Enhanced photoelectrochemical hydrogen production efficiency of MoS$_2$-Si heterojunction

ABEER ALARAWI,1,4 VINOTH RAMALINGAM,2,4 HUI-CHUN FU,2 PURUSOTHAMAN VARADHAN,2 RUSEN YANG,3 AND JR-HAU HE2,*

1Material Science and Engineering (MSE) Division, King Abdullah University of Science & Technology (KAUST), Thuwal 23955-6900, Saudi Arabia
2Computer, Electrical, and Mathematical Sciences and Engineering (CEMSE) Division, King Abdullah University of Science & Technology (KAUST), Thuwal 23955-6900, Saudi Arabia
3School of Advanced Materials and Nanotechnology, Xidian University, Xi’an 710126, China
4Equal contribution
*jrhau.he@kaust.edu.sa

Abstract: Photoelectrochemical water splitting is one of the viable approaches to produce clean hydrogen energy from water. Herein, we report MoS$_2$/Si-heterojunction (HJ) photocathode for PEC H$_2$ production. The MoS$_2$/Si-HJ photocathode exhibits exceptional PEC H$_2$ production performance with a maximum photocurrent density of 36.33 mA/cm$^2$, open circuit potential of 0.5 V vs. RHE and achieves improved long-term stability up to 10 h of reaction time. The photocurrent density achieved by MoS$_2$/Si-HJ photocathode is significantly higher than most of the MoS$_2$ coupled Si-based photocathodes reported elsewhere, indicating excellent PEC H$_2$ production performance.

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1. Introduction

Solar-driven water splitting is one of the most promising approaches to utilize renewable energy to produce clean H$_2$ fuel [1,2]. The water splitting method can be categorized into two approaches which include electrochemical and solar-driven photoelectrochemical (PEC) H$_2$ production [3-6]. In general, PEC cell consists of two essential components i) photo-absorbing semiconductor to generate electron-hole pairs upon light illumination and ii) co-catalyst that facilitates charge transfer from semiconductor to the electrolyte and thereby induce the H$_2$ production process [7]. Among the wide range of light absorber materials, Si-based photocathodes have been widely adopted because of its low cost in the conventional solar industry [8,9]. Moreover, many theoretical studies have been illustrated that Si with the appropriate band-gap can perfectly align with the water oxidation–reduction potential levels [10].

In the PEC systems, $p$-type Si has been widely used as a photocathode for PEC H$_2$ production due to its downward band-bending in electrolyte, inexpensive and suitable band gap (~1.1 eV) to absorb solar light effectively. However, $p$-Si/H$_2$O junction causes an intrinsically low open-circuit voltage ($V_{oc}$), which greatly hampers the solar to H$_2$ conversion efficiency in PEC [9]. In contrast, replacing $p$-Si/electrolyte junction with a built-in $p$-$n$ junction by adding an $n^+$-layer to the $p$-Si can boost the photovoltage [11]. For example, Lewis demonstrated that the onset potential could be improved to about 0.56 V when Pt is used as a co-catalyst, and $p$-Si is used that features a high level of $n^+$ surface doping [11]. This is because of the $n^+$-layer provides a built-in depletion region at the semiconductor-liquid junction [11]. Therefore, adding $p^+$-Si layer on the back of the $n^+$-$p$ Si junction helps to facilitate the majority carrier collection, improving the device fill factor (FF) and overall performance [12].
Platinum and other noble metals are the best-known electrocatalysts for hydrogen evolution reaction (HER), but the high cost and scarcity have significantly hindered their large-scale commercial usage [13,14]. Consequently, intensive research is devoted to exploring a new catalyst that possesses characteristics such as earth-abundant, inexpensive, and non-toxic and has a highly efficient catalytic performance towards HER. For example, metal alloys [15], chalcogenides [16], nitrides [17], phosphides [18], borides [19], transition metal dichalcogenides (TMDs) [20], perovskites [21], and carbides [22]. In fact, most of these new materials have only been utilized as standalone electrocatalysts, and few of them have been integrated with photocathodes for PEC H₂ production [23]. Furthermore, the appearance of interfacial defect states causes charge recombination sites due to the unappropriated band alignment of the light absorber/co-catalyst/electrolyte bands [24]. Also, there are fabrication issues related to control the morphology, thickness, and uniform deposition when using the direct synthesis of co-catalyst on the light absorbing substrate [25]. Molybdenum disulfide (MoS₂) as a co-catalyst has been widely integrated with Si photocathodes due to its electrochemical stability in the acidic environment, excellent HER activity, the direct controllable synthesis method, and favorable band-gap alignment with Si [26].

