

Hydrogen evolution by ternary metal selenide at biomembrane-like soft interfaces

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Abstract

Two phase reactions are the analogy of biomembranes, which are polarized by Galvani potential difference at interface between two immiscible electrolyte solutions. Energy conversion reactions such as oxygen reduction reaction or hydrogen evolution reaction have been great drawn attention at soft interfaces due to the similarity of natural biochemical reactions. In this study, copper-based ternary metal selenide (copper tungsten selenide, Cu_2WSe_4) was first reported in the literature for hydrogen evolution reaction catalysis at the water/1,2-dichloroethane interface. The synthesized Cu_2WSe_4 catalyst is characterized by morphological and structural techniques. Catalytic activity of Cu_2WSe_4 at liquid-liquid interfaces by lipophilic dexamethylferrocene as the sacrificial electron donor agent. This catalytic activity was tracked by four-electrode voltammetry at the water/1,2-dichloroethane interface and biphasic reactions monitored by gas chromatography. The rates of the hydrogen evolution reaction catalyzed by the Cu_2WSe_4 were found to be approximately 160-fold than the rate for the reaction performed in the absence of a catalyst.

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1. Introduction

Hydrogen is seen as a future energy carrier by virtue of the fact that it is renewable, does not evolve the "greenhouse gas" CO_2 in combustion and is easily converted to electricity by fuel cells. Nowadays hydrogen is generally produced by using fossil fuels, which release greenhouse gases and other climate-changing emissions. Hydrogen production from water is biggest candidate to control of climate change due to the not releasing greenhouse gases. Catalysts need to use to produce hydrogen because of positive Gibbs free energy of water splitting into hydrogen and oxygen gases [1]. Most common and efficient catalyst, platinum (Pt), is used as catalysts in the hydrogen evolution reaction (HER). However, Pt is scarce and expensive and there is more study to find as an alternative to Pt with more abundant and cheaper than noble metal catalysts. Well-known noble metal-free MoS_2 , WS_2 , MoSe_2 and WSe_2 are drawn attention as an alternative to Pt in hydrogen evolution reaction (HER) [2-5]. Molybdenum selenide and tungsten selenide displayed high electrocatalytic HER performance because of having the large amount of active edge sites [6]. 3D dendritic [7,8], graphene-like nanosheet [9], thin film [10] and monolayer nanosheet [11] shapes of WSe_x have been investigated in the electrocatalytic

HER as the electrocatalyst. In addition, tungsten selenide photoelectrode has been studied by coating noble metal catalysts such as Ru and Pt, which are displayed $> 7\%$ solar-to-hydrogen conversion efficiency on photoelectrochemical HER in a broad pH range [12]. Copper incorporated molybdenum and tungsten sulfides have aroused interest in photocatalytic and electrocatalytic HER due to their advanced physical properties, novel chemical and unique structures [13]. Although, Cu_2WS_4 is used in the electrochemical hydrogen evolution [14], there is no report HER by using Cu_2WSe_4 in the literature up to now.

The analogy with biomembranes of an interface between two immiscible electrolyte solutions (ITIES) has been drawn a great deal of attention. Herein, liquid/liquid interfaces (LLI) are used as a model system for the catalytic hydrogen evolution. Electrochemistry at LLI has found applications in important areas such as chemical sensing, drug release, phase-transfer catalysis and energy-conversion systems by mimicking of the biological membranes [15]. LLI afford a unique platform to investigate hydrogen evolution reactions at which protons in the aqueous phase react with electron donors in the organic phase in the absence or presence of different catalysts by proton-coupled electron-transfer (PCET) reaction

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[16]. Herein, water/organic interfaces can be polarized either application of an external potential by a potentiostat or chemically by dissolving a common ion in both phases. Some metallocenes such as cobaltocene, osmocene, decamethyl-osmocene, decamethylruthenocene and decamethylferrocene (DMFc) were used at LLI for the catalytic HER as organic electron donor [17-22]. DMFc is most common electron donor for HER catalysis at the water/1,2-dichloroethane (DCE) interface [22]. Metallic nanoparticles [23, 24], metal oxides [25], metal carbide and metal boride [26], binary metal sulfides [27-29], ternary metal sulfides [30], amorphous ternary metal chalcogenides [31-33], quaternary metal sulfides [34] and also its nanocomposites [35-39] supported on mesoporous carbon, graphene or carbon nanotube is used as the catalyst for HER by DMFc at water/DCE interface. However, there is no study reported for the metal selenide HER catalysts at LLI.

