Hierarchical 0D–2D Co/Mo Selenides as Superior Bifunctional Electrocatalysts for Overall Water Splitting

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Introduction

Hydrogen is a promising energy source that boasts a high power density and environmental friendliness; therefore, electrolysis of water is hotly pursued as a renewable, efficient, and pollution-free technique (Amiinu et al., 2017; Luo et al., 2018; Zhu et al., 2018). Electrocatalytic water splitting consists of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), and electrocatalysts as the chemical reaction centers play a critical role in the water splitting electrolyzer. Although some noble metal oxide catalysts (RuO2 and IrO2) have high electrocatalytic performance for the OER and some noble metal catalysts (Pt and Ir) deliver good electrochemical property in the HER, the high cost and scarcity restrict their wide industrial application (Trasatti, 1972, 1984). Therefore, noble-metal-free catalysts with high stability and efficiency are crucial to large-scale hydrogen production from water splitting. Currently, the OER activity in alkaline solution is the
bottleneck in overall water splitting due to the sluggish kinetics arising from the multiproton-coupled electron transfer steps (Jamsh and Sun, 2018). In practice, the HER catalyst in the electrolyzer should be compatible with the OER catalyst and functions in the same medium. Hence, development of suitable bifunctional noble-metal-free electrocatalysts with both high HER and OER performance in alkaline media is of great significance.

In recent years, transition metal dichalcogenides (TMDs) have attracted significant research interests owing to their earth-abundant reserves and acceptable activity for electrocatalytic HER (Xie et al., 2013; Zhang et al., 2017a; Xue et al., 2018; Wang et al., 2019). Particularly, layered MoSe₂ has been considered as a promising HER electrocatalyst because of its unique structure features and high electrochemical activity (Shi et al., 2015; Chen et al., 2018a; Zhang et al., 2018). Theoretical research has demonstrated that the Gibbs free energy for H atom absorption on the edge of MoSe₂ is lower than that of MoS₂ due to the more metallic nature of MoSe₂, revealing the higher HER performance (Tang et al., 2014; Lai et al., 2017; Yang et al., 2018). In addition, it has been experimentally confirmed that the unsaturated Se edges in MoSe₂ nanosheets are extremely active as the S edges in MoS₂, which is responsible for the high HER activity (Jaramillo et al., 2007; Tang and Jiang, 2016). However, similar to MoS₂, the HER activity of layered MoSe₂ is largely limited by its poor conductivity and serious aggregation or restacking during the synthesis procedure (Mao et al., 2015; Qu et al., 2015), inhibiting the practical application of MoSe₂ catalyst. Therefore, it is significant to improve the electrochemical activity of MoSe₂-based catalyst. Recent works have shown that coupling MoSe₂ with other transition metal selenides and constructing heterostructured materials could be an effective approach to further enhance the electrocatalytic performance of MoSe₂. For instance, Wang et al. found that the MoSe₂@Ni₀.85Se nanowire delivered enhanced kinetics and performance for HER in alkaline conditions due to the high density of active edges of MoSe₂ and the good conductivity of Ni₀.85Se (Wang et al., 2017a). Zhang et al. synthesized 2D MoSe₂/NiSe₂ nanowires, which significantly enhanced HER activity with a low Tafel slope and overpotential in 0.5 M H₂SO₄, because the 3D structure affords more active sites (Zhang et al., 2017a). Liu et al. fabricated MoSe₂-NiSe@carbon heteroanastructures and achieved glorious HER catalytic properties and excellent durability in both acidic and base conditions (Liu et al., 2018). In addition, the hierarchical mesoporous MoSe₂@CoSe/N–C composite also exhibits outstanding HER activity (Chen et al., 2019b). Despite significant success, most of previous reports mainly focused on the improvement of HER performance, while the OER activity of MoSe₂ catalyst in alkaline media has been ignored. Hence, the rational design and fabrication of MoSe₂-based bifunctional electrocatalysts with satisfactory activity and stability toward overall water splitting in alkaline solution still remain a big challenge.

