HER and OER. For example, Pt-based materials remain the most efficient metal-based electrocatalysts, while Ir- or Ru-based electrocatalysts are still the benchmark for OER. However, Ir-based homologues are unsatisfactory during the HER process. Therefore, the development of bifunctional electrocatalysts for various electrolyte systems is an urgent issue in this field.

Although IrSe$_2$ is a superior oxygen evolution catalyst, its electronic structure lacks active sites for hydrogen production and hinders its use as a bifunctional catalyst. The intercalation of Bi atoms into the IrSe$_2$ framework regulates its electronic structure with the improvement of performance. Herein, novel bismuth inserted iridium-based selenide (BiIr$_4$Se$_8$) is synthesized via solid-state reaction. Interestingly, BiIr$_4$Se$_8$ exhibits impressive activities with dual functionality in pH-universal electrolytes. It achieves small overpotentials at 10 mA cm$^{-2}$ toward hydrogen evolution (85 mV in acid and 252 mV in alkali) and oxygen evolution (379 mV in acid and 364 mV in alkali), which overmatches the benchmarking noble metal-based electrocatalysts. When served as the bifunctional electrocatalyst to drive a water electrolyzer, BiIr$_4$Se$_8$ affords 10 mA cm$^{-2}$ at a voltage of 1.56 and 1.52 V$_{RHE}$ in 0.5 M H$_2$SO$_4$ and 1 M KOH, far exceeding the Pt/C||RuO$_2$ and other published materials. Theoretical calculations show that a narrow bandgap is obtained due to the induced intermediate band derived from the combination of the $p$ orbitals of Bi atoms and structure reconstruction, which promotes the electrocatalytic performance. This research introduces a new strategy to design channel structures and sheds light on their applications for water splitting.
enhanced performances. The interaction strength between the interlayer spacing can be regulated via the insertion of dopants or the carrier injection to the interlayer. Along with structure adjustments, the localization characteristics and transfer paths of carriers have changed, thus leading to the enhanced performance. For example, Pd atoms are disorderly inserted into the NbS\textsubscript{2} lattice to achieve atomic dispersal of noble metal Pd. The dispersive electron distribution and elevated density of state near Fermi level by Pd 4d and S 3p hybridization further improve the electrocatalytic performance beyond NbS\textsubscript{2}.\textsuperscript{15} Semiconductive Ir\textsubscript{2}Se\textsubscript{4} with 1D channel is another important TMD, and its open framework can be performed as a structural motif to design new functional materials. By introducing heteroatoms to occupy open structural channels and modify its electronic structure, it may bring new potential applications.

Here, we report the synthesis of bismuth inserted iridium-based selenide (BiIr\textsubscript{4}Se\textsubscript{8}) for the first time. Its structure is determined by single-crystal X-ray diffraction (XRD), which possesses a channel crystal structure and unique delocalized electronic states along the b-axis. Apart from the novel structure, metallic BiIr\textsubscript{4}Se\textsubscript{8} can be used in overall water splitting as an efficient electrocatalyst. BiIr\textsubscript{4}Se\textsubscript{8} achieves small overpotentials toward both the HER and OER, which overmatches the benchmarking noble metal-based electrocatalysts. When served as cathode and anode materials to drive a water electrolyzer, it affords 10 mA cm\textsuperscript{-2} at a cell voltage of 1.56 and 1.52 V in 0.5 M H\textsubscript{2}SO\textsubscript{4} and 1 M KOH solution, respectively, far exceeding the performance of Pt/C||RuO\textsubscript{2} and published materials before. The current research not only introduces a new route for the synthesis of ternary iridium–based chalcogenides but also develops its application as a bifunctional electrocatalyst for overall water splitting.

