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# From Molecular 2Fe-2Se Precursor to FeSe<sub>2</sub> Acting as Highly Efficient Electrocatalyst for Overall Water-Splitting

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**Abstract:** A highly active  $FeSe_2$  electrocatalyst for durable overall water-splitting has been prepared from a molecular 2Fe-2Se precursor. The as-synthesized  $FeSe_2$  was electrophoretically deposited on nickel foam and applied for both oxygen (OER) and hydrogen evolution reaction (HER) in alkaline media. When used as an oxygen-evolution electrode, merely 245 mV of overpotential was achieved at a current density of 10 mAcm<sup>2</sup>, representing outstanding catalytic activity and stability due to the formation of  $Fe(OH)_2/FeOOH$  active sites at the surface of  $FeSe_2$ . Remarkably, the system is also favorable for HER. Moreover, an overall water-splitting set up was fabricated using a two-electrode cell displaying low cell voltage and high stability. In summary, the first iron selenide material is reported which can be used as superiorly active bifunctional electrocatalyst for OER and HER as well as overall water-splitting.

Today's one of the most fundamental scientific and technological challenge remains in the development of alternative clean energy sources to the current fossil based fuels.<sup>[1]</sup> Large scale production of H<sub>2</sub> through splitting of water is the key to generate chemical fuels that are clean and sustainable.  $\ensuremath{^{[2]}}$  While several efficient catalysts are accessible for the hydrogen evolution reaction (HER),[3] the oxygen evolution reaction (OER) is considered to be the bottle-neck to watersplitting as it comprises of multiple proton coupled electron transfer (PCET) steps involving high energy intermediates.<sup>[2]</sup> The current state of-the-art catalysts that perform both OER and HER are based on noble metals, which are unsuitable for practical large-scale applications owing to their scarcity and high cost.<sup>[4]</sup> Tremendous research efforts have been devoted in this direction to design inexpensive catalysts based on earthabundant transition metals that can perform OER and HER with very high efficiency.<sup>[5]</sup> This includes cheap transition-metal based materials, including oxides, [2a, 2c-f] chalcogenides[6] and pnictides<sup>[6b,7]</sup> that have been explored as alternative OER, HER

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Supporting information for this article is given via a link at the end of the document. and overall water-splitting catalysts.

Although numerous transition-metal selenides are known to be efficient for HER, high performance OER catalysts based on selenides were discovered only very recently.<sup>[6]</sup> Early 2017, Gao et al. reported on using FeSe<sub>2</sub> for OER with considerable low overpotential of 330 mV at a current density of 10 mAcm<sup>-2</sup>.<sup>[8]</sup> In accordance with previous observations, however, the same catalyst seems unsuitable for HER.<sup>[6b]</sup> While there is one iron sulfide that has been identified with moderate activity for OER and HER,<sup>[6c]</sup> there is – as of now and to the best of our knowledge – no report on an iron selenide material that has been utilized for overall water-splitting catalysis. This prompted us to investigate whether the size, structural, morphological, and the electronic properties of FeSe<sub>2</sub> can be fine-tuned to achieve not only high performance for bifunctional OER and HER but also for overall water-splitting.

Usually metal chalcogenide materials are synthesized by conventional synthetic routes (e.g. precipitation method) leading to a random distribution of aggregates and an infinite number of nanostructures among which only few are catalytically active. [9a-b] To overcome this, the "low-temperature molecular precursor" approach is a convenient method to control the composition and size distribution of nanomaterials and to enable high catalytic activity.<sup>[9c-g]</sup> Applying this concept, the synthesis of FeSe<sub>2</sub> from a molecular 2Fe-2Se precursor that shows superior catalytic activity for both OER and HER is promising. The 2Fe-2Se cluster core in the latter represents a heavy analog of 2Fe-2S clusters in iron-sulfur proteins responsible for multi-electron transfer processes in Nature.[10] Unlike isolable 2Fe-2S clusters,<sup>[11]</sup> related 2Fe-2Se clusters are still scarce. By the seminal work of Holm and co-workers, several Fe-Se clusters could be synthesized with a range of iron nuclearities (2, 3, 4 and 6); thus, aiming at the development of an understanding of electronic effects exerted by a heavy element, such as selenium, in these clusters and the elucidation of their functionality in biological systems.[11c,11d,11g,12]

Here, we present (i) the synthesis of a bioinspired molecular 2Fe-2Se cluster core supported by a  $\beta$ -diketiminato ligand, (ii) the fabrication of FeSe<sub>2</sub> nanomaterials from the molecular 2Fe-2Se clusters via a versatile thermolytic approach, (iii) the utilization of immobilized FeSe<sub>2</sub> as an outstanding electrocatalytic material for bifunctional OER and HER, and for overall water-splitting catalysis, and (iv) the elucidation of surface-structural phenomena, the nature of the active species, and structure-activity relationships. In comparison to known iron selenide systems, the catalytic activity of FeSe<sub>2</sub> attained here renders them to be one of the highly active catalysts so far.

The  $\beta$ -diketiminato supported all ferric molecular 2Fe-2Se cluster **2**, and its one electron reduced form **3** were prepared as similar to the related 2Fe-2S clusters (Scheme 1, *Supporting Information*).<sup>[11a]</sup> Both **2** and the anion in **3** displayed similar geometrical features (Figure 1) as the analogous 2Fe-2S clusters.<sup>[11a]</sup> Detailed spectroscopic investigations were undertaken to ascertain that **2** consists of high spin Fe<sup>III</sup>/Fe<sup>III</sup>,

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Scheme 1. Synthesis of the 2Fe-2Se clusters 2 and 3.

whereas **3** involves mixed valence  $Fe^{II}/Fe^{III}$  centers,<sup>[13]</sup> such that the electronic structures of both **2** and **3** (Table S5) are akin with those observed for the 2Fe-2S analogue.<sup>[11a]</sup>

When 2 was subjected to thermal degradation under hot injection conditions, FeSe<sub>2</sub> was obtained in 72% yields. We hypothesize that in the process of thermolysis, instant dissociation of the weakly bound  $\beta$ -diketiminato ligand takes place followed by Fe-Se core. As successful nucleation occurs: a thermodynamically more stable orthorhombic FeSe<sub>2</sub> phase is obtained.<sup>[14]</sup> The as-prepared FeSe<sub>2</sub> was characterized by powder X-ray diffraction analysis (PXRD) and scanning electron microscopy (SEM) (Figure S16-17). Transmission electron microscopy (TEM) and high resolution (HR) TEM revealed that the agglomerates consists of very small crystalline particles ranging from 4-10 nm in diameter and the resulting lattice spacing of 0.256 nm reflected the (111) plane of FeSe<sub>2</sub> (Figure 2a, 2b and S18).<sup>[15]</sup> In addition, the rings in the selected area diffraction pattern (SAED), extracted from the HR-TEM, revealed the spacing of 0.302, 0.256, 0.201, 0.161, and 0.149 nm corresponding to the (101), (111), (112), (211), and (023) planes, respectively (Figure 2c).<sup>[15]</sup> The as-prepared FeSe<sub>2</sub> crystallizes in the orthorhombic marcasite structure (space group Pnnm) consisting of octahedrally surrounded Fe<sup>II</sup> atoms coordinated to six Se atoms; each tetrahedrally coordinated Se atom of the Se<sub>2</sub><sup>2-</sup> moieties is ligated to three Fe centers (Figure 2d).<sup>[14]</sup> The phase and composition of FeSe<sub>2</sub> were confirmed by energy dispersive X-ray analysis (EDX) and inductively coupled plasma atomic emission spectroscopy (ICP-AES; Table S6, Figure S19). In X-ray photoelectron spectroscopy (XPS), it is known that the binding energy of Fe2p<sub>3/2</sub> is about 709 eV for Fe<sup>II</sup>, and 711 eV for Fe<sup>III.[15]</sup> The peak of the Fe2p<sub>3/2</sub> regions, obtained at 710.4 eV indicate that both Fe<sup>II</sup> and Fe<sup>III</sup> are present at the surface of FeSe2.[16] Similarly, the peak corresponding to 2p1/2 was located at 723.8 eV confirming the Fe<sup>IVIII</sup> character originating from partial corrosion of Fe at the surface, which is in agreement with previously reported analyses of FeSe2.[9b] Further details on the Fe2p and Se3d XPS are given in supporting information (Figure S20).[17,18] The attained Fe:Se ratio on the surface is about 1:2 which is in accordance with the ICP-AES and EDX analyses.

The electrocatalytic OER was examined by depositing FeSe<sub>2</sub> on nickel foam (NF) using a three electrode set-up (SI) and the overpotential exhibited at 10 mAcm<sup>-2</sup> was merely 245 mV, while at 100 mAcm<sup>-2</sup>, the overpotential was only 308 mV (Figure S21a, b). The resulting overpotentials are not only one of the lowest in the series of chalcogenides but also lower than most of the high-performance transition-metal based catalysts (Tables S7, S8). While cycling between 1.22 and 1.44 V vs RHE, a small reversible redox couple was attained (prior to the OER) for FeSe<sub>2</sub>/NF. This is attributed to the presence of Fe<sup>II</sup>/Fe<sup>III</sup>, and is typical for first-row transition-metal based materials with



Figure 1. Molecular structures of 2 and 3 (ion pair with potassium-crownetheracetone).

M(OH)<sub>2</sub>/MOOH phase formation (Figure S21c).<sup>[19]</sup> In order to gather more insights on the redox process, we compared bare NF with the FeSe<sub>2</sub>/NF (Figure S21b) and found that, a slight oxidation to Ni<sup>2+</sup> in NF is unavoidable, however, the redox peaks were gradually shifted during water oxidation in FeSe2/NF indicating the oxidation of Fe<sup>2+</sup>. To entirely rule out whether the redox peaks are from active Ni2+, we studied redox behavior of FeSe<sub>2</sub> on fluorine doped tin oxide (FTO) that exhibited a clear redox couple and is solely ascribed to Fe<sup>2+</sup>/Fe<sup>3+</sup>. The catalytic activity of FeSe<sub>2</sub>/NF outperformed that of the noble metal-based RuO<sub>2</sub>/NF, IrO<sub>2</sub>/NF, Pt wire and bare NF catalysts, which were also measured under similar conditions (Figure 3). FeSe<sub>2</sub> displayed extremely high stability towards chronopotentiometric (CP) analysis over 18 h with improving overpotentials of ~ 230 mV (Figure S22). After the CP measurements, a CV was measured again for comparison (Figure S22) with the initial CV and the difference was found to be marginal when compared at 100 mAcm<sup>-2</sup>. Similarly, the FeSe<sub>2</sub> and other noble metal-based materials were deposited on FTO and the linear sweep voltammetry (LSV) in each case was measured and the details are given in (Figure S23). The catalytic activities for both FeSe<sub>2</sub>/NF and FeSe<sub>2</sub>/FTO are better than any iron selenide and one of the best among both chalcogenides as well as other firstrow transition metal based materials (Tables S7 and S8 for details).

HER was performed similar to the OER conditions in 1 M KOH. Figure S24 shows the catalytic HER activity of FeSe2/NF and those of commercial IrO2/NF and Pt catalysts. A strong redox response was observed in the lower current density region for FeSe<sub>2</sub>/NF indicating the reduction of Fe from mixed +2/+3 to a more reduced state akin to what was reported for FeOx type materials.<sup>[19b,20]</sup> Due to the interfering redox response at the region of lower current densities (-10 mAcm<sup>-2</sup>), the overpotentials were defined and compared at a current density of -100 mAcm<sup>-2</sup> (Table S10). The overpotential was determined to be at 262 mV for FeSe2/NF, 334 mV for IrO2/NF, and Pt showed the best with 135 mV. In addition, the influence of scan rates on polarization current was also conducted where the current was slightly decreased with decrease in scan rates from 20 mV/s to 1 mV/s (Figure S24b) and the overpotential at -10 mAcm<sup>-2</sup> was 178 mV. The activity comparison with existing materials indicates the moderate efficiency of FeSe<sub>2</sub> (Tables S9,



Figure 2. TEM images (a), HR-TEM (b) SAED (c) images and the orthorhombic marcasite crystal structure (d) of FeSe<sub>2</sub>.

