**MOF-derived copper selenides implanted in octahedral carbon matrix for efficient hydrogen evolution reaction**

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**Abstract**

The development of durable, efficient catalysts is vital in electrochemical water dissociation. Metal-organic frameworks (MOFs) based nanomaterials have been explored due to their well-distribution metal nodes and stability, but the shortage of efficient cathode compounds for electrochemical hydrogen evolving restricted their industrial applications. Herein, Cu2Se nanocrystals embedded in the octahedral carbon frameworks (Cu2Se/C) were fabricated using a copper-related MOF template through a one-step selenization technique. Interestingly, the catalytic efficacy of Cu2Se/C is better than that of Cu/C and Cu-MOF as catalysts for hydrogen generation in an acidic medium. In particular, Cu2Se/C shows a moderate overvoltage of 220 mV at a current density of 10 mA cm-2 and a low Tafel slope of 54.5 mV dec-1. Also, this catalyst presents outstanding durability with 2000 cycling operations and 12 hours of testing by chronoamperometry. The high efficiency is assigned to the synergistic effect of Cu2Se nanoparticles and carbon frameworks, which plays essential roles in increasing exposed catalytic sites and protected active centers. The results may open potential direction to prepare economical hydrogen-evolving electrocatalysts*.*

**Keywords**: copper, copper selenides, electrolysis, water splitting, carbon matrix

1. Introduction

Nowaday, the consumption of energy is highly elevated since the ever-increasing global energy demand. As a result, the drastical deplention of tranditional norenewable fuel resources, e.g, fossil fuel, natural gases, etc, is inevitable [[1](#_ENREF_1)]. Therefore, the seek of a new clean and sustainable energy resources is urgent to meet future global energy demands. During the past decades, renewable energy resources (e.g., solar, wind, and hydraulic power) have been explored as sustainable alternatives to traditional fossil fuels; however, their utilization is usually limited by the spatial and temporal intermittencies. In this circumtance, hydrogen was identified as the promissing fuel to replace coal, and gasoline in the future since its high energy density (between 120-140 MJ kg-1) and environmental friendliness.be with respect to gasoline, natural gas, and coal [[2-7](#_ENREF_2)]. Therefore, various techniques were conducted to produce hydrogen in the industry such as coal gasification, methane forming, and water electrolysis. The coal gasification and methane reforming methods have been studied and extensively carried out in both research and industrial level, however, the great hurdle of these two method is CO2 emission. a cause of “green house” effect and global warming. Contrary to the coal gasification and methane reforming methods, water electrolysis method is considering as an eviromental friendly (net-zero CO2 emissions) and cost-effective method to produce hydrogen [[8](#_ENREF_8)]. This method simply uses water as an initial source to generate hydrogen via a facile electrochemical water splitting process [[9-14](#_ENREF_9)]. In the electrochemical water splitting process, catalytic materials play a crucial role to accelerate reaction performance, determining the electrochemical hydrogen evolution reactions (ECHER) . Up to now, precious metals-based electrocatalysts, platium group elecments (e.g Pd or Pt), gives the best performances for ECHER in both acidic (2H + 2e- → H2) and alkaline media (4H2O + 4e- →H2 + 4OH-) [[15-22](#_ENREF_15)]. However, The use of these materials for ECHER are still not meet the requiment of commercial applications due to their high-cost (~ 33 USD g-1) and low natural reverse (the presence of Pt and Pd is < 0.005 ppm on Earth’s crush). Thus, they are still far from conveniently substituting the diminishing fossil fuels [[23](#_ENREF_23), [24](#_ENREF_24)]. Hence, extensive efforts have been devoted toward the development of the cost-effective and durable materials for ECHER to replace the precious metals. For instance, the exploitation of non-precious materials such as transition metal -nitrides, -dichalcogenides, , -phosphides, -carbides and metal -oxides, -selenides for ECHER have been extensively reported [[25-34](#_ENREF_25)].