2. Results and Discussion
2.1. Structural Characterization of BiIr\textsubscript{4}Se\textsubscript{8}

The crystal structure of BiIr\textsubscript{4}Se\textsubscript{8} was determined by single-crystal XRD. BiIr\textsubscript{4}Se\textsubscript{8} belongs to the monoclinic system with a space group of C\textsubscript{2}2\textsubscript{1}m (No. 12). As shown in Figure 1, both Ir\textsubscript{8}Se\textsubscript{2} and BiIr\textsubscript{4}Se\textsubscript{8} feature 1D channel structures and have Se–Se bonds in the structures. In the structure of BiIr\textsubscript{4}Se\textsubscript{8}, Bi atoms reside in the open channel of Ir\textsubscript{8}Se\textsubscript{2} framework along the b-axis. The hollow covalent framework is composed of four edge-sharing [IrSe\textsubscript{4}] octahedra double chains along the b-axis. Every two-neighboring edge-sharing [IrSe\textsubscript{4}] octahedra chains were connected by edge-sharing and Se–Se bonds. The average Ir–Se bond distance in BiIr\textsubscript{4}Se\textsubscript{8} is 2.476(0) Å, which is nearly the same as IrSe\textsubscript{2}. The Se–Se bond distance is 2.591(5) Å, which is greater than IrSe\textsubscript{2}.\textsuperscript{16} The inserting of Bi atoms into Ir\textsubscript{8}Se\textsubscript{2} framework is equivalent to electron injection, which makes the Se atoms in BiIr\textsubscript{4}Se\textsubscript{8} at a higher energy level, resulting in an increase in the Se–Se bond distance.

With weak bonding along the b-axis, much larger displacement is found in Bi site (Figure S1a, Supporting Information), and the Bi atoms reside in the channel of [Ir\textsubscript{8}Se\textsubscript{2}] octahedra framework. Bi atoms are bonded with four Se atoms to form [BiSe\textsubscript{4}] paralellogram. Such a coordination leads to the violent vibration of Bi atoms along the channel (dynamic disorder\textsuperscript{15}), resulting in a larger thermal displacement. The thermal displacement U\textsubscript{22} = 0.290(6) Å\textsuperscript{2} along the b-axis is about 7 times bigger than U\textsubscript{11} = 0.044(1) Å\textsuperscript{2}. Therefore, we split one Bi site (2a) into three Bi sites (2a, 4g, and 4g) in BiIr\textsubscript{4}Se\textsubscript{8} during the crystal structure refinement process. It can be seen that the flexible Bi atoms are inserted into the Ir\textsubscript{8}Se\textsubscript{2} structure, and the Ir\textsubscript{8}Se\textsubscript{2} skeleton is rearranged, thereby resulting a stable frame with a larger channel size. Meanwhile, the introduction of Bi may lead to unusual electrical behaviors.

