Interface engineering-inspired electron regulation in Pt/Pd hetero-metallene for methanol-assisted hydrogen evolution

| Journal:        | *Energy Lab*                                                      |
|-----------------|------------------------------------------------------------------|
| Manuscript ID   | ENLAB-2022-0005.R1                                               |
| Manuscript Type | Original Article                                                 |
| Date Submitted  | 27-Sep-2022                                                      |
| by the Author   |                                                                  |
| Complete List of Authors: | Liu, Songliang; Zhejiang University of Technology  |
|                  | Yin, Shuli; Zhejiang University of Technology                    |
|                  | Cui, Lin; Zhejiang University of Technology                      |
|                  | Yu, Hongjie; Zhejiang University of Technology                   |
|                  | Deng, Kai; Zhejiang University of Technology                     |
|                  | Wang, Ziqiang; Zhejiang University of Technology                 |
|                  | Xu, You; Zhejiang University of Technology                       |
|                  | Wang, Liang; Zhejiang University of Technology                   |
|                  | Wang, Hongjing; Zhejiang University of Technology                |
| Keywords:        | Pt/Pd hetero-metallene, interface engineering, electrocatalysis, hydrogen evolution reaction, methanol oxidation reaction |
| Speciality:      | energy, electrocatalysis, Nanocatalysis, water splitting         |

SCHOLARONE™
Manuscripts
Interface engineering-inspired electron regulation in Pt/Pd hetero-metallene for methanol-assisted hydrogen evolution

**Author list**

**Songliang Liu**
State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.
E-mail: 1310568013@qq.com

**Shuli Yin**
State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.
E-mail: 1134287078@qq.com

**Lin Cui**
State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.
E-mail: 731661138@qq.com

**Hongjie Yu**
State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.
E-mail: 527432719@qq.com

**Kai Deng**
State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.
E-mail: 347026380@qq.com
Ziqiang Wang  
State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.  
E-mail: zqwang@zjut.edu.cn

You Xu  
State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.  
E-mail: yxu@zjut.edu.cn

Liang Wang  
State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.  
E-mail: wangliang@zjut.edu.cn

Corresponding Author(s)*  
Hongjing Wang*  
State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.  
E-mail: hjw@zjut.edu.cn  
ORCID ID: https://orcid.org/0000-0003-0641-3909
Abstract

The small molecule oxidation reaction instead of oxygen evolution reaction coupled with hydrogen evolution reaction can greatly reduce the reaction overpotential of electrochemical water splitting, which is a very efficient and energy-saving hydrogen evolution strategy. Herein, we report an interface engineering constructed two-dimensional ultrathin curled Pt/Pd hetero-metallene for efficient electrocatalytic hydrogen evolution assisted by methanol. The thin-sheet structure of Pt/Pd hetero-metallene provides a large specific surface area and exposes numerous surface atoms that could act as reactive sites, thus accelerating the reaction mass transfer process. More importantly, the constructed Pt/Pd hetero-metallene possesses abundant Pt/Pd heterointerface, which can maximize the strong metal-metal interaction and increase the utilization of metal atoms, thereby optimizing the adsorption and activation of reactants during the reaction. Pt/Pd hetero-metallene can produce hydrogen stably and efficiently in 1 M KOH + 1 M CH₃OH, and the voltage only needs 0.83 V at @100 mA cm⁻² when used in electrocatalytic hydrogen evolution, which is much lower than the voltage required for the traditional electrochemical water splitting process (1.94 V). This work not only provides a powerful approach to rational design and construction of hetero-metallene through interface engineering, but also builds a bridge between hetero-metallene and methanol-assisted hydrogen evolution.