Herein, it is firstly reported that hydrogen evolution reaction catalysis by using copper tungsten selenide (Cu_2WSe_4) at the biomembrane-like water/DCE interface by the organic reducing agent DMFc. The catalytic HER activity of Cu_2WSe_4 catalyst at LLI is investigated by four-electrode voltammetry and biphasic reactions using electrochemical and chromatographic techniques, respectively. The HER rate was relatively increased in the presence of the Cu_2WSe_4 catalysts with 4.8 μmol hydrogen measured after only 30 min of biphasic reactions (the maximum stoichiometric amount of hydrogen is 5 μmol). In addition, HER kinetic is calculated and Cu_2WSe_4 catalyst is enhanced the reaction rate about 160-times when compared to non-catalyzed reaction.

2. Materials and Methods

2.1. Synthesis of Cu_2WSe_4 nanostructures

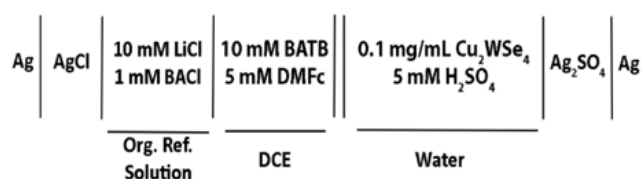
Cu_2WSe_4 have been synthesized by using hot-injection method according to reported literature [40,41]. Herein, stoichiometric amount of copper (II) chloride dihydrate (134.45 mg) and tungsten (IV) chloride (162.825 mg) were mixed with oleylamine (OLA) (12 mL) in a two-neck flask and evacuated at room temperature for 30 min under Ar flow. Then, another solution was prepared, which is included with 64 mg Se powder dissolved in 2 mL OLA, under magnetic stirring, until the OLA was dissolved (reddish-black). Afterwards, the first solution was heated to 300°C and the OLA-Se solution was rapidly injected about to 180 °C; then the temperature mixture solution was kept for 30 minutes by stirring. The reaction was finished by stopped of the heating mantle and allowed to cool

down to room temperature effortlessly. The product was washed two times with toluene-ethanol mixtures.

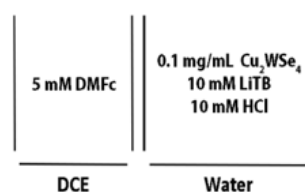
2.2. Hydrogen evolution experiments at liquid/liquid interfaces

Hydrogen evolution reaction at liquid/liquid interfaces (LLI) have been tracked by electrochemical polarization and chemical polarization. Electrochemical and chemical polarization were provided according to Scheme 1 a and b, respectively. BACl, BATB, DMFc and LiTB are the abbreviations of bis (triphenylphosphoranylidene) ammonium chloride, bis (triphenylphosphoranylidene) ammonium tetrakis (pentafluorophenyl) borate, ecamethylferrocene and lithium tetrakis (pentafluorophenyl) borate, respectively, in the Scheme 1. Organic supporting electrolyte BATB was prepared by metathesis as reported previously [42]. Electrochemical polarization was carried out by using four-electrode voltammetry in the presence of H_2SO_4 and BATB in the aqueous and organic phases, respectively, as the supporting electrolyte by using a CHI 760 D potentiostat with a four-electrode cell (geometric area is 1.53 cm^2) under oxygen free conditions. Galvani potential difference across the water/DCE interface determined by standard ion transfer potential of the tetraethylammonium cation (TEA^+) as 0.019 V [37]. Biphasic reactions were figured out by using DMFc and LiTB as the electron donor and proton transfer catalyst, respectively, under oxygen free conditions in the 10 mL volume glass flasks by magnetic stirring in the absence and presence of Cu_2WSe_4 catalyst. The evolved hydrogen amount was measured by gas chromatography (Shimadzu GC2010Plus), which calculated with calibration curve by using standard samples of H_2 in N_2 .