The well-crystallized BiIr\textsubscript{4}Se\textsubscript{8} was synthesized with rod-like morphology, as shown in the inset of Figure 2a. To check the purity of BiIr\textsubscript{4}Se\textsubscript{8} powder, the powder X-ray diffractogram (PXRD) pattern was refined using Fullprof Software,\textsuperscript{16} in which the simulated curve fits the experimental data well. BiIr\textsubscript{4}Se\textsubscript{8} adopts C\textsubscript{2}2\textsubscript{1}m space group with a = 16.0949(5) Å, b = 3.7272(1) Å, c = 11.2506(3) Å, and β = 126.8389(8)\degree, which is consistent with single-crystal structure. In terms of electrical resistivity for BiIr\textsubscript{4}Se\textsubscript{8} powder, Figure 2b shows its resistivity increases slowly from 300 to 60 K, and then increases rapidly below 50 K, indicating a semiconducting behavior. The resistivity of BiIr\textsubscript{4}Se\textsubscript{8} is 0.0012 Ω m, which is much smaller than Ir\textsubscript{8}Se\textsubscript{2} (0.11 Ω m) at room temperature. To obtain the activation energy, Arrhenius-type equation\textsuperscript{17} was fitted to the temperature-dependent resistivity data. The activation energy was determined to be 30 meV for BiIr\textsubscript{4}Se\textsubscript{8}, which is smaller than that of Ir\textsubscript{8}Se\textsubscript{2} (90 meV).\textsuperscript{14} The energy-dispersive X-ray spectroscopy (EDS) indicates the existence of Bi, Ir, and Se elements for BiIr\textsubscript{4}Se\textsubscript{8} crystal (Figure S3, Supporting Information). According to the semi-quantitative analysis, the molar ratio of Bi to Ir is 1:3.20 for BiIr\textsubscript{4}Se\textsubscript{8} crystal, approaching the results from refined crystal structure.
To use BiIr$_2$Se$_8$ as electrocatalyst, it should be downsized via high energy ball milling. The elemental ratio of Ir to Bi for powder is slightly higher than the value for crystal confirmed by the result of Table S8 and S9, Supporting Information, which is due to the high energy ball-milling process. The transmission electron microscopy (TEM) images of BiIr$_2$Se$_8$ powders further demonstrate its microstructures. The corresponding high-resolution transmission electron microscopy (HRTEM) image (Figure S5b, Supporting Information) reveals the distinct lattice fringes with a spacing of 2.26 and 3.03 Å for the (203) and (313) planes, respectively, and the selected area electron diffraction (SAED) result also confirms its high crystallization characteristics. The Bi, Ir, and Se elements in BiIr$_2$Se$_8$ are distributed evenly with no apparent separations or aggregations (Figure S5c, Supporting Information). X-ray photoelectron spectroscopy (XPS) is conducted to determine the chemical composition and valence state. The chemical composition result via XPS was BiIr$_{3.53}$Se$_{5.92}$, which is consistent with EDS results (Table S10, Supporting Information). The high-resolution Bi 4f spectrum (Figure S5d, Supporting Information) can be well fitted into four peaks at 158.04, 158.67, 163.36, and 164.03 eV, corresponding to Bi 4f$_{5/2}$ and 4f$_{7/2}$, respectively. The existence of Bi–O peaks attribute to the slight oxidation of BiIr$_2$Se$_8$ powder during the high energy ball-milling process. And the fact that there is no observation of oxide peaks indicates that the oxidized species on the surface is mainly amorphous phase. In Ir 4f XPS spectrum (Figure S5e, Supporting Information), two major peaks at 61.43 and 64.44 eV can be identified as Ir 4f$_{5/2}$ and 4f$_{7/2}$. The existence of Se element is confirmed by the peaks of 55.42 eV (Se 3d), 161.51 eV (Se 3p$_{3/2}$), and 167.18 eV (oxidized Se).