In recent decades, transition metal nitrides have exhibited promising ECHER performance under alkaline evironments due to their unique electronic structure, similar to Pt and Pd, distinguished conductivity and good corrosion resistance [[35](#_ENREF_35)]. Nevertheless, long-term stability at high current is the main challenge of metal nitrides for ECHER owing to their undesirable morphological and/or crystalline structure changes during electrochemical process which made these materials are far from practical applications [[36](#_ENREF_36)]. Transition metal-phosphides and -carbides are another group of materials that garnered attention due to their typical intrinsic electronic structure. The ECHER activity metal-phosphides and -carbides is mainly determine by P and C atoms in their crystalline structure (the ability of P and C atoms to grip electrons from metal atoms) [[37](#_ENREF_37)], which can be further improved via composition engineering techniques (doping and hybrdiztion) [[38](#_ENREF_38), [39](#_ENREF_39)]. However, the real mechanism of the ECHER for these materials still requires much exploration [[40](#_ENREF_40)]. Besides, one of the immediate challenges toward their, large-scale application is the availability of low-cost and efficient electrocatalysts for ECHER. As for transition metals-dichalcogenides, MX2 (M= transition metal dichacogenides and X= S, Se, Te), both theoretical and experimental studies has clarified the H+ absorption capability (free Gibbs energy ~ 0.08 eV for H+ absorption) of unsaturated X atom at the edges of semiconducting 2H (trigonal prismatic) which acts an active site for ECHER [[41](#_ENREF_41), [42](#_ENREF_42)]. However, there are several drawbacks of MX2 still exsisting such as the scalability of production, high production cost, low electronic conductivity and uncontrollable phase changing during electrochemical process [[43](#_ENREF_43), [44](#_ENREF_44)]. Although metal-oxides are able to provide efficient electrocalysis active sites via O vacancies and large number of metal ions for ESCHE, there are plenty of drawbacks such as low intrinsic electrical conductivity, complicated fabrication process and unstable electrochemical stability due to their fast oxidation in ECHER operation, hampering the comercial applications of these materials [[45](#_ENREF_45)].

Among the aforementioned catalysts, metal selenides, e.g., NiSe2, Ni3Se2, CoSe2 and Co7Se8 have gained considerable attention due to their exceptional electrocatalytic activity toward ECHER in both acidic and alkaline media [[46-48](#_ENREF_46)]. However, apart from enhanced performance, reducing the electrocatalyst cost without negative effect on performance has still been the most important aim of further research and tremendous eﬀorts have been carried out to figure out the solution. In term of “hydrogen economy”, one of the easiest and fastest way to significantly reduce the cost is to design the catalyst from the earth abundant and cheap elements. In this context, copper has been regconized as a proper material because is widely available in the Earth’ s crust and cheaper than most metals including Ir, Ni, Co, etc. Therefore, copper selenides are emerging as potential candidates for altering other metal selenides as well as noble materials in ECHER since their low-cost, high catalytic activity, diverse composition, and tunable morphology. Besides, copper selenides can be easily synthesized via electrodeposition and hydro-, solvo-thermal methods [[49](#_ENREF_49)]. In term of material tailoring and design, variety of strategies were implemented to increase the ECHER activity of copper selenides. For instance, Durairaj et al. fabricated a thin film of Cu2Se nano architecture through a hydrothermal technique [[50](#_ENREF_50)]. This electrode exhibits a better ECHER performance than the bare Cu electrode, attributed to the fast electron transport of copper selenide. Lv et al. prepared Cu2-xSe nanosheets on copper foam (CF) as an efficient electrode for ECHER [[51](#_ENREF_51)]. Ray et al. fabricated Cu2O−Cu2Se nanosheets embedded on nickel foam as an outstanding cathode for water splitting in various pH conditions [[52](#_ENREF_52)]. The study of Das and co-workers reported the preparation of hybrid architecture Cu2Se/CoSe2 on CF as an efficient electrode for water dissociation with a low overvoltage (110 mV at a current density of 10 mA cm–2) [[53](#_ENREF_53)]. Xiao et al. found that copper selenide has the low Gibbs free energy (~0.3 eV) of hydrogen by calculating density function theorywhich is related to its good ECHER activity [[25](#_ENREF_25)]. Apart from the specific intrinsic properties of material, the excellent ECHER performance also related to material structures, e.g, nanosheets, nanoclusters, hollow structures, etc., that brings out the novel effect of high surface area, resulting in large active sites for electrocatalytic reactions. In this regard, strategies using metal-organic frameworks (MOFs) as precursors to create electrocatalysts have drawn a lot of attetions in recent years. The novel structure of MOFs is constructed by the coordination between organic ligands as linkers and metal ions as nodes, resulting in the generation of unfolded crystalline framework structures with large surface areas (frequently 600−7000 m2 g-1) which is favourable to electrochemical active sites in ECHER [[54](#_ENREF_54)]. Moreover, the periodic network crystalline structures of MOF is mainly formed via organic linkers, containing a conjugate base of a carboxylic acid or anions of organo-compounds. In the view of water splipting, the MOF utilizing carbon based organic linker is one of the attractive materials because of its sufficient “synergetic effect”. That is, carbon materials in MOF usually act as a good electrical conductive matrix for the well-dispersion metal components, providing more exposed surface area [[55](#_ENREF_55)]. Thus, constructing MOF hybrid materials of metal /carbon can not only tune the electronic structure by electron transfer on the hetero-interface, but also effectively boost the electrochemical properties of the active materials, e.g., more exposed active sites, higher electrical conductivity and faster electron transfer, for ECHER [[56-59](#_ENREF_56)]. For instance, Do et al. proved that the MOF plays a vital role in improving the stability of cobalt selenides for ECHER. [[26](#_ENREF_26)] Recently, the efficient electrocatalyst of Co3O4@Co-MOF was reported by S. Zheng et al. for ECHER. The uniformly distributed Co3O4  nanocubes supported on a high-surface-area Co-MOF enable the large active sites of electrocatalyst, indicating high catalytic activity of Co3O4@Co-MOF hybrid.