In this work, we developed a facile in situ phase separation strategy to construct a novel hierarchical heterostructure consisting of 0D–2D CoSe₇/MoSe₂ via the selenization of CoMoO₄ nanosheets supported on a carbon cloth (CC) (Figure 1). Due to the in situ phase transformation, CoSe₂ nanoparticles are uniformly anchored on MoSe₂ nanosheets in the integrated structure, which can not only enhance reaction kinetics because of the synergetic effects, thus boosting the electrocatalytic activity, but also effectively suppress the aggregation/restacking of MoSe₂ nanosheets, thereby improving the structural stability. Moreover, the hierarchical structure assembled by 0D–2D CoSe₇/MoSe₂ could provide abundant active sites for the electrochemical reactions. As a result, the designed CoSe₇/MoSe₂ architecture exhibits outstanding OER and HER performance in alkaline media. More specifically, a small overpotential of 280 mV is achieved at a current density of 10 mA cm⁻² for OER with a small Tafel slope of 86.8 mV dec⁻¹, and the overpotential is 90 mV at a current density of 10 mA cm⁻² for HER with a Tafel slope of 84.8 mV dec⁻¹ in 1 M KOH. Moreover, the symmetrical electrolyzer assembled with the CoSe₇/MoSe₂ catalysts delivers a small cell voltage of 1.63 V at 10 mA cm⁻² toward overall water splitting.

**EXPERIMENTAL SECTION**

**Synthesis of CoMoO₄ Nanosheet**

Firstly, a pristine carbon cloth (CC) was treated with nitric acid solution overnight, subsequently ultrasonicated in deionized (DI) water and dried in an oven at 80°C for 2 h. After that, 1 mmol cobalt acetate, 1 mmol ammonium molybdate, 2 mmol urea, and 5 mmol ammonium fluoride were dissolved in 30 mL DI water, followed by ultrasonication for 30 min. Then, the homogeneous solution was poured into a 50-mL Teflon-lined electrodeposition of Co precursor was reacted with 0.5 g selenium powder under an Ar/H₂ (90%/10%) atmosphere at 450°C for 1 h. After cooling to room temperature, the CC was washed with DI water for several times and dried in a vacuum freeze-dryer overnight. Finally, the obtained sample was treated at 400°C for 2 h with a ramp rate of 5°C min⁻¹ in an argon atmosphere.

**Synthesis of CoSe₂/MoSe₂**

The as-prepared CoMoO₄ precursor was reacted with 0.5 g selenium powder at 450°C for 1 h under an Ar/H₂ (90%/10%) atmosphere to form the CoSe₂/MoSe₂.

**Synthesis of CoSe₂**

The CoSe₂ was prepared through two steps. Firstly, the treated CC was immersed in a 0.1 M Co(NO₃)₂ solution for the electrodeposition of Co (Yang et al., 2015). Then, the collected sample was reacted with 0.5 g selenium powder under an Ar/H₂ (90%/10%) atmosphere at 450°C for 1 h.

**Synthesis of MoSe₂**

Firstly, MoS₂ was prepared via hydrothermal reaction with the CC at 200°C for 12 h, followed by heating at 400°C for 2 h to form MoO₃ (Wu et al., 2018). Then, the obtained MoO₃ was reacted with 0.5 g selenium powder at 450°C for 1 h under an Ar/H₂ (90%/10%) atmosphere.

**Preparation of Pt/C**

Four milligrams of 20% Pt/C and 20 μL 5% Nafion solution were added into 1 mL solution of isopropanol and DI water (9:1) and then sonicated to form a uniform solution. Finally, the 11 cm²
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FIGURE 1 | Schematic illustration of the fabrication of CoSe$_2$/MoSe$_2$.

CC was soaked in the homogeneous solution and dried in air at atmospheric temperature.

**Preparation of RuO$_2$**

Four milligrams of RuO$_2$ and 20 µL 5% Nafion solution were added into 1 mL solution of isopropanol and DI water (9:1), and then the sample was sonicated to form a uniform solution. Finally, the 1*1 cm$^2$ CC was soaked in the homogeneous solution and dried in air at atmospheric temperature.