Herein, we demonstrate MoS₂/Si-HJ as an efficient photocathode for PEC H₂ production. The MoS₂/Si-HJ photocathode shows an ability to address the shortcoming of each component. We have achieved a half cell solar-to-hydrogen (STH) conversion efficiency of 5.57% under AM 1.5G illumination with a maximum photocurrent density of 36.33 mA/cm² and an onset potential of 0.5 V vs. RHE. Besides, the electrochemical impedance spectroscopy (EIS) elucidates that the integration of MoS₂ significantly reduced the charge transfer resistance and thereby enhanced the PEC H₂ production performance of MoS₂/Si-HJ photocathode. Accordingly, the integration of Si (excellent light harvesting) and MoS₂ (HER catalytic ability, and chemical protection) results in fabricating of an earth-abundant catalyst coupled photocathode that has an efficient and stable PEC H₂ production characteristics.

2. Experimental details

2.1 Synthesis of MoS₂

The thermal annealing method was used for the synthesis of MoS₂ [27]. The different concentrations of ammonium tetrahiomolybdate (0.5 to 1.5 M) was prepared in dimethylformamide (DMF) solution and subsequently ultra-sonicated for 30 min [28]. Then, the prepared precursor solution was spin coated (500 rpm for 30 s and then 1500 rpm for 45 s) on a fluorine-doped tin oxide (FTO) substrates and heated at 80 °C for 20 min in a vacuum oven. Afterward, the spin-coated MoS₂ film was transferred into a tube furnace and annealed at 450 °C for one h under Ar: H₂ (8:2) atmosphere to obtain MoS₂ thin film [28]. Importantly, H₂ gas plays a critical role to avoid creating MoO₃ during the growth process and improves the MoS₂ film quality. Equation (1) shows the thermal decomposition reaction involved for synthesis the MoS₂ from the initial precursor [28].

\[(NH₄)_2MoS₄ + H_2 \rightarrow 2NH_4 + 2H_2S + MoS_2 \]  

2.2 Fabrication of MoS₂/Si-HJ photocathode

The photocathode includes several components. Firstly, n-type layers of (100) Si wafer with a thickness of 150 μm contains a dopant concentration of 5 × 10¹⁵ cm⁻³ that were fabricated on both sides of the cell by using an electrodeless chemical etching process [Solution of potassium hydroxide (KOH, 45 vol. %) and isopropyl alcohol (IPA)] to create a micro-pyramidal surface structure. Secondly, an emitter layer includes a 300 nm of p⁺-Si with a dopant concentration of 9 × 10¹⁹ cm⁻³ which is formed by utilizing the thermal diffusion of BCl₃. Thirdly, the back surface field layer contains a 300 nm of n⁻-Si with the dopant concentration of 3 × 10²⁰ cm⁻³ that is fabricated by the thermal diffusion process of POCl₄.
By utilizing the techniques of atomic layer deposition and plasma-enhanced chemical vapor deposition, the 7 nm of Al₂O₃ and 50 nm of Si₃N₄ were deposited on the top of the emitter layer, respectively. Finally, both Al₂O₃ and Si₃N₄ layers were etched by HF, and then the photolithography and lift-off processes were applied to both materials, to deposit 300 nm of Ag on the top side of the cell. Furthermore, the p⁺-layer side function is to harvest the light (light harvesting layer), due to its nearest location to the interface of the p⁺-n junction position. Before MoS₂ deposition, Si cell was treated with buffer oxide etchant (BOE) to remove the native oxide layer followed by O₂ plasma for 3 min to make the hydrophilic Si surface for the better integration of MoS₂ precursor with Si photocathode. MoS₂ film on Si photocathode was prepared by drop-casting MoS₂ precursor solution on the n⁺ side of Si and subsequently thermally annealed as described in MoS₂ synthesis (section 2.1).