In this work, we constructed a hydrid strucure of MOF-derived copper selenides implanted in octahedral carbon matrix. Our strategy exploited the use of Cu-based MOF as a sacrificial platform to produce copper selenides (Cu2Se) anchored on a carbon skeleton for ECHER via a facile solvothermal process. This strategy brings beneficial effects, the carbon matrix inherited from MOF structure helps to avoid aggregation of Cu2Se particles, leading to the significant increase in electrochemical active sites. Besides, the carbon matrix plays an important role in preserving metal sites in acidic environments, further improving stability. The abundant synergistic active sites obtained between carbon and Cu2Se promote electron transfer and modulated the chemical environment.Consequently, Cu2Se/C gives a good ECHER efficiency with a low overpotential and high durability, which is attributed to the Cu2Se nanoparticles and carbon frameworks.

**2. Material and Methods**

**2.1. Chemical**

Copper(II) nitrate trihydrate (99.9%), trimesic acid (95%), Selene powder (99.99%), and were obtained from Sigma-Aldrich. Nafion™ 117 containing solution was supplied by the Chemours company. N,N-dimethylformamide (DMF), H2SO4 (97%), and 98% ethanol (C2H5OH), Trimesic acid (H3BTC) were purchased from Daejung. A glassy carbon electrode (GCE) was supplied by the BASi company.

**2.2. Fabrication of Cu-MOF**

Cu-MOF material is synthesized by the solvothermal method, modified from a previous study [[60](#_ENREF_60)]. Notably, 4.15 g Cu(NO3)2.3H2O was dissolved in 30 ml DI water to generate A solution. B solution was created by dissolving 2.01 g H3BTC in a co-solvent of 30 mL DMF and 40 ml ethanol. Then, mix A and B in a Teflon-lined stainless autoclave, heating at 100C for 10h. The blue crystals of Cu-MOF were washed by centrifugation with ethanol and dried at 80C for 12 h.

**2.3. Fabrication of Cu2Se/C**

Here, 0.2 g Cu-MOF precursor was blended with 0.2 g selenium powder in a ceramic cup and annealed at 450 °C for 2 h under N2 flow to create Cu2Se/C.

**2.4 Fabrication of Cu/C**

The Cu-MOF crystals were put into a ceramic boat before being put into a furnace. The structure of copper implanted in the carbon skeleton (Cu/C) was generated by calcination of Cu-MOF at 450C for 2 hours under N2 gas pressure.