**CHARACTERIZATION**

The phase composition of the samples were characterized by X-ray diffraction (XRD, Bruker D8A A25), and the chemical states were determined through X-ray photoelectron spectroscopy (XPS, ESCALB 250Xi). The morphology and microstructure were recorded via field emission scanning electron microscopy (FE-SEM, FEI Nova NANOSEM 400) and high-resolution transmission electron microscopy (HR-TEM, JEM-2100 UHR STEM).

**ELECTROCHEMICAL MEASUREMENTS**

All samples made use of a three-electrode system performed by a biologic VSP300 type electrochemical workstation (Biologic Science Instruments, France). The sample of CoSe$_2$/MoSe$_2$ was put on the electrode holder as the working electrode with a mass loading of 4 mg/cm$^2$, the saturated calomel electrode (SCE) was the reference electrode, and a carbon rod served as the counter electrode. The electrolyte was 1 M KOH solution with saturated N$_2$. Linear sweep voltammetry (LSV) was characterized by polarization curves of OER with a scanning rate of 5 mV s$^{-1}$ from 0 to 0.8 V vs. SCE. Similarly, the polarization curves of HER were determined under the same condition from 0 to −0.8 V vs. SCE. The potentials were standardized by a reversible hydrogen electrode (RHE) as shown in the following: E (RHE) = E (SCE) + 0.059 × pH with instrument automatic 85% iR compensation. The electrochemically active surface area (ECSA) was calculated by cyclic voltammetry (CV) performed from −0.3 to −0.2 V vs. SCE with different scanning rates of 40, 60, 80, 100, and 120 mV s$^{-1}$. Electrochemical impedance spectroscopy (EIS) measurements were conducted by biologic VMP3 (Biologic Science Instruments, France) from 100 KHz to 0.1 Hz. The overall water-splitting electrolyzer was performed with CoSe$_2$/MoSe$_2$ as electrodes and 1 M KOH as the electrolyte.

**RESULTS AND DISCUSSION**

Figure 2A presents the FE-SEM image of the as-prepared CoMoO$_4$ precursor, which presents uniform nanosheets (with a lateral size of 2 µm) perpendicularly grown on the CC substrate with high coverage. After a selenization process, the obtained CoSe$_2$/MoSe$_2$ sample well maintains the pristine morphology of the CoMoO$_4$ precursor (Figure 2B). Moreover, the high-magnification SEM image further reveals that lots of nanoparticles are well dispersed on the surface of the nanosheet (Figure 2C), implying the structure and phase evolution during the selenization treatment. The elemental maps in (Figure 2D) show that Mo, Co, and Se are uniformly distributed throughout the nanosheets. In addition, the low-resolution TEM images in (Figures 2E,F) display that nanoparticles are uniformly distributed on the nanosheet during the thermal reduction procedure, forming the 0D/2D structure. Furthermore, the high-resolution TEM (Figure 2G) shows the lattice fringes of 0.26 nm and 0.65 nm corresponding to the (111) and (002) planes of CoSe$_2$ and MoSe$_2$, respectively (Qu et al., 2016; Liu et al., 2017), demonstrating the successful formation of the CoSe$_2$/MoSe$_2$ after the selenization reaction.

To investigate phase evolution during the selenization process, the crystal structure and phase composition of the obtained samples were characterized by X-ray diffraction (XRD) analysis (Figure 3A). The diffraction peaks of CoMoO$_4$ precursor (in the black line) can be well indexed to the CoMoO$_4$ phase (JCPDS No: 21-0868) (Wang et al., 2016). After the thermal reduction, some
new diffraction peaks can be observed. The diffraction peaks at around 13.7 °, 27.6 °, 31.4 °, and 37.8 ° can be assigned to the MoSe₂ phase (JCPDS No: 77-1715) (Qu et al., 2016), while the other peaks could be attributed to the phase of CoSe₂ (JCPDS No:53-0449) (Liu et al., 2017). The XRD result clearly manifests the successful phase separation of the CoSe₂ and MoSe₂ from the CoMoO₄ precursor via the selenization process.