For packing MoS₂/Si-HJ photocathode, Ga-In eutectic alloy (Sigma-Aldrich) was deposited on the electrode to make an Ohmic contact. The photocathode was subsequently connected with a Cu wire using silver paste. Samples then were embedded in Epoxy (Hysol 11C), and the only part that was covered with MoS₂ was exposed to the electrolyte. Epoxy then was dried at 80 °C for 30 min. The sample areas were then measured through the ImageJ software before the PEC measurements.

2.3 Characterizations

Raman spectroscopy measurements were carried out using a micro-Raman spectrometer. The samples were excited with a visible light laser [wavelength (λ = 473 nm)]. An objective lens at 100x magnification was used to focus the excitation laser on the desired spot of the MoS₂ thin film. Photoluminescence (PL) spectra of MoS₂ film was obtained using a Lab RAM spectrometer. X-ray photoelectron spectroscopy (XPS) studies were carried out in a Kratos Axis Supra DLD spectrometer equipped with a monochromatic Al Ka X-ray source (hv = 1486.6 eV) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of ~10⁻⁹ m bar. X-ray diffraction patterns (XRD) were collected at room temperature using a Bruker D8 Advance powder diffractometer. We used a field-emission scanning electron microscope (FE-SEM, Magellan and FEI) to observe the surface morphology. The TEM instrument used for this study was a probe Cs-corrected FEI-ST Titan 80–300 kV (ST) microscope. The high angle annular dark field-scanning electron microscopy (HAADF-STEM) were obtained using Titan Themis-Z TEM (TFS) at an operating voltage of 300 kV.

2.4 Electrochemical and photoelectrochemical (PEC) measurements

We evaluated the HER activity of the MoS₂ thin film at 25 °C in 0.5 M H₂SO₄ electrolyte using a standard three-electrode system, consists a MoS₂ electrode as the working electrode, Pt wire as the counter electrode, and Ag/AgCl (1 M KCl) as the reference electrode. All electrode potentials were converted with respect to RHE scale, according to Eq. (2). Also, all the HER curves were iR corrected to reflect the intrinsic behaviors of the catalysts.

\[
E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197V
\]  (2)

The electrochemical impedance spectroscopy (EIS) of the samples were measured at a frequency changing from 200 KHz to 100 MHz. For PEC measurements, AM 1.5G illumination was achieved with a 150 W halogen-lamp-based solar simulator. The chronoamperometry measurement was carried out using a three-electrode cell under one sun illumination in 0.5 M H₂SO₄. The amount of H₂ gas evolved during PEC experiments was measured using an online gas chromatography instrument (Agilent Technologies, 7890B GC system equipped with TCD detector).
3. Results and discussion

Fig. 1. (a) XRD patterns, (b) Raman spectra, (c) PL emission spectra, (d) XPS survey scan spectra, (e) High resolution Mo 3d XPS spectra and (f) High resolution S 2p XPS spectra of MoS$_2$ thin film.