2.2. Electrocatalytic Performances of BiIr$_2$Se$_8$

The electrocatalytic performances of BiIr$_2$Se$_8$ for HER are tested by a typical three-electrode configuration. To make the comparison, the corresponding catalytic activities of IrSe$_2$, Bi$_2$Se$_3$, and commercial Pt/C (20 wt.%) are also tested in our experiment. BiIr$_2$Se$_8$ exhibits a prominent activity toward HER, much higher than those of IrSe$_2$ and Bi$_2$Se$_3$ (Figure 3a,b). In fact, BiIr$_2$Se$_8$ exhibits a current density of 10 mA cm$^{-2}$ at an overpotential ($\eta$) of 85 and 252 mV in 0.5 M H$_2$SO$_4$ and 0.1 M KOH, respectively. Two electrolytes are selected as the representative environment, which are also commonly used in literatures. However, IrSe$_2$ needs a much higher $\eta$ (301 mV in acid) to reach 10 mA cm$^{-2}$. By extracting the slope from Tafel plots, the catalytic activities can be further understood (Figure S7, Supporting Information). The lowest Tafel slope of 75.3 mV dec$^{-1}$ is obtained for BiIr$_2$Se$_8$ between IrSe$_2$ (129.6 mV dec$^{-1}$) and Bi$_2$Se$_3$ (248.2 mV dec$^{-1}$) in 0.5 M H$_2$SO$_4$, indicating its excellent activity. From the slope it is concluded that the reaction follows a Volmer–Heyrovsky (Volmer: $\text{H}^+ + \text{e}^- \rightarrow \text{H}_2$ in acid, $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2 + \text{OH}^-$ in base; Heyrovsky: $\text{H}_2\text{O} + \text{e}^- + \text{H}^+ \rightarrow \text{H}_2 + \text{OH}^-$ in base) mechanism as rate determining step. To make the comparison, the corresponding catalytic activities of IrSe$_2$, Bi$_2$Se$_3$, and RuO$_2$ as a comparison. BiIr$_2$Se$_8$ displays a lower onset potential (1.48 V$_{\text{RHE}}$ in acid and 1.42 V$_{\text{RHE}}$ in alkali) than that of Bi$_2$Se$_3$ and higher activity toward OER than that of IrSe$_2$. Even BiIr$_2$Se$_8$ is comparable with RuO$_2$ with a larger current density at the same overpotential and low onset potential. More specifically, driving a current density of 10 mA cm$^{-2}$, BiIr$_2$Se$_8$ demands overpotentials of 379 mV in acid and 364 mV in alkali, which are far superior to RuO$_2$. In terms of the kinetics, Tafel slope of BiIr$_2$Se$_8$ (89.8 mV dec$^{-1}$) is smaller than IrSe$_2$ and RuO$_2$ in acid; meanwhile, BiIr$_2$Se$_8$ also presents smaller value of 64.0 mV dec$^{-1}$ than those of IrSe$_2$, Bi$_2$Se$_3$, and RuO$_2$ in alkali. When analyzing the kinetic parameters for BiIr$_2$Se$_8$, a Tafel slope of 89.8 mV dec$^{-1}$ in acid and 64.0 mV dec$^{-1}$ in alkali solution can be found. In the literature, different mechanisms have been discussed based on the value of
Tafel slope. The electrochemical oxide path, for instance,\textsuperscript{[20]} proceeds via the formation of $\text{M}–\text{OH}$, the oxidation to $\text{M}–\text{O}$, and the final recombination of two adsorbed $\text{O}_{\text{ad}}$. Another model\textsuperscript{[21]} is based on the discharge of an $\text{OH}^-$ ion and the succeeding hydrogen peroxide formation, and has gained attention on iron-doped nickel electrodes.\textsuperscript{[22]} Lyons and Brandon found that the activity strongly depends on the amount and composition of the active materials but that the mechanism of the OER stays the same. The electrochemical surface area (ECSA) values are shown in Figure S8, Supporting Information. BiIr$\text{Se}_8$ provides a larger ECSA of 2.45 cm$^2$ in the acid than that of basic electrolyte (1.89 cm$^2$). And it exhibits a higher surface roughness and exposes more active sites than that of Ir$\text{Se}_8$, leading to the enhanced electrochemical performance.

To clarify the practical possibility for application, the performance of overall water splitting is researched in a two-electrode configuration. Although the BiIr$_4\text{Se}_8||$BiIr$_4\text{Se}_8$ electrolyzer shows a larger onset potential in acid, its current density surpasses the Pt/C||RuO$_2$ electrolyzer over 35 mA cm$^{-2}$ (Figure 3d). In 1 M KOH solution, our electrolyzer has similar performance with noble metal–based electrolyzer (Figure S9a, Supporting Information). These results indicate BiIr$_4\text{Se}_8$ is a multifunctional and efficient electrolyzer during water splitting process, and it has the potential to constitute the symmetrical electrolyzer in various electrolytes. Its catalytic activity and stability are better than previously reported bifunctional electrolycatalysts\textsuperscript{[23]} (see in Table S12, Supporting Information, and radar chart of Figure 3f). The volumes of $\text{H}_2$ and $\text{O}_2$ are recorded at intervals of 60 min through the water–gas displacement method (Figure S10, Supporting Information). The volume ratio (2.05) of hydrogen to oxygen is close to the theoretical ratio, which reveals its nearly 100% Faradaic yield for water splitting in acid.