(a)



(b)



Scheme 1. (a) Electrochemical and (b) biphasic polarization of the water/DCE interface

3. Results and Discussion

3.1. Characterization of Cu_2WSe_4

Morphological and structural characterizations of Cu_2WSe_4 catalysts were carried out by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), elemental mapping, X-ray diffraction (XRD) and energy dispersive x-ray (EDX) spectroscopy techniques. SEM image of Cu_2WSe_4 shows uniform dispersity of particles (Figure 1a). Morphology and particle shape of Cu_2WSe_4 were investigated by TEM technique as shown in Figure 1b-c. According to TEM images, Cu_2WSe_4 catalyst displayed square and rectangular sheet-like shapes with approximately 50 nm of edge sizes [41]. Selected area electron diffraction (SAED) pattern shows that Cu_2WSe_4 has a single crystalline and well crystallized [40,43]. In addition, elemental composition and distribution were examined by SEM-EDX techniques with area mapping (Figure 1d). Moreover, crystalline formation and phase purity of Cu_2WSe_4 catalyst were investigated by using XRD technique. As shown in Figure 1e, XRD pattern displayed a pure tetragonal P42m symmetry with primitive phase of Cu_2WSe_4 ($P\text{-Cu}_2\text{WSe}_4$, PDF no: 01-081-1159), which corresponding crystal structure is seen in the inset of Figure 1e [44]. The crystalline structure, which is obtained by XRD, is also in the harmony with SAED pattern. Furthermore, chemical composition of Cu_2WSe_4 was determined by EDX (Figure 1f) and it is very close to the ideal stoichiometry (2:1:4). The undefined peaks approximately 0, 1, 2 and 4 keV based on the used surfactant OLA and gold coating for the EDX analysis along with imaging of SEM.

3.2. Catalytic hydrogen evolution at liquid/liquid interfaces

Catalytic hydrogen evolution reaction (HER) activity of Cu_2WSe_4 at the water/DCE interface was investigated by using four-electrode voltammetry and biphasic reactions for the first time. Electrochemical polarization of water/DCE interface was figured out by using four-electrode cell as shown in Scheme 1a under anaerobic condition. First of all, potential window has been determined by transfer potential of SO_4^{2-} and H^+ at the negative and positive potentials, respectively (Figure 2, black solid line). Then, while organic electron donor DMFc added to organic phase, current density is increased and onset potential is shifted to negative potentials at the positive potentials (Figure 2, orange solid line). The return peak observed in the back