Keywords

Pt/Pd hetero-metallene, interface engineering, electrocatalysis, hydrogen evolution reaction, methanol oxidation reaction

Main text

1 Introduction

With the continuous consumption of fossil energy and increasingly serious environmental problems, there is an urgent need to find clean energy to replace fossil energy.¹⁻³ Hydrogen (H₂) is considered the most potential renewable energy source to replace fossil energy due to its high energy density and environmental non-pollution characteristics.⁴⁻⁵ The methods of producing H₂ mainly include biological methods, thermal methods, chemical methods and electrochemical methods.⁶⁻⁹ Among them, electrochemical water splitting is a green, efficient and sustainable way of H₂ evolution.¹⁰⁻¹³ Electrochemical water splitting consists of two half-reactions, the
anodic oxygen (O$_2$) evolution reaction (OER) and the cathodic H$_2$ evolution reaction (HER).\textsuperscript{14-16} It is worth noting that the traditional electrochemical water splitting OER process requires high overpotentials and generates low value-added O$_2$ (which may be explosive when mixed with H$_2$).\textsuperscript{17,18} Despite the development of many efficient catalysts to attempt to solve this problem, the desired efficiency has not been achieved.

Recently, the oxidation-assisted water electrolysis of small molecules (alcohols, hydrazine, glycerol, etc.) has attracted much attention.\textsuperscript{19-21} Compared with traditional water electrolysis, it can not only greatly reduce the overpotential, but also may produce high value-added products.\textsuperscript{22,23} Among them, methanol (CH$_3$OH) is regarded to be an ideal small molecule for oxidation-assisted water electrolysis due to its advantages of easy storage, low price, and low toxicity.\textsuperscript{24-26} Therefore, replacing OER with methanol oxidation reaction (MOR) to assist water electrolysis is a very efficient and energy-saving strategy. The key to driving methanol-assisted H$_2$ evolution (HER at the cathode and MOR at the anode) lies in the controllable preparation of high catalytic activity catalysts. It is well known that Pt is the most effective electrocatalyst for HER and MOR.\textsuperscript{27-29} However, the high price and scarcity of Pt severely limit its widespread commercial application.\textsuperscript{30,31} It is crucial to design and construct efficient Pt-based catalysts to enhance the catalytic activity as well as to improve the utilization of Pt in the catalyst.

Pd has a similar electronic structure to Pt, so it has similar physicochemical characteristics to Pt, and it is feasible to use Pd to replace most of the Pt in the catalyst.\textsuperscript{32-34} The controllable construction of morphology is one of the effective strategies to improve the catalytic performance of Pd-based nanomaterials. In which, two-dimensional (2D) nanomaterials exhibit unique strain effects, interfacial effects and ligand effects that can greatly improve the catalytic performance.\textsuperscript{35-39} It is noteworthy that defect-rich metallene, which has a similar structure to graphene, has been efficiently used in electrocatalytic reactions due to its high electrical conductivity, high specific surface area and fast mass transfer.\textsuperscript{40-43} For example, Guo and co-authors have prepared high-quality PdMo bimetallene with sub-nanometer thickness by a simple one-pot method, and the quantum size effect exhibited by the catalyst optimized the electronic structure between metals, resulting in excellent electrocatalytic performance.\textsuperscript{44} In addition, the construction of bimetallic catalysts to change the electronic configuration of the catalyst surface through ligand effects and induce facet effect to increase the catalyst active area is also an effective way to improve the catalytic performance.\textsuperscript{45-47} Among them, the hetero-interface is constructed by depositing ultra-small metal nanoparticles on the metal interface, and
the strong interaction between metal and metal is generated to amplify the interface
effect, which could greatly improve the utilization rate of metal atoms. Therefore,
the development of ultrathin metallene with Pt/Pd heterointerface is expected to
efficiently stimulate the methanol-assisted H₂ evolution.

Herein, we construct ultrathin and highly wrinkled 2D Pt/Pd hetero-metallene
through interface engineering. On the one hand, the unique 2D ultrathin nanosheet-
like structure of Pt/Pd hetero-metallene has a very large specific surface area, thus
exposing abundant catalytic active centers. On the other hand, Pt/Pd hetero-metallene
is composed of abundant uniform ultra-small Pt nanoparticles anchored on the surface
of Pd metallene. The formed abundant Pt/Pd heterointerface could spontaneously
generate a unique built-in electric field to optimize the electronic configuration at the
interface, thereby enhancing the adsorption and activation of reaction intermediates.

The constructed Pt/Pd hetero-metallene exhibit excellent HER catalytic performance
in both 1 M KOH and 1 M CH₃OH + 1 M KOH. In addition, when Pt/Pd hetero-
metallene is applied to methanol-assisted H₂ evolution, the voltage could be reduced
to 0.83 V at @100 mA cm⁻², which is significantly better than the traditional
electrolysis of water for H₂ evolution (1.94 V). This study provides a novel strategy
for the design and preparation of hetero-metallene and offers insights into how to
efficient and energy-saving produce H₂.