**2.4 Characterization and Catalytic Activity Evaluation**

The X-ray diffraction (XRD) of Cu2Se/C, Cu/C, and Cu-MOF was analyzed on a PANalytical X-ray powder diffractometer with Cu Kα radiation (λ = 1.5418 Å). Samples (powders) are ground and squeezed on quartz substrate. Field Emission-Scanning electron spectroscopy (FE-SEM) from JEOL JSM-7500 FA was adopted with an accelerating potential of 5 kV to evaluate the surface of the material. Transmission electron microscopy (TEM) of Cu2Se/C was collected by utilizing JEOL microscope, operated at 100 kV. X-ray photoelectron spectrometer (XPS) data was obtained utilizing equipment of ThermoFisher Scientific with an Al Kα X-ray source, operated at 20 mA and 15 kV. The pass energy of 10 eV and energy step of 0.1 eV were apply to acquire high-resolution spectra. The photoelectrons are detected at a take-off angle (*e.g.*, the angle defined by the sample surface normal and the position of the detector) φ = 0 with respect to the surface normal. The pressure in the analysis chamber is maintained below 10-6 Pa for data acquisition. The Raman spectra of samples were acquired via Renishaw inVia confocal Raman microscope with laser excitation wavelength of 514.5 nm (incident power of ~1 mW on the samples) and a 100× objective..

Catalytic activity evaluation was investigated at room temperature (25°C) with a solution of 0.5 M H2SO4 in a three-electrode system through a with a Biologic MPG2 potentiostat/galvanostat. In particular, a graphite rod as the counter electrod. An Ag/AgCl (NaOH, 1 M) as a reference electrode, and GCE coated catalysts as working electrode. In cathode fabrication, 48 mg catalysts and 0.08 mL Nafion were ultrasonicated with 8 mL DMF for 3 hours to produce a homogeneous ink. Then catalyst ink was dropped-casting onto the GCE with the loading of material to be 0.3 mg/cm2. Linear sweep voltammetry was implemented at a scan rate of 5 mV s-1 with IR compensation. Obtained potentials were converted by the formula, ERHE = E0Ag/AgCl + EAg/AgCl + 0.059\*pH. Impedance spectra were analyzed in frequency windows from 10-1 to 105 Hz. The durability of the material was confirmed by the cyclic voltammetry (CV) technique and chronoamperometry after 12 hours.

**3. Result and discussion**

The preparation pathway of copper selenide from Cu-based MOF is displayed in **Figure 1**. First, Cu-MOF crystals were prepared by solvothermal process; then they are used as sacrificial templates to create Cu2Se/C through the selenization technique at 450 °C for 2 h. The crystal structure of Cu-MOF and Cu2Se/C were analyzed by XRD methodology. XRD pattern verified the good crystallinity of the as-synthesized Cu-MOF. The characteristic peaks of 6.84°, 9.64°, 11.77°, 13.59°, 19.19°, and 26.07° were attributed to the (200), (220), (222), (400), (440), and (731) crystal planes of Cu-MOF, as shown in **Figure S1** [[61-63](#_ENREF_61)]. **Figure 2a** displays the XRD plot of the Cu2Se/C sample. Well-defined typical peaks were recorded at 26.8, 44.9, and 53.1 which are in agreement with the Cu2Se cubic phase (JCPDS 88-2043). These peaks corresponded to the (111), (220), and (311) crystal facets [[64-66](#_ENREF_64)]. In addition, the XRD of pyrolyzed samples obtained at 450 °C (Cu/C) is displayed in **Figure S2**. Raman spectra of Cu2Se/C only exhibit one peak at 256 cm-1, which indicates the stretching modes of the Se-Se bond, as shown in **Figure 2b**. **Figure 3a** depicts the SEM images of Cu2Se/C, which have an octahedral morphology with a rough surface. TEM images (**Figure 3b)** matched well with SEM images for Cu2Se/C sample. The high-resolution-TEM image in Figure 3c indicates that a d-spacing of 0.34 nm is attributed to the (111) crystal facet of Cu2Se. Interestingly, a thin carbon layer was observed on the surface of the Cu2Se phase, which plays an essential role in protecting active sites and uniform distribution copper selenide phase in the material. **Figure 3d-g** depicts scanning TEM and a corresponding elemental mapping of Cu2Se/C provides the well-distribution of elements (Cu, Se, C). This implies that active sites also were uniformly distributed in samples. **Figure 4a** proves the existence of Cu, Se, and C in the Cu2Se/C product. The high-resolution XPS of Cu 2p, Se 3d, and C1s were thoroughly fitted to determine the chemical state of the elements. Notably, the HR-XPS of Cu 2p3/2 (**Fig. 4b**) in Cu2Se/C exhibited two peaks 932.3 eV and 952.1 eV, which can be attributed to Cu1+ 2p3/2, and Cu1+ 2p1/2, respectively. The other peaks at 934.1 eV and 953.9 eV are ascribed to the chemical state of Cu2+ [[64](#_ENREF_64)]. In the region of Se 3d spectrum (**Figure 4c**) peaks at 54.4 eV and 53.54 eV could be attributed to the Se 3d5/2 and Se 3d3/2**.** These peaks have orbit-splitting energy of 0.86 eV, which corresponds Se2- state. As depicted in the C 1s XPS, the peaks located at 284.6, 285.9, and 288.2 eV could be indexed into C−C/C=C, C−OH, and C-O, respectively [[67](#_ENREF_67)].