In addition, BiIr$_4\text{Se}_8||$BiIr$_4\text{Se}_8$ electrolyzer shows excellent stability during 12 h for overall water splitting (Figure 3e). By contrast, Pt/C||RuO$_2$ cannot hold the stable potential under acid media due to the instability nature of carbon matrix and RuO$_2$. Although the commercial Pt/C catalyst possesses great stability in acid electrolyte (Figure 3c), RuO$_2$ is unstable and apt to be oxidized soluble species. From linear sweep voltammogram (LSV) curves of corresponding initial and long-term tests, BiIr$_4\text{Se}_8||$BiIr$_4\text{Se}_8$ has a more stable performance than the noble metal–based electrolyzer. Even compared with the performances of many representative water splitting catalysts, it has smaller overpotential at 10 mA cm$^{-2}$ in both acidic and basic electrolytes, indicating that BiIr$_4\text{Se}_8$ can be a promising candidate for bifunctional electrolycatalyst in various conditions. It also exhibits great durability in 1 M KOH, which is more favorable than that of commercial Pt/C||RuO$_2$ (Figure S9b, Supporting Information). Apart from the conventional electrochemical workstation, the water-splitting electrolyzer could be driven by an AA battery with the open-circuit voltage of 1.5 V (Figure S11, Supporting Information). To investigate the compatibility of BiIr$_4\text{Se}_8||$BiIr$_4\text{Se}_8$ electrolyzer, a solar-driven water-splitting system is built by connecting cathode and anode materials with home-made solar cells in tandem under AM1.5 illumination (Figure S12, Supporting Information). The system can convert solar energy into hydrogen energy, making the utilization of clean energy more practicable and alleviating the energy crisis effectively.
To further investigate the durability of BiIr$_2$Se$_8$ after the long-term electrolysis, various characterization methods (such as XRD, Raman, XPS, and TEM) are performed. The XRD patterns after aging show that the initial XRD peaks for BiIr$_2$Se$_8$ still maintain with the additional signals of graphene substrate (Figure S13, Supporting Information). There are obvious Raman peaks from graphene substrate and underlying BiIr$_2$Se$_8$ electrocatalyst in the 1 m KOH and 0.5 m H$_2$SO$_4$, respectively, thus implying its stability in pH universal electrolytes. After long-term electrolysis for both acidic and basic media, BiIr$_2$Se$_8$ maintains the valence states of Ir, Bi, and Se with the initial samples proved by the XPS results (Figure S14, Supporting Information) and its morphology confirmed by the TEM image with the SAED pattern in Figure S15, Supporting Information. And the catalyst possesses the amorphous layer and crystalline core confirmed by the HRTEM image.

2.3. Theoretical Calculation for BiIr$_2$Se$_8$

To deeply understand the unique property of BiIr$_2$Se$_8$, we applied the first-principle calculation to investigate its electronic property, together with IrSe$_2$ for comparison. The projected electronic density of state (PDOS) and electronic distribution results show that IrSe$_2$ and BiIr$_2$Se$_8$ are both semiconductors. The bandgap of IrSe$_2$ is 0.45 eV, larger than that of BiIr$_2$Se$_8$ (0.15 eV). As is well known, the increase of bandgap for electrocatalyst will hinder electronic transportation and result in poor electro-catalytical performance. The PDOS of IrSe$_2$ also provides that the valence band maximum (VBM) is mainly contributed by p orbital of Se, and conduction band minimum (CBM) is consisted of d orbital of Ir, similar to other chalcogenides. However, it can be found that VBM and CBM of BiIr$_2$Se$_8$ are mainly contributed by p orbital of Bi, which suggests that the smaller bandgap may origin from the Bi atom implanting. It should be noted that compared with IrSe$_2$, intermediate electronic states between Ir 5d and Se 3p orbitals generated by the hybridization of Bi p and Se p orbitals lead to the smaller bandgap of BiIr$_2$Se$_8$.