X-ray photoelectron spectroscopy (XPS) measurement was carried out to analyze the composition and chemical state of as-prepared samples. (Figure 3B) illustrates the high-resolution Co 2p peaks at 778.8 eV (Co 2p₁/₂), 793.7 eV (Co 2p₁/₂), 780 eV (Co 2p₃/₂), and 796 eV (Co 2p₁/₂), corresponding to CoSe₂ and cobalt–oxide bond, while those peaks at 784.1 eV and 801.5 eV are the satellite peaks (Mu et al., 2016; Wang et al., 2017b; Gao et al., 2018). Furthermore, the fine Mo 3d XPS spectrum (Figure 3C) shows the main peaks at 228.8 eV and 231.9 eV, which represent the Mo 3d₃/₂ and Mo 3d₅/₂ of MoSe₂ (Wang et al., 2018a,b). Additionally, the peak located at 230 eV can be ascribed to the Se 3s of MoSe₂ (Zhao et al., 2018). The Se 3d XPS spectrum (Figure 3D) displays the characteristic of CoSe₂ and MoSe₂ at 54.5 eV and 55.4 eV in agreement with the Se 3d₃/₂ and Se 3d₅/₂, respectively (Gao et al., 2018). Moreover, the peak at around 59.8 eV is confirmed to correspond to the selenium–oxygen bond (Kong et al., 2014). According to these results, the selenization process induced the phase separation from CoMoO₄ into the nanoscale CoSe₂ and MoSe₂.

It is generally recognized that highly efficient electrocatalysts worked in alkaline solution is the bottleneck for large-scale application of overall water splitting. Linear sweep voltammetry (LSV) at a scanning rate of 5 mV s⁻¹ was characterized by the electrocatalytic HER and OER capacities of the samples by a three-electrode system in 1 M KOH solution with saturated N₂. By contrast, CoSe₂, MoSe₂ (Figure S1), RuO₂, and Pt/C catalysts were performed in the same condition. The HER polarization curves and corresponding Tafel slopes
are depicted in (Figures 4A,B). The overpotential ($\eta_{10}$) and Tafel slope of CoSe$_2$/MoSe$_2$ are 90 mV and 84.8 mVdec$^{-1}$, which are better than those of CoMoO$_4$ (277 mV, 123.6 mVdec$^{-1}$), CoSe$_2$ (205 mV, 195.2 mVdec$^{-1}$), and MoSe$_2$ (199 mV, 152.4 mVdec$^{-1}$). CoSe$_2$ has a metallic character, which can promote the dissociation of water and provide protons under alkaline conditions, thus improving the HER performance of MoSe$_2$ (Kwak et al., 2016). In addition, the hierarchical nanosheet array assembled by the CoSe$_2$/MoSe$_2$ provides abundant active sites for the electrochemical reaction at the phase interface, which can further enhance the HER performance (Zhang et al., 2017a). Therefore, the CoSe$_2$/MoSe$_2$ catalyst exhibits improved HER performance benefiting from the synergistic effect. The catalyst of Pt/C illustrates an overpotential ($\eta_{10}$) (59 mV) and Tafel slope (36.9 mVdec$^{-1}$) in 1 M KOH that are similar to those in other literatures (Chen et al., 2018b; Wan et al., 2018). Moreover, the overpotential of CoSe$_2$/MoSe$_2$ is superior to those of recently reported selenide catalysts such as NiSe NWS/Ni Foam (96 mV) (Tang et al., 2015), EG/cobalt selenide/NiFe–LDH (260 mV) (Hou et al., 2016), o-CoSe$_2$/P (104 mV) (Zheng et al., 2018), CoSe$_2$ NCs (520 mV) (Kwak et al., 2016), Co$_{0.75}$Ni$_{0.25}$Se/NF (106 mV) (Liu et al., 2019), 1T MoSe$_2$/NiSe (120 mV) (Zhang et al., 2019), and SWCNTs/MoSe$_2$ (219 mV) (Najafi et al., 2019) (Table S1).