The hydrogen production performance of the as-synthesized materials was evaluated in a conventional system of three electrodes with a solution of 0.5 M H2SO4. **Fig. 5a** presents the polarization curves of different materials in the same working conditions. The Cu2Se/C catalyst exhibited the lowest overvoltage (232 mV) to obtain a current density of 10 mA cm−2, implying higher ECHER catalytic activity than Cu/C (290 mV) and Cu-MOF (720 mV). These outcomes can be explained that copper selenide is higher in ECHER than pristine copper as it has negatively polarized selenide anions with relatively lower free energy for hydrogen adsorption [[68](#_ENREF_68)]. Moreover, Cu/C has better activity than Cu-MOF, which was attributed to the removing organic component in pyrolysis Cu-MOF, leading to improve conductivity of the material. The ECHER activity of Cu2Se/C could be commensurate with the reported copper selenide-based materials for ECHER (**Table S1**). Also, Cu2Se/C provides a moderate Tafel slope of 54.5 mV dec−1, which are lower quantities than those of Cu/C (61.4 mV dec−1) and Cu-MOF (120.4 mV dec−1) (**Figure 5b**). These results reveal that the ECHER process of as-synthesized materials undergoes a Volmer–Heyrovesky pathway. Impedance spectra were evaluated on Cu-MOF, Cu/C, and Cu2Se/C at a potential of −200 mV to verify the reaction kinetics at the electrode/electrolyte interface for hydrogen production [[69](#_ENREF_69), [70](#_ENREF_70)]. As depicted in **Figure 5c**, the electron transport impedance (Rct) of Cu2Se/C (149.2 Ω) is smaller than those of Cu/C (1501 Ω) and Cu-MOF (4847 Ω), revealing that the selenization process can accelerate the chare transpỏt in the ECHER kinetics of Cu2Se/C. Furthermore, the electrochemically active surface area (EASA) was computed adopting the double-layer capacitance (Cdl) determined by the CV methodology (**Fig. S3**). As presented in **Figure 5d**, the Cdl value of Cu2Se/C is 1.34 mF cm−2, which is higher than those of Cu/C (1.10 mF cm−2) and Cu-MOF (0.13 mF cm−2), indicating a higher EASA and more catalytic species for hydrogen production (**Table S2**).

To compare the intrinsic catalytic properties of the materials, the turnover frequencies (TOFs) were computed at a potential of −200 mV (versus RHE), as shown in **Figure 6a**. The TOFs of Cu-MOF, Cu/C, and Cu2Se/C were 0.00039, 0.00074, and 0.00172 s−1, respectively. This indicates that Cu2Se/C displayed a higher efficiency of the catalytic sites in the HER process. The stability of the working electrode needs to be tested to evaluate its ability in the industry. This was conducted for Cu2Se/C through cyclic voltammetry, and using the chronoamperometry methodology (**Figure 6b**). The polarization plots of Cu2Se/C were only slightly altered after the 2000 cyclic testing. In addtion, the chronoamperometric responses of Cu2Se/C at an overvoltage of 240 mV (inset **Figure 6b**) presented only a negligible reduction over 12 h of hydrogen production. Also, the went down current density is assigned to the interference of the hydrogen gas on the active catalytic sites. The outcomes show the efficacy of the carbon frameworks in boosting the durability of the Cu2Se catalyst.

**4. Conclusion**

This study aims to design a stable and efficient material of Cu2Se nanoparticles implanted on carbon skeletons from a Cu-MOF template and investigate its HER properties. This approach provides the vital role of carbon frameworks, inherited from MOF structure, which is favorable for the well-distribution of Cu2Se nanoparticles. Besides, carbon skeletons play a crucial role in protecting active sites in extreme conditions, leading to the enhanced durability of catalysts. As a result, Cu2Se/C exhibited high efficiency for electrochemical HER. Notably, Cu2Se/C only requires a low overpotential of 220 mV to deliver a current density of 10 mA cm-2. Moreover, this material preserves catalytic performance after 12 h operation by chronoamperometry method in an acidic solution. This work may provide a promising approach for the preparation of metal selenides/carbon by utilizing MOFs as sacrificial agents for electrochemical water splitting.