To confirm this result, the electronic density distribution near Fermi level for these two structures is examined (Figure 4c,d). As for IrSe$_2$, the electrons near Fermi level are strongly localized at Se and Ir atoms of Ir—Se bonds, while none at Se—Se bonds. This localized behavior is consisting with a large bandgap. Except for electron distribution at Ir atoms, a large number of electrons are localized at Bi atom for BiIr$_2$Se$_8$. Furthermore, these localized electrons at Bi atoms can connect with each other forming an electronic string, leading to a delocalized electron state like electron gas in metal. Therefore, a smaller bandgap and faster electronic transport will achieve in BiIr$_2$Se$_8$, which can be deduced that BiIr$_2$Se$_8$ has a better electrocatalytic performance than IrSe$_2$.

3. Conclusion

In summary, a novel iridium-based selenide with monoclinic structure and specific electronic structure is synthesized using solid-state reaction. Its unprecedented structure and uniform elemental distribution are characterized by single-crystal XRD. BiIr$_2$Se$_8$ possesses diversity structure with the specific Se—Se bonds. Based on its unique property, it can be used as a bifunctional water splitting electrocatalyst in the pH universal electrolytes. When served as cathode and anode electrodes, BiIr$_2$Se$_8$ exhibits 10 mA cm$^{-2}$ at 1.56 and 1.52 V$_{RHE}$ in 0.5 m H$_2$SO$_4$ and 1 m KOH, far exceeding the performance of Pt/C/RuO$_2$ and published materials. This study not only opens a new way for the synthesis of bifunctional water splitting electrocatalyst in the pH universal electrolyte, but also has some enlightenment for its potential commercial application.

4. Experimental Section

Chemicals and Materials: Bi, Ir, and Se powders were purchased from Macklin Inc., and stored in glove box filled with Ar. H$_2$SO$_4$, KOH, and Super P were purchased from Sinopharm Chemical Reagent Company.
Preparation of BiIr$_2$Se$_8$ Single Crystal and Powder: BiIr$_2$Se$_8$ single crystal was synthesized via a routine high-temperature solid-state reaction method. Stoichiometric amounts of Bi, Ir, and Se powders were weighed and mixed to yield 2g for BiIr$_2$Se$_8$. They were fully ground, pressed into a pellet, and fire-sealed in evacuated silica tubes. Then the tube was placed in a programmable temperature-controlled muffle furnace, and the temperature rose slowly to 1175 K during 10 h, and maintained at that temperature for 5 days. Later, the furnace was shut down and the sample was cooled down to room temperature. The product was made of shiny, rod-like crystals, and several suitable single crystals were selected to do the single-crystal diffraction. To carry out electrochemical measurement, the powders were synthesized by ball milling for 3 h.

Characterizations: The PXRD data were collected by a powder diffractometer (Bruker D8 Advance). The data were gathered in a $θ$–$2θ$ scan range of 5–90° at a rate of 6° min$^{-1}$. Suitable rod-like single crystal was selected. Lattice cell parameters determination and data collection were done on a Bruker D8 Venture. The integration of raw data and the semi-empirical absorption corrections were done using the program SADABS and SADABS software, respectively. Crystal structure of BiIr$_2$Se$_8$ was solved by direct methods, and then refined by full matrix least-squares methods on F$^2$ using SHELXL. Much larger displacement was found in Bi site. The Bi atoms reside in the channel of framework formed by [Ir$_2$Se$_6$] octahedra, and there is no bonding along channel direction, which leads to the larger thermal displacement. Therefore, one Bi atom was split into five Bi atoms in BiIr$_2$Se$_8$, to reduce the large thermal displacement. Specific details of the data collection, crystallographic parameters, and selected atomic distances are shown in Table S1–S5, Supporting Information. Raman spectra were collected via Raman microscope with laser excitation at 532 nm. XPS data were recorded with an Axis Ultra imaging photoelectron spectrometer. The C 1s line (284.8 eV) was used as the reference to calibrate the binding energies. A JEM-2100 electron microscope (JEOL, Japan) operating at 200 kV was used for the TEM investigations. The microtopography and compositions were detected by the scanning electron microscopy (SEM, JSM-6510). The optical absorption spectra of samples were conducted on the UV–vis–near-infrared (NIR) spectrometer (Hitachi U4100).