The electrocatalytic OER properties are determined by LSV and polarization measurements as shown in (Figures 4D,E). The CoSe$_2$/MoSe$_2$ catalyst shows a lower overpotential ($\eta_{10}$ of 280 mV) than those of the CoMoO$_4$ (352 mV), CoSe$_2$ (322 mV), MoSe$_2$ (404 mV), and RuO$_2$ (318 mV), respectively. More importantly, the OER performance of the designed CoSe$_2$/MoSe$_2$ sample exceeds those of recently reported selenide catalysts in OER, for instance, the Ag–CoSe$_2$ (320 mV) (Zhao et al., 2017), CoSe$_2$ NCs (430 mV) (Kwak et al., 2016), CoSe$_2$/DETA (392 mV) (Guo et al., 2017), NiCo$_2$Se$_2$ holey nanosheets (295 mV) (Fang et al., 2017), NiSe–Ni$_{0.85}$Se/CP (300 mV) (Chen et al., 2018a), SWCNTs/MoSe$_2$ (295 mV) (Najafi et al., 2019), 1T/2H MoSe$_2$ (397 mV) (Li et al., 2019), and CoSe$_2$@MoSe$_2$ (309 mV) (Chen et al., 2019c) (Table S2). Furthermore, the corresponding Tafel slope of CoSe$_2$/MoSe$_2$ is 86.8 mVdec$^{-1}$, which is smaller than those of the CoMoO$_4$ (101.8 mVdec$^{-1}$), CoSe$_2$ (124 mVdec$^{-1}$), MoSe$_2$ (130 mVdec$^{-1}$), and RuO$_2$ (93.4 mVdec$^{-1}$). The CoSe$_2$/MoSe$_2$ has lower overpotential and smaller Tafel, which can be attributed to its unique hierarchical heterostructure, facilitating electron transfer and accelerating OER kinetics. In this heterostructure, the transfer of electrons from CoSe$_2$ phase to
MoSe$_2$ phase in the CoSe$_2$/MoSe$_2$ interface can result in electron-poor Co species and electron-rich Mo species (Liu et al., 2018). It is believed that the Se anion can affect the electron transfer between Co and Mo species, which is important for boosting catalytic ability (Yan et al., 2019). Besides, the formation of CoOOH is the primary cause to promote OER activity (Liu et al., 2015), and the increased 3d−4p repulsion between the center of the metal d band and the center of the p band of the Se site further promotes the rapid transfer of dioxygen molecules, thus improving OER performance (Li et al., 2017).

To understand the effects of the structure and composition of prepared catalyst on the electrochemical performance, several CoSe$_2$/MoSe$_2$ catalysts were collected at different selenization temperatures and the HER and OER performance were evaluated...
FIGURE 5 | Electrochemical double-layer capacitance with the CV curves acquired at different scanning rates from 40, 60, 80, 100, and 120 mV s$^{-1}$: (A) CoSe$_2$/MoSe$_2$, (B) CoSe$_2$, and (C) MoSe$_2$; (D) current densities ($\Delta j = j_{\text{anode}} - j_{\text{cathode}}$, at 0.82 V) as a function of scanning rates of CoSe$_2$/MoSe$_2$, CoSe$_2$, and MoSe$_2$ with the corresponding slope being twice that of the $C_{dl}$ values.

by LSV analysis (Figure S2). It can be seen that the CoSe$_2$/MoSe$_2$ sample obtained at 450°C (CoSe$_2$/MoSe$_2$-450) possesses better electrocatalytic properties than other counterparts, which can be ascribed to its superior structure. As shown in (Figure S3), with the selenization temperature increasing, the size of nanoparticles on the surface of nanosheets increased as well, indicating higher crystallinity. Generally, larger particle size will reduce the active surface of catalyst (Zhang et al., 2017b; Chen et al., 2019a). Therefore, when the selenization temperature elevated to 500°C (CoSe$_2$/MoSe$_2$-500), the catalytic performance slightly declined owing to its larger particle size and lower active surface. In addition, (Figure S4) displays the composition of the CoSe$_2$/MoSe$_2$ catalysts achieved at a different selenization temperature. As can be seen, when the selenization process proceeded at low temperature, the obtained CoSe$_2$/MoSe$_2$ catalyst has poor MoSe$_2$ phase and low crystallinity, which are responsible for the poor electrochemical catalytic performance of the catalysts (CoSe$_2$/MoSe$_2$-350 and CoSe$_2$/MoSe$_2$-400). Therefore, the catalyst synthesized at 450°C shows the best performance, benefiting from the appropriate crystal structure and phase composition.