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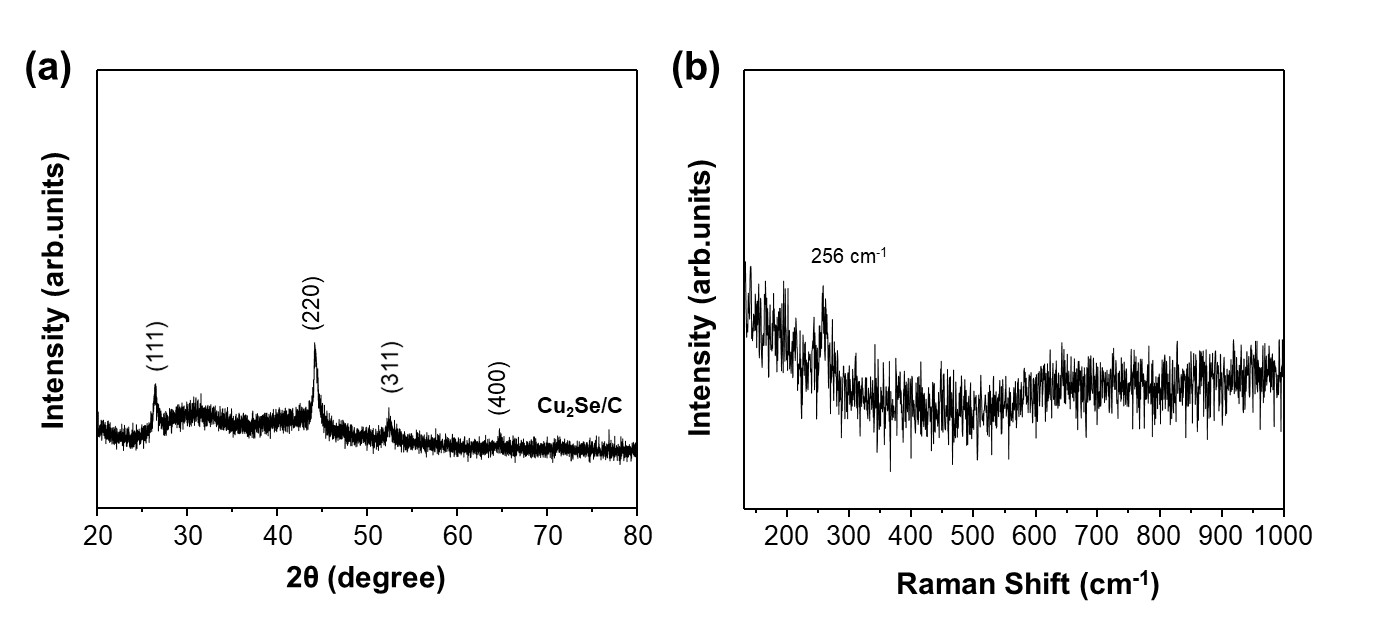
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**Figure 1**. Schematic illustration of the preparation of Cu-MOF and Cu2Se/C.



**Figure 2**. (a) XRD patterns and (b) Raman spectra of Cu2Se/C.

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**Figure 3**. (a) SEM, (b) TEM, (c) high-resolution TEM, (d) STEM images of Cu2Se/C with EDS mapping of (e) Cu, (f) Se, and (g) C elements.

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**Figure 4** (a) XPS survey spectrum. High-resolution XPS spectra (b) Cu 2p, (c) Se 3d and (d) C 1s of Cu2Se/C.

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Figure 5. HER performance: (a) Polarization curve of Cu-MOF, Cu/C, Cu2Se/C, and Pt/C (b) Tafel slope of electrocatalysts, (c) Impedance spectra were recorded on the various samples, (d) Double-layer capacitances of different electrocatalysts.

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Figure 6. (a) TOFs of Cu-MOF, Cu/C, and Cu2Se/C at an overpotential of 200mV and (b) Polarization curves were recorded first cycle and after 2000 cycling testing. Inset: Current-time plot of Cu2Se/C at a potential of -0.240 V for 12 h.