Electrical Conductivity and Activation Energy: BiIr$_2$Se$_8$ sample was pressed into a pellet, annealed at 300°C for 5 h, and then the pellet was incised into rectangle shape. The resistivity data for BiIr$_2$Se$_8$ sample were collected using four-probe method on physical property measurement system (PPMS) (Quantum Design). Arrhenius-type equation with linear form was used to fit the temperature-dependent resistivity data from 300 to 200 K to determine the activation energy $E_a$. In $\rho$ was plotted versus 1/T.

$$\rho = \rho_0 \exp \left( \frac{E_a}{k_B T} \right)$$

$$\ln \rho = -\frac{E_a}{k_B T} + \ln \rho_0$$

where $\rho$, $E_a$, and $k_B$ are the resistivity, activation energy, and Boltzmann’s constant, respectively.

Electrochemical Measurements: All electrochemical tests were performed with CHI 660 E Electrochemical Workstation. Rotating disk electrode (RDE) modified with catalyst film is the working electrode (WE) and Pt wire (Sigma-Aldrich) served as counter electrode. As reference electrode, a Hg/HgO (1 M NaOH) in base (0.1 M KOH) and an Ag/AgCl (1 M KCl) in acid (0.5 M H$_2$SO$_4$) were used. The slurry of catalyst (concentration: 5.0 mg mL$^{-1}$) was prepared by dispersing target materials in Nafton/alcohol solution (0.5 wt%), and then sonication for 30 min. Suitable slurry (10 μL) was dropped onto the RDE, the loading mass of catalyst film is 250 μg cm$^{-2}$. The WE was rotated at 2000 rpm to minimize mass transport limitations. Catalyst blocking by bubbles could be circumvented and resulting bubble overpotential could be minimized. All the electrolytes during the HER or OER were purged N$_2$ or O$_2$ for 30 min. Electrochemical aging was performed between $-0.43$ and 1.77 V$_{RHE}$ using a scan rate of 50 mV s$^{-1}$ until the cyclic voltammetry (CV) curves remain unchanged. LSV in base (0.1 M KOH) and in acid (0.5 M H$_2$SO$_4$) was collected at the scan rate of 10 mV s$^{-1}$ and rotating rate of 2000 rpm. To compare with the benchmark material, the commercial Pt/C (20 wt%) and RuO$_2$ were tested under the same condition. Durability measurements using the chronoamperometry were performed for 12 h at 50 mA cm$^{-2}$ and rotational speed of 2000 rpm. The electrochemical surface area (ECSA) was calculated based on the double-layer capacitance ($C_D$) referred to the literature before. The Faradic efficiency was calculated as the ratio of the amount of H$_2$ or O$_2$ during the experiments to the expected values based on theoretical conditions. The electrochemical impedance spectroscopy (EIS) was measured from 10$^{-2}$ to 10$^5$ Hz with an amplitude of 5 mV versus reference electrode. The ohmic contribution was estimated from the Nyquist plots. In base electrolyte, the standard electrode potential of Hg/HgO/0.1 M KOH (MMO) was 0.098 V. The overpotentials ($\eta_{OER}$ and $\eta_{HER}$) were calculated using Equation (3, 4).

$$\eta_{OER} = \frac{E_{applied} + 0.098 + 0.059 \times pH - i \times R}{C_0}$$

$$\eta_{HER} = \frac{0 - (E_{applied} + 0.098 + 0.059 \times pH - i \times R)}{C_0}$$

where $E_{applied}$ is the applied potential (vs MMO) in 0.1 M KOH, R is the compensated resistance, i is the measured current, and pH is 13 for 0.1 M KOH. The current densities were normalized by dividing geometric surface areas of RDE (0.1963 cm$^2$).