The electrochemically active surface area (ECSA) of as-prepared catalyst was evaluated by the double-layer capacitance ($C_{dl}$), which was measured by CV in a non-Faradaic reaction potential range (Deng et al., 2015). The $C_{dl}$ values of the CoSe$_2$/MoSe$_2$ (1.6 mF cm$^{-2}$) is higher than those of CoSe$_2$ (0.63 mF cm$^{-2}$) and MoSe$_2$ (0.8 mF cm$^{-2}$), as shown in (Figure 5), suggesting more active sites of the CoSe$_2$/MoSe$_2$ catalyst. Furthermore, the smaller $R_{ct}$ value for the CoSe$_2$/MoSe$_2$ catalyst in the EIS measurement (Figure S5) implies the promoted charge transfer and boosted kinetics, which can be ascribed to the abundant interfaces and synergetic effect between the CoSe$_2$ and MoSe$_2$.

The structural stability is another significant parameter for catalysts in HER and OER. (Figures 4C,F) show a galvanostatic for CoSe$_2$/MoSe$_2$ catalyst in both the HER and OER processes. The morphology and composition of the catalyst after galvanostatic cycling are characterized by SEM and XPS. The
CoSe$_2$/MoSe$_2$ could well inherit the pristine sheet-like structure, demonstrating good structural stability. In addition, the fine XPS spectra of the Co 2p, Mo 3d, Se 3d acquired from the sample of CoSe$_2$/MoSe$_2$ after galvanostatic measurement confirm the reservation of CoSe$_2$ and MoSe$_2$ (Figure S6), indicating phase stability during the electrochemical reactions.

To investigate its practical application of the obtained catalyst, an overall water splitting electrolyzer is assembled with CoSe$_2$/MoSe$_2$ as electrodes in 1 M KOH. It can decompose water at a low cell voltage of 1.63 V (current density at 10 mA cm$^{-2}$) (Figure 6A), and the efficiency is similar to those constituting of the noble-metal-based cathode and anode (RuO$_2$ vs. Pt/C). Moreover, the overall water splitting performance of the CoSe$_2$/MoSe$_2$ is better than those of other recently reported non-noble metals at the same current density, such as (Ni,Co)$_{0.85}$Se NSAs (1.65 V) (Xiao et al., 2018), a-CoSe/Ti mesh (1.65 V) (Liu et al., 2015), CoO$_2$-CoSe (1.64 V) (Xu et al., 2016), Co$_{0.85}$Se@NC (1.76 V) (Meng et al., 2017), Co$_2$B/CoSe$_2$ (1.73 V) (Guo et al., 2017), NiSe$_2$/Ni (1.64 V) (Zhang et al., 2018), 1T/2H MoSe$_2$/MXene (1.64 V) (Li et al., 2019), and Ni$_3$Se$_2$/CF (1.65 V) (Shi et al., 2015) (Table S3). Additionally, CoSe$_2$/MoSe$_2$ electrolyzer exhibits a slight increase in the potential after being cycled for 12 h in alkaline solution (Figure 6B).

CONCLUSION

In summary, a novel hierarchical 0D−2D Co/Mo selenide was developed by a facile in situ phase separation strategy. Benefiting from its unique structure and composition, the constructed CoSe$_2$/MoSe$_2$ catalyst exhibits small $\eta_{10}$ of 280 mV and 90 mV and Tafel slopes of 86.8 mV·dec$^{-1}$ and 84.8 mV·dec$^{-1}$ for OER and HER, respectively. Furthermore, the electrolyzer comprising CoSe$_2$/MoSe$_2$ as the bifunctional catalyst shows a small water splitting cell voltage of 1.63 V at a current density of 10 mA·cm$^{-2}$. This work provides insights into rational design and development of economical and valid bifunctional catalysts for overall water splitting.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/Supplementary Material.

AUTHOR CONTRIBUTIONS

LX implemented the experiment, analyzed the data and wrote the article. HS, XL, XZ, and BG participated in the formulation of the experimental scheme. YZ, KH, and PC revised the article.

FUNDING

This work was financially supported by the National Natural Science Foundation of China (Nos. 51572100, 61434001, and 3150783).

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2020.00382/full#supplementary-material

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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