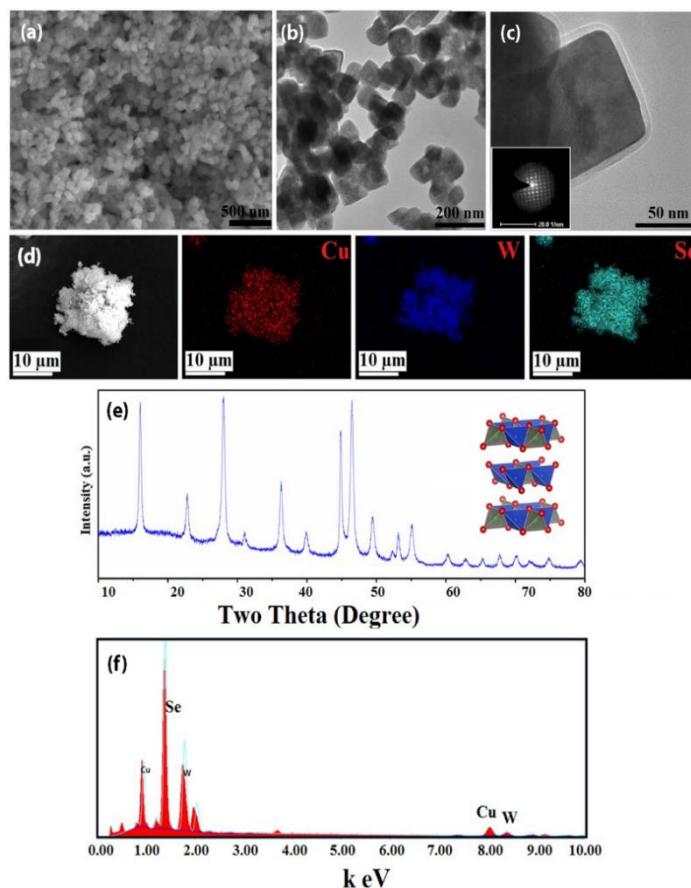


Figure 1. (a) Scanning electron microscope (SEM), (b-c) transmission electron microscope images (TEM, HR-TEM and SAED pattern) and (d) elemental mapping, (e) X-Ray diffraction (XRD) patterns with corresponding crystal structure (inset) and (f) energy dispersive X-ray (EDX) spectrum of the Cu_2WSe_4

scan can be attributed to the backward transfer of protons from DCE to the water phase. Herein, the proton, which is in the form of DMFcH^+ , was either consumed at a very slow rate or unconsumed in the organic phase because of the deficiency of chemical reactions to produce H_2 and DMFc^+ . In the presence of both Cu_2WSe_4 and DMFc added to the aqueous and organic phases, respectively, both onset potential is more shifted to negative and current density is more increased irreversibly with no back peak when compared to using only DMFc in the organic phase (Figure 2, green solid line) because protons adsorbed on the surface of Cu_2WSe_4 catalyst undergo rapid electron transfer with DMFc, which the protons are consumed fully [28]. No eligible current response was observed by using only Cu_2WSe_4 in the aqueous phase without DMFc (Figure 2, black dashed line) when

compared to the blank cell. In addition, the catalytic activity can be pursued by magnitude of reversible DMFc⁺ transfer peak, which is seen about -0.27 V. Herein, DMFc⁺ transfer peak is increased by using Cu₂WSe₄ and DMFc in the aqueous and organic

phases, respectively, when compared using only DMFc in the organic phase. These results proofed the catalytic activity of Cu₂WSe₄ by using organic electron donor DMFc.

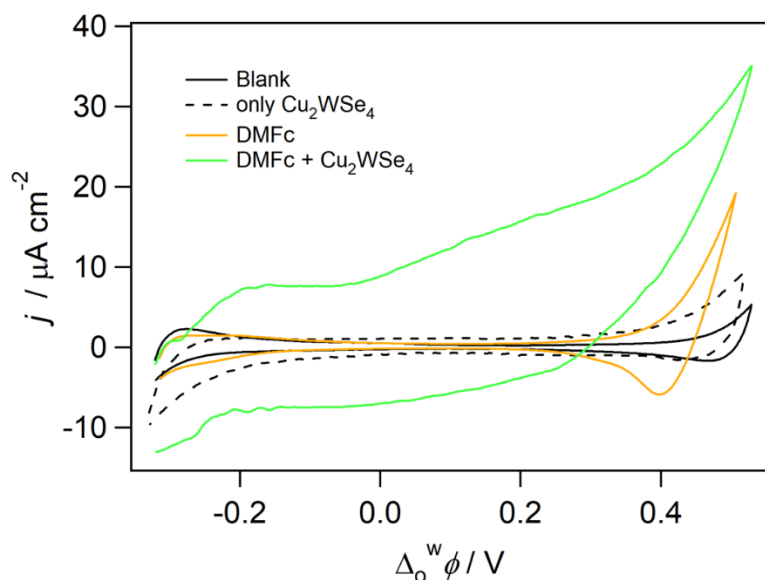
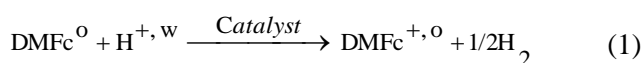


Figure 2. Cyclic voltammograms of four-electrode voltammetry by using only supporting electrolytes BATB and H₂SO₄ in the organic and aqueous phases, respectively (black solid line), in the presence of only Cu₂WSe₄ in the aqueous phase (black dashed line), in the presence of only DMFc in the organic phase (orange solid line), and in the presence of both DMFc and Cu₂WSe₄ in the organic and aqueous phases, respectively (green solid line).