Figure 1(a) shows the X-ray diffraction (XRD) patterns of as-synthesized 1M MoS$_2$ film on FTO substrate. A high intense peak noted at 2θ = ~14.6° corresponds to (002) plane of 2H-MoS$_2$ [29]. In addition, many smaller XRD peaks indicate the formation of polycrystalline multilayer MoS$_2$ film [30]. Figure 1(b) displays the Raman spectra of MoS$_2$ thin film. Two characteristic Raman peaks identified at ~379.3 cm$^{-1}$ and 406.82 cm$^{-1}$ are assigned to E$_{1g}^{2g}$ and A$_{1g}$ mode of MoS$_2$. The peak positions confirmed the formation of MoS$_2$ after thermal annealing process [31,32]. Additionally, the 27.52 cm$^{-1}$ separation between A$_{1g}$ and E$_{1g}^{2g}$ peaks indicates the presence of multilayer MoS$_2$ thin film [33]. The absence of vibrational peaks at 150 cm$^{-1}$, 219 cm$^{-1}$, and 327 cm$^{-1}$ indicates that 2H-MoS$_2$ was obtained [34]. In order to investigate the semiconducting phase of the obtained MoS$_2$ film, we evaluated the
photoluminescence (PL) spectra as illustrated in Fig. 1(c). We observed that the thermal annealing of the MoS₂ precursor at 450 °C leads to a high-intensity PL feature at around 610 nm resulted from the 2H-MoS₂ excitons. The PL emission spectra for the multilayer film reflects the semiconductor phase of MoS₂ with a direct band gap of around 2 eV [35]. The peak at 610 nm reflects the energy of excitons which are radiatively recombining from the direct band gap. Moreover, it suggests that the observed PL arises from the intrinsic electronic properties of the multilayer MoS₂ and not from structural defects or chemical impurities [33]. The chemical state of MoS₂ film was further studied by X-ray photoelectron spectroscopy (XPS). The survey scan XPS spectra of 1M MoS₂ shows the existence of Mo and S elements, reveals the formation of MoS₂ thin film [Fig. 1(d)]. The high-resolution Mo3d XPS spectrum is depicted in Fig. 1(e). The Mo3d spectrum consists of binding energy peaks at around 229.3 eV and 232.4 eV, which correspond to Mo3d₅/₂ and Mo3d₃/₂ orbitals, respectively [29]. Additionally, a small binding energy peak centered at 226.8 eV is related to S₂s. Likewise, high-resolution S2p XPS spectrum displays two peaks at 163.5 eV and 162.0 eV, which are assigned to S₂p₁/₂ and S₂p₃/₂ orbitals, respectively, that further indicates the presence of 2H-phase of MoS₂ [36]. Moreover, the Mo and S binding energies are in good agreement with previously reported values [37]. These results strongly suggest that the 2H-phase of MoS₂ is well preserved when the thermal annealing process is carried out at 450 °C.

Electrocatalytic HER activity of MoS₂ film was evaluated in 0.5 M H₂SO₄ electrolyte. Figure 2(a) displays the HER polarization curves of MoS₂ electrodes prepared using different precursor concentrations. The 0.5 M MoS₂, 1 M MoS₂ and 1.5 M MoS₂ catalysts exhibit an overpotentials of 0.177 V, 0.156 V and 0.136 V, respectively to reach 10 mA/cm² [Fig. 2(a)]. Interestingly, 1M MoS₂ shows excellent HER activity by offering low overpotential value at
high current density. For example, 1M MoS₂ exhibits an overpotential of 0.191 V to attain 60 mA/cm², which is smaller than the overpotential of MoS₂ prepared using 0.5M MoS₂ and 1.5M MoS₂ catalysts to achieve same current density. Based on the HER performance, MoS₂ catalyst prepared using 1M initial precursor solution was found to be the optimized HER catalyst. Moreover, the observed overpotential is almost similar to that of previously reported metallic MoS₂ nanosheets [38]. In order to gain more insights in reaction kinetics during HER, Tafel slope values were extracted from Tafel plots as shown in Fig. 2(b). The Tafel slope value of 1 M MoS₂ electrode is calculated to be 64 mV/decade, while 0.5 M and 1.5 M MoS₂ shows high Tafel values of 96 and 81 mV/decade, respectively. The smallest Tafel value offered by 1 M MoS₂ suggests that the mechanism of hydrogen adsorption/desorption is close to the Heyrovsky reaction regime (40 mV/decade) and the rate-limiting step here is the electrochemical desorption step [39]. Moreover, the Tafel value noted for 1 M MoS₂ quite agrees with previous reports of MoS₂ crystals, which range from 55 to 60 mV/ decade [40]. Overpotential and Tafel slope values comparison shows that 1 M MoS₂ is found to be optimized to achieve improved HER activity [Fig. 2(c)]. Stability is one of the most important factors used to evaluate the performance of a robust catalyst. Figure 2(d) shows chronocoulometry measurement that was used to analyze the long-term stability of the 1 M MoS₂ electrode at an overpotential of −0.1 V vs. RHE. The 1M MoS₂ is found to be stable up to 20h of continuous reactions with slight degradation in its performance, indicating excellent stability of MoS₂ in acidic environment.