In acid electrolyte, the standard electrode potential of Ag/AgCl/1.0 M KCl was 0.222 V. The overpotentials $\eta_{OER}$ and $\eta_{HER}$ were calculated using Equation (5, 6).

$$\eta_{OER} = \frac{E_{applied} + 0.222 + 0.059 \times pH - i \times R}{C_0}$$

$$\eta_{HER} = \frac{0 - (E_{applied} + 0.222 + 0.059 \times pH - i \times R)}{C_0}$$

where $E_{applied}$ is the applied potential in 0.5 M H$_2$SO$_4$, and pH is 0 for 0.5 M H$_2$SO$_4$.

The overall water splitting measurement was performed in a conventional two electrodes system via the sample/3D graphene as both cathode and anode. Ink (1 mL) was dripped to 1 cm$^2$ 3D graphene current collector (loading mass: 2.5 mg cm$^{-2}$). This kind of current collector possesses large surface area and superior electroconductibility; thus, it is an excellent substrate for overall water splitting measurement. LSV curves were collected from 1.2 to 2 V for the polarization curves. For the comparison, the benchmark materials (commercial Pt/C as cathode and RuO$_2$ as anode) are tested under the same condition. The stability test was fixed at a constant potential of 1.74 V. Theoretical Calculation: All the calculated results are used by the density functional theory (DFT) method implemented in the Vienna Ab initio Simulation Package (VASP) program. Perdew–Burke–Ernzerhof (PBE) functional is performed for the exchange–correlation term based on the generalized gradient approximation (GGA). We set the energy cutoff at about 500 eV for the plane wave basis, where the accuracy is checked by higher cutoffs. The convergence criterion of the self-consistency process is set to 10$^{-6}$ eV between two electronic steps. The Brillouin zone was sampled by the Monkhorst-Pack scheme with a $Γ$-centered grid of $2 × 10 × 6$ k points for IrSe$_2$ and $4 × 4 × 3$ k points for BiIr$_2$Se$_8$ primitive cell. The structures are fully relaxed before calculating the relevant properties until the residual force is less than 0.001 eV Å$^{-1}$ on each atom. The van der Waals (vdW) interaction is also considered and corrected by DFT-D3 approach. As pure PBE seriously underestimates the bandgap, a more accurate functional based on HSE06 is used to describe the electronic property. First, it can be found that IrSe$_2$ owns the Pnma space group, consisting of 8 Ir atoms and 16 Se atoms in the unit cell. Unlike general chalcogenides, this structure contains Se-Se bonds and channels inside. The relaxed lattice parameters of IrSe$_2$ are about $a = 20.97$ Å, $b = 3.77$ Å, and $c = 5.95$ Å. According to the coordination environment of Se atom, the bond distance of $\text{Ir}–\text{Se}$ can be classified into two types (fourfold Se atom of 2.44–2.48 Å and threefold Se atom of 2.52–2.56 Å), and Se-Se bond is about 2.58 Å. As for BiIr$_2$Se$_8$, it owns the C2/m group, containing 1 Bi atom, 4 Ir atoms, and 8 Se atoms in the primitive cell. The main difference is that the Bi atom is induced into the empty channels of IrSe$_2$ to form BiIr$_2$Se$_8$ by experiment. The corresponding lattice parameters of BiIr$_2$Se$_8$ are about $a = b = 8.27$ Å, and $c = 20.97$ Å.
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Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
This work was financially supported from the China Postdoctoral Science Foundation (grant no. 2019M650173), the Certificate of postdoctoral research grant in Henan province, the National Natural Science Foundation of China (grant nos. 21871008 and 21801247), and the Key Research Program of Frontier Chinese Academy of Sciences (grant no. QYZDJ-SSW-JSC013).

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that supports the findings of this study are available in the supplementary material of this article.

Keywords
bifunctional electrocatalysts, BiIr₄Se₈, electronic structures, intercalations, water splitting

Received: November 13, 2020
Revised: December 19, 2020
Published online: May 5, 2021

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