The catalytic activity of Cu₂WSe₄ catalyst is also investigated by two phase system to supply Galvani potential difference without any external bias, which is named as “two-phase reaction” or “shake-flask” experiments. The chemical polarization of water/DCE interface is supplied by distribution of a common ion tetrakis-(pentafluorophenyl)borate anion (TB⁻), which is fixed Galvani potential difference to 0.58 V in order to transfer of proton from aqueous to organic phase [22]. The protons can be reduced in the organic phase by organic sacrificial agent DMFc into H₂ gas, according to their redox potentials in DCE as 0.04 V and 0.55 V vs SHE for DMFc and H⁺, respectively [22]. The reaction between DMFc and H⁺ is written as:



where o and w denote the organic and aqueous phases, respectively. According to these values, aqueous H⁺ can be reduced by DMFc with higher Galvani potential difference than 0.55 V [22]. Catalytic hydrogen evolution experiments were carried out according to Scheme 1b in the absence and presence of Cu₂WSe₄. Gas chromatograms and reaction cells are given in the Figure 3a and 3b, respectively, after 30 min of shaking in the absence and presence Cu₂WSe₄. Herein, hydrogen evolution rate is increased in the presence of Cu₂WSe₄ when compared to non-catalyzed reaction. In addition, color of organic phase in is changed rapidly from yellow to green the presence of Cu₂WSe₄ because of changing DMFc (absorption wavelength = 425 nm) into DMFc⁺ (absorption wavelength = 779 nm) [27], which is indirectly related to hydrogen evolution rate according to Equation (1).

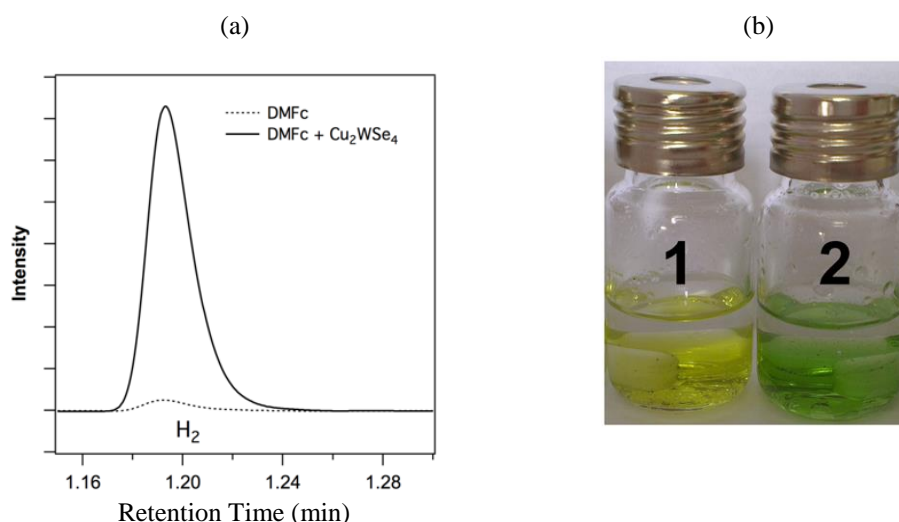


Figure 3. (a) Gas chromatograms of the headspace with (solid black line) or without (dashed black line) Cu_2WSe_4 catalyst after 30 min of biphasic reactions by using headspace cells (b) in the absence (flask 1) and presence (flask 2) of Cu_2WSe_4 catalyst.