A top view scanning electron microscopy (SEM) image of MoS₂ film reveals a continuous, ordered and compressed, featuring grains that cover the entire n⁺ side of Si cell [Fig. 3(a)]. As shown in Fig. 3(b), SEM image of the front side of Si cell shows micro-pyramidal structure. Figure 3(c) shows the SEM image of MoS₂/Si-HJ PEC cell in which a conformal and smooth MoS₂ thin film catalyst is uniformly covered the Si micro-pyramidal surface with a thickness of ~1–1.5 µm. In addition, top view TEM shows that the thick flakes of MoS₂ with different sizes are covered the pyramidal Si surface [Fig. 3(c) inset]. Figures 3(d)-3(f) depicts the HR-TEM images of MoS₂/Si-HJ. The lattice fringes values (0.607 nm and 0.31 nm) correspond to MoS₂ noted in Figs. 3(d) and 3(e) indicates the successful integration of MoS₂ with Si. Also, the HR-TEM images confirm the nanosheets layer-by-layer growth mode on the faceted n⁻-Si layer where the interface area appeared between the two materials. Figures 3(g) and 3(h) depict the HR-TEM image and its corresponding EDX mapping image at the interface between MoS₂ and Si. The HAADF-STEM image and its EDX mapping further reconfirm the integration of MoS₂ with Si. Furthermore, the mapping images confirm the existence of Mo, S and Si elements in MoS₂/Si-HJ [Figs. 3(i) and 3(l)].
Fig. 3. (a) Top view SEM image of MoS2 film, (b) SEM image of front surface of Si, (c) TEM image of MoS2 coated Si (inset, top view TEM image of MoS2/Si-HJ photocathode), (d-f) HR-TEM images of MoS2/Si-HJ, (g, h) TEM image and its corresponding mapping and (i-l) HAADF-STEM mapping images of Mo, S and Si elements in MoS2/Si-HJ.

The PEC H2 production performance of the photocathode was evaluated in 0.5 M H2SO4 using a three-electrode assembly. Illumination of the working electrode was simulated by solar irradiance and calibrated to “one sun” based on the AM 1.5G standard [41]. Figure 4(a) illustrates the schematic structure of MoS2/Si-HJ photocathode for PEC H2 production. Figure 4(b) shows the LSV curves of bare Si and MoS2/Si-HJ photocathodes under AM1.5 G illumination. As expected, bare Si photocathode exhibits poor PEC performance by offering large negative onset-potential value of −0.4 V vs. RHE and a maximum saturation photocurrent density value of about 26.2 mA/cm2. Impressively, MoS2/Si-HJ photocathode achieves an excellent PEC H2 production performance with a positive onset potential of 0.5 V vs. RHE, which is similar to the Voc of the Si-MP solar cell. Besides, MoS2/Si-HJ photocathode has achieved a maximum photocurrent density of 36.33 mA cm−2 at 0 V vs. RHE, indicating an exceptional catalytic activity of MoS2 as a co-catalyst in MoS2/Si-HJ photocathode. Moreover, the achieved current density and onset potential values are higher than most of the literature reported on MoS2/Si-based photocathodes (Table 1). Because of the superior characteristics of the Si cell since it possesses the ability to minimize the charge reduction and improve the light harvesting. In addition, integration MoS2 to this Si cell leads to reduce the charge transfer resistance and provide a complete corrosion protective layer thereby enhanced the solar to H2 conversion performance. Most importantly, the high saturation current density values that can be obtained from the MoS2/Si-HJ photocathode is close to the short circuit current density (JSC) of Si MP solar cell, suggesting a minimal optical loss due to the efficient light-trapping properties of the Si MP structure. Figure 4(c) displays the MoS2/Si-HJ photocathode response to ON/OFF light illumination. Besides, Fig. 4(d) demonstrates the stability measurement of MoS2/Si-HJ photocathode in which the MoS2/Si-HJ photocathode is found to be stable up to 600 min of reaction time. To explain the excellent
PEC H₂ production performance of the MoS₂/Si-HJ photocathode, we carried out electrochemical impedance spectroscopy (EIS). Figure 4(e) demonstrates the EIS spectra for bare Si cell and MoS₂/Si-HJ photocathodes measured under one sun illumination. Si photocathode without MoS₂ shows large charge transfer resistance, indicating poor interaction between electrolyte and Si surface. However, the MoS₂/Si-HJ photocathode has two distinguishable semicircles compared to that of bare Si cell [Fig. 4(e) inset]. The semicircles shape confirms the reduction of kinetics transport resistivity in MoS₂/Si-HJ photocathode. Furthermore, the semicircles proved the positive impact of the integration of the MoS₂ with Si, since more irreversible electrons can travel from Si to MoS₂ and thereby increasing its conductivity. Moreover, the unique Si cell structure increased the charge separation and decreased the recombination probability within the MoS₂/Si interface [42]. All of these factors played a significant role in increasing the MoS₂ electrons contribution for achieving efficient PEC H₂ production performance.