2. Experimental section

2.1. Materials and methods

Palladium (II) acetylacetonate (Pd(acac)₂, 99%) and K₂PtCl₄ (≥ 99.9%) were
purchased from Sigma-Aldrich. Tungsten hexacarbonyl (W(CO)₆, 99.9%) and acetic
acid (CH₃COOH, ≥96%) were received from Aladdin. ethylene glycol (EG, 98%) and
N, N-Dimethylformamide (DMF, 99.5%) were obtained from Xilong Scientific Co.
Ltd.

2.2. Synthesis of the Pt/Pd hetero-metallene

The Pd metallene was fabricated by our previous report method with minor
alteration. For a typical synthesis, W(CO)₆ (20 mg) and Pd(acac)₂ (10 mg) were
added to 8 mL of DMF to dissolve ultrasonically and then put it in an oil bath at 50 °C,
follow by adding 2 mL of acetic acid for 1 h. After that, the product washed by
ethanol for 5 times, and dissolved in 1 mL of water for further use. In the typical
synthesis of Pt/Pd hetero-metallene, 0.2 mL of newly-prepared Pd metallene added to
4.8 mL EG under sonication. After complete dissolution, 20 μL K₂PtCl₄ (20 mM) was
injected to the above solution, which was maintained in a water bath at 65°C for 2 h. Finally, the product was separated by centrifugation at 10000 rpm for 10 mins, washed several cycles with water and ethanol.

3. Results

Figure 1. (a) Schematic illustration for the synthesis of the Pt/Pd hetero-metallene. (b) HAADF-STEM and (c and d) TEM images of the Pt/Pd hetero-metallene. (e) False-color HRTEM image of the Pt/Pd hetero-metallene. (f) The particle size distribution of figure 1d. The insets in (e) display the lattice fringes and corresponding atomic absorption intensity profile of the square region.

Figure 1a illustrates the preparation of Pt/Pd hetero-metallene, by in situ generation abundant Pt/Pd hetero-interfaces densely on Pd metallene via a two-step synthesis method. Firstly, Pd metallene with ultrathin thickness was synthesized in high yield using W(CO)$_6$ as a structure directing agent.$^{51}$ Secondly, K$_2$PtCl$_4$ was injected into the Pd metallene EG solution to slowly form a large number of uniform Pt/Pd hetero-interfaces. The high-angle circular dark-field scanning transmission electron microscope (HAADF-STEM) and transmission electron microscope (TEM) images
show that the obtained Pd metallene have a graphene-like morphology with porous-rich surface (Figures. S1a-S1e). The selected area electron diffraction (SAED) pattern shows concentric ring profile, indicating that Pd metallene is polycrystalline (Figure. S1f). The lattice spacings of 0.225 nm in the high resolution TEM (HRTEM) image can be ascribed to the (111) plane of the face-centered cubic (fcc) Pd metallene (Figure. S1g). In addition, the average thickness of Pd metallene is determined to approximately 0.9 nm by the atomic force microscopy (AFM) (Figures. S1h and S1i).

Figure 2. (a) HRTEM image of the Pt/Pd hetero-metallene. (b) HAADF-STEM and EDS mapping images of the Pt/Pd hetero-metallene.

After the deposition of Pt nanoparticles (Pt NPs), the obtained Pt/Pd hetero-metallene still displayed ultrathin wrinkled nanosheet morphology (Figures. 1b, 1c and S2a-S2c). The ultrasmall Pt NPs with an average size of 2.4 nm are uniformly anchored on Pd metallene (Figures. 1d and 1f). The thickness of Pt/Pd heterometallene is 2.4 nm, suggesting that the Pt NPs are uniformly supported on the Pd metallene (Figure S2c and S2d). The abundant Pt/Pd heterointerfaces formed between Pt NPs and Pd metallene can regulate the local electronic configuration between Pt and Pd, which evolves into highly catalytically active centers. False-color HRTEM image illustrates the presence of Pt/