Herein, kinetic experiments have been carried out by using Cu_2WSe_4 catalyst. Firstly, non-catalytic reaction was carried out in the absence of catalyst according to Scheme 1b. Accordingly, HER rate is very low and reached $0.8 \mu\text{mol}$ after 24 hours [27]. However, the amount of hydrogen was reached $4.8 \mu\text{mol}$ after 30 min in the presence of Cu_2WSe_4 (Figure 4a). These results pointed out approximately 96% efficiency according to Equation (1), which is limited by initial concentration of DMFc. In the absence of Cu_2WSe_4 , the amount of H_2 is only $0.061 \mu\text{mol}$ after 30 min. These results displayed that Cu_2WSe_4 catalyzed well to HER by DMFc at water/DCE interface.

The HER rate catalyzed by Cu_2WSe_4 is assumed as 1st order kinetics according to DMFc concentration as displayed in Equation (2) [36].

$$v = k[\text{DMFc}] \quad (2)$$

Reaction kinetic are explained by integrated rate law as shown in Equation (3) [36].

$$kt = \ln \frac{[\text{DMFc}]_0}{[\text{DMFc}]_0 - [\text{DMFc}^+] } \quad (3)$$

Herein, rate constants (k, min^{-1}) were calculated from slopes of straight lines in the absence and presence of Cu_2WSe_4 (Figure 4b). k was found out to be 0.00042 min^{-1} without any catalyst. However, k was increased to the 0.0662 min^{-1} in the presence of Cu_2WSe_4 . For the rate constant ratios in the presence and absence of Cu_2WSe_4 , increasing of catalytic activity was turned out to be about 160-fold by using Cu_2WSe_4 catalyst.

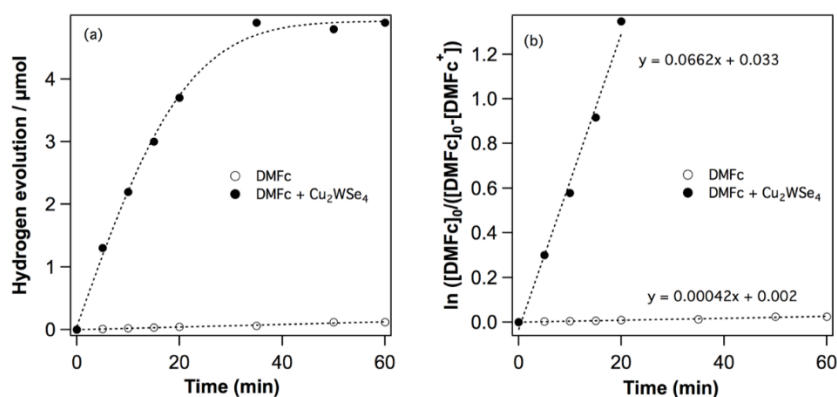


Figure 4. (a) Time dependent hydrogen evolution amount in the absence and presence of Cu_2WSe_4 catalyst. (b) Rate constant (k) determination: plots of the integrated rate law versus time (min) for the HER, indicating 1st order kinetics. The slopes of the straight lines illustrate the rate constants (k, min^{-1}) for a 1st order reaction.

The catalytic activity of Cu_2WSe_4 can be compared with the similar structure of Cu_2WS_4 , which is reported by our group in 2016 [30], at the water/DCE interface by DMFc for hydrogen evolution. Herein, catalytic activity of Cu_2WSe_4 is found out lower than that of Cu_2WS_4 (Table 1). These differences can be explained by the atomic radii of sulfur and selenium. Catalytic activities of selenium based catalysts are lower than sulfur based catalysts because they may be prone to high recombination rates [13]. In addition, higher radius of selenium than sulfur might be supplied to keep the more electrons on the surface in stable and it is not prone to react in the ternary metal chalcogenides [13]. Moreover, the catalytic activity differences

between Cu_2WSe_4 and Cu_2WS_4 is able to related band gap and energy band levels of catalysts. Band gaps and energy band levels of Cu_2WX_4 catalysts were calculated by our previous published paper for the determination of differences photocatalytic activities for HER (Table 1) [41]. According to conduction band levels of Cu_2WX_4 catalyst, having close conduction band level, which is -0.16 V vs. NHE for Cu_2WS_4 to H^+/H_2 (0 V vs. NHE) is more apt to react. Herein, the lower catalytic activity of Cu_2WSe_4 than Cu_2WS_4 could be based on the conduction band level of Cu_2WSe_4 , which is far from H^+/H_2 . Eventually, in this study catalytic activity differences of catalysts are able to explain with two factor proof.