Fig. 4. (a) Schematic illustration of MoS₂ integrated Si photocathode for PEC H₂ production (b) LSV curve of bare Si cell and MoS₂/Si-HJ photocathode in 0.5 M H₂SO₄ at a scan rate of 20 mV/s upon AM 1.5G illumination, (c) MoS₂/Si-HJ photocathode response to ON/OFF
Finally, the half-cell solar-to-hydrogen conversion efficiency ($\eta_{STH}$), which refers to the relationship between the input energy (solar irradiation) to the output energy (electric or chemical energy via hydrogen evolution subtracted from the input applied potential) has been calculated using the following Eq. (3) [41].

$$\eta_{STH} (\%) = \frac{V_{oc} \times FF \times J_{sc}}{P_{in}} (\%)$$

where $J_{sc}$, FF and $V_{oc}$ represents the photocurrent density, fill factor and open-circuit potential of the PEC device [41]. Based on Eq. (3), the MoS$_2$/Si-HJ photocathode achieves a half-cell $\eta_{STH}$ of 5.5%. The amount of H$_2$ gas evolved by MoS$_2$/Si-HJ photocathode under light illumination was measured using an online gas chromatography instrument (Fig. 5). The H$_2$ gas produced by MoS$_2$/Si-HJ photocathode matches well with theoretically calculated H$_2$ value. The Faradaic efficiency of MoS$_2$/Si-HJ photocathode was estimated to be about 100%, suggesting the outstanding PEC H$_2$ production performance of MoS$_2$/Si-HJ photocathode.

![Graph showing calculated and experimental data for hydrogen evolution.](image)

**Fig. 5.** Theoretically calculated and experimentally evolved amount of H$_2$ using MoS$_2$/Si-HJ photocathode under AM1.5G light illumination

<table>
<thead>
<tr>
<th>Photocathode Structure</th>
<th>Electrolyte</th>
<th>Photocurrent Onset Potential ($V$ vs. RHE)</th>
<th>Photocurrent Density ($mA/cm^2$ at 0 $V$)</th>
<th>Stability (h)</th>
<th>Ref.</th>
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<td>0.5 M H$_2$SO$_4$</td>
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<td>36.34</td>
<td>10</td>
<td><em>This work</em></td>
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<tr>
<td>MoS$_2$/n$^+$ p Si</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>-0.20 to -0.10</td>
<td>17</td>
<td>100</td>
<td>[43]</td>
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**Table 1.** Comparison on the PEC H$_2$ production performance of MoS$_2$/Si-HJ photocathode with the reported MoS$_2$-integrated Si photocathodes.
4. Conclusion

In conclusion, MoS2/Si-HJ photocathode reported herein exhibited a maximum half-cell $\eta_{\text{STH}}$ of 5.5% with a high photocurrent density of 36.33 mA/cm$^2$, an open circuit potential of 0.5 V vs. RHE, and stability up to 10 h of continuous reaction time. The EIS measurement demonstrated that the integration of MoS2 significantly reduced the charge-transfer resistances across either the MoS2/Si-HJ interface or the MoS2/electrolyte interface and thereby significantly enhance the PEC H$_2$ production efficiency. The excellent PEC H$_2$ production performance of the integrated photocathode provides a promising alternative for non-noble metal co-catalysts toward solar-driven hydrogen production. Importantly, this will also lead to additional research and exploration to employ the semiconducting metal chalcogenides for PEC applications.

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