S10). The CP was recorded for FeSe<sub>2</sub>/NF maintaining constant current of -10 mAcm<sup>-2</sup> (Figure S25). Although a good overpotential was achieved initially (176 mV), the long-time stability was further decreased and the resulting overpotential increased to ~ 260 mV. The CV after the CP showed a decrease in the current density (-640 to -440 mAcm<sup>-2</sup>) as well as slight increase in the overpotential at -100 mAcm<sup>-2</sup> (260 mV to 320 mV). The LSVs of FeSe<sub>2</sub> and the commercially available noble metal-based catalysts deposited on FTO were carried out and compared (Figure S26, Tables S9, S10).

To gather insights on the nature of the active species as well as the structural and morphological transformations occurring at the near-surface zone during electro-catalysis, the FeSe<sub>2</sub> was characterized after the electrochemical OER and HER, i.e., post CV (CV OER and CV HER) as well as post CP (CP OER and CP HER). In the case of CV OER, the TEM and HR-TEM images revealed a thin amorphous shell, which appeared to be started growing on the surface of the particles confirming the immediate changes on the surface at applied potentials (Figure S27), while the thickness of the amorphous shell was further increased after CP OER (Figure S28). This observation suggests the formation of Fe(OH)<sub>2</sub>/FeOOH on the surface, which could also be observed from CV cycling during OER measurements (Figure S21), and is consistent with respective literature reported data for iron based catalysts.[19] Both HRTEM and SAED pattern showed that the core of the particle was intact (Figure S28).<sup>[15]</sup> Clearly, the Fourier transform infrared (FT-IR) spectra exhibited broad bands that are indicative for hydroxylation in comparison to the FeSe<sub>2</sub>, where such bands were absent (Figure S29). Interestingly, ICP-AES disclosed a tiny loss of Se during CV OER but the amount of Se loss increased after CP OER suggesting corrosion of FeSe<sub>2</sub>. This surface change for selenides has already been reported for the Ni<sub>0.8</sub>Fe<sub>0.2</sub>Se<sub>2</sub> catalyst.<sup>[21]</sup> In the XPS spectra (Figure S30), the Fe2p<sub>3/2</sub> of CV OER showed a peak at 710.7 eV, while CP OER exhibits a peak at 711 eV evidencing an increase in the oxidation state of Fe from mixed Fe<sup>2+</sup>/Fe<sup>3+</sup> to Fe<sup>3+</sup>.<sup>[15]</sup> Similarly, the 2p1/2 for CV OER and CP OER were found to be at the binding energy of 724.7 eV and 724.9 eV, respectively. The values obtained clearly indicate, that the surface of the catalysts



Figure 3. Current-potential curves of  $FeSe_2$  and commercial noble metal-based catalysts deposited on nickel-foam (NF) with a scan rate of 20 mV/s in 1M KOH.

was oxidized from mixed Fe<sup>2+</sup>/Fe<sup>3+</sup> to Fe<sup>3+</sup>, consistent with literature-reported examples.<sup>[17,22]</sup> The Se3d peaks were slightly shifted from the initial spectrum and a minor peak at ~ 58.3 eV suggests oxidation of the selenium surface (Figure S31).<sup>[23]</sup> In addition, the XPS analysis revealed the loss of surface Se (~ 40%) supporting the results of ICP-AES. The O1s XPS spectra of both CV OER and CP OER of FeSe<sub>2</sub> could be deconvoluted into small O1 and broad O2 peaks (Figure S32). The O1 peak ~ 529.2 eV (O1) could be assigned to the formation of iron-oxygen bonds on the surface, due to the surface passivation of FeSe<sub>2</sub> to form FeO<sub>x</sub> species. The peak at ~ 531.7 eV (O2) is due to large dominance of oxyhydroxide/hydroxides.<sup>[2b,2c,2d,2e,7]</sup>

In case of CV HER and CP HER, no indication for the formation of amorphous shell was observed in the HR-TEM (Figure S33). The SAED pattern displayed rings corresponding to FeSe<sub>2</sub> phase (Figure S33). Unlike post-OER, only a negligible amount of Se was detached from the particles as observed from ICP-AES. In the XPS spectra (Figure S34), the Fe2p<sub>3/2</sub> of CV HER and CP HER, also exhibited a peak at ~ 710.7 eV (similar to OER) indicative of a slight increase in the oxidation state; presumably because of surface passivation when exposed to oxygen in the atmosphere and/or placing the electrode in strong alkaline media.  $^{\left[ 17,24\right] }$  Similarly, the  $2p_{1/2}$  for CV HER and CP HER were found to be close to 724.4 eV. Interestingly, the satellite peak at ~719 eV completely disappeared and a new peak appeared at ~ 716 eV, which corresponds to the  $Fe2p_{3/2}$  satellite for Fe<sup>II.[17,22]</sup> The Se3d peak of FeSe<sub>2</sub> located at 55.5 eV matched well to that of CV HER and CP HER (Figure S35). However, the minor peak at ~ 58.3 eV, implicating the surface oxidation of Se species, was increased strongly from CV to CP.<sup>[23]</sup> The O1s XPS spectra of both CV HER and CP HER of FeSe<sub>2</sub> could be deconvoluted into small O1 and broad O2 peaks and could be described akin to the OER CP (Figure S36).<sup>[2b,2c,2d,</sup> 2e,7]

Based on the aforementioned results, the outstanding OER activity of  $FeSe_2$  can be attributed to the (i) advantageous use of **2** as molecular precursor enabling very small and defined particle size and enrichment of significantly higher active sites (ii) formation of Fe-rich amorphous shell consisting of  $Fe(OH)_2/$ 





Figure 4. Current - potential curve for FeSe2 || FeSe2 on NF in a two-electrode set-up for overall water-splitting solution with a scan rate of 5 mV/s in alkaline medium. The long-term stability of the catalysts is shown in the inset.

FeOOH species at the surface, and (iii) the formation of defect structure with anionic vacancies due to the loss of Se from the particle surface. The active species on the surface of the catalysts can thus facilitate the adsorption of OH- ions and stimulate transport of electrons to have simple recombination of two oxygen atoms to promote efficient oxygen evolution.<sup>[25]</sup> Activity of FeSe<sub>2</sub> in HER can be correlated to the bond strength of Se that plays a crucial role. In principle, HER electrocatalyst should have neither too weak nor too strong bonding, but should have moderate bonding state with the intermediates and products. Interestingly, within chalcogenides, the bond strength of Se-H (276 kJ mol<sup>-1</sup>) is much lower compared to S-H (363 kJ mol<sup>-1</sup>) and it can trap protons by acting as bases and accelerates deprotonation to release H<sub>2</sub>.<sup>[6b,7]</sup>

An alkaline water electrolyzer was constructed (twoelectrode configuration) using FeSe<sub>2</sub>/NF as both anode and cathode (FeSe<sub>2</sub> || FeSe<sub>2</sub>) where the water-splitting reaction initiated at a potential of 1.52 V and reached 1.73 V at a current density of 10 mAcm<sup>-2</sup> (Figure 4, S37). The potential acquired here are very much in the range of highly aspiring water-splitting catalysts<sup>[6b,26]</sup> and stability test showed that the electrodes are very stable over a period of 24 hours (Figure 4 inset).

In conclusion, we have synthesized bioinspired molecular 2Fe-2Se compounds 2 and 3 analogous to 2Fe-2S clusters of iron-sulphur proteins. Using 2 as low temperature molecular precursor, FeSe<sub>2</sub> can be produced that exhibits remarkable catalytic activity towards both OER and HER with considerably low overpotentials, exceedingly high current density and longterm stability. Subsequently, insightful information on the nature of active species, surface structural arrangement, and a structure-activity relation in FeSe2 during OER and HER was obtained. Finally, an overall water-splitting set-up was constructed using a two-electrode cell, displaying low cell voltage and remarkable durability. This is the first report on iron selenide investigated for bifunctional OER, HER, and for overall water-splitting catalysis

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## COMMUNICATION

**Bridging the gap**: For the first time, a superiorly active iron selenide electrocatalyst could be prepared at low temperature from a bioinspired 2Fe-2Se molecular complex and applied for bifunctional oxygen and hydrogen evolution reactions as well as for overall watersplitting. The nature of active sites and structure-activity relationships were uncovered.



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From Molecular 2Fe-2Se Precursor to FeSe<sub>2</sub> Acting as Highly Efficient Electrocatalyst for Overall Water-Splitting