Table 1. Catalytic parameters and band gap structure differences of Cu_2WS_4 and Cu_2WSe_4 .

Catalyst	Cu_2WS_4	Cu_2WSe_4
Hydrogen evolution in 5 min (μmol)	2.9	1.3
Reaching time for maximum theoretical stoichiometric amount of hydrogen (min)	10	35
Reaction increment by factor	1005	160
Optical band gap (eV)	1.80	1.65
Electrochemical band gap (eV)	1.66	1.80
$E_{\text{Valance Band}}$ (V vs. NHE)	1.50	1.24
$E_{\text{Conduction Band}}$ (V vs. NHE)	-0.16	-0.56

The mechanism of hydrogen evolution can be explained by proton coupled electron transfer (PCET). Hydrogen evolution is based on assisted proton transfer (APT) from aqueous to organic phases by electron donor DMFc in the absence of catalysts [22]. However, HER is actualized by adsorbed protons on catalyst while in the presence of catalyst. Herein, HER is figured out by adsorbed protons on the active surface on the Cu_2WSe_4 catalyst with giving electrons from DMFc as displayed in Figure 5.

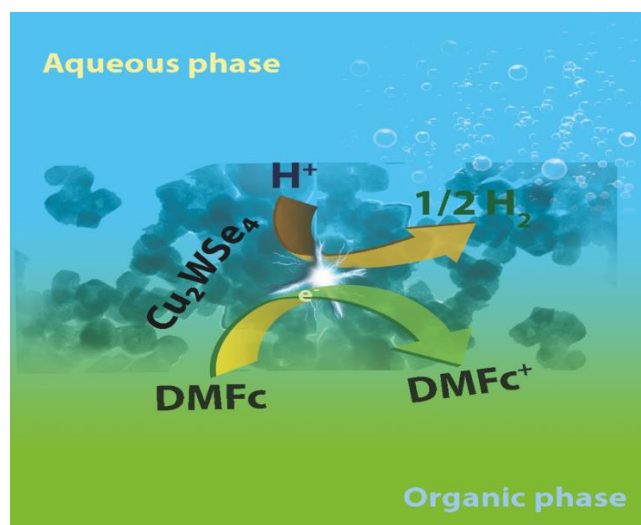


Figure 5. The proposed mechanism of hydrogen evolution by using Cu_2WSe_4 catalyst at the water/DCE interface.

4. Conclusions

The catalytic activity of square / rectangular sheet-like shapes of copper-based ternary metal selenide (Cu_2WSe_4) catalyst are investigated at the polarized water/1,2 dichloroethane (DCE) interface for the reduction of aqueous protons to molecular hydrogen by the organic electron donor DMFc for the first time. Catalytic HER activity is improved by Cu_2WSe_4 sheet-like structures at the biphasic water/DCE system using DMFc electron donor in the organic phase when compared to non-catalyzed reaction. In addition, the catalytic activity differences between Cu_2WS_4 and Cu_2WSe_4 are compared according to atomic radius and energy band structure of catalysts. The main advantages of this work are that catalytic activities of ternary metal chalcogenides can be explained by molecular and electronic structures of catalyst. These results open new perspectives for the exploration for the observing different selenide-based catalyst on the HER at the soft interfaces. First time reported catalytic activity of Cu_2WSe_4 paves the way that ternary metal selenide-based materials will be used in the different energy conversion reactions such as solar cell, batteries, supercapacitors, and so on.

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Conflicts of interest

The authors state that there is no conflict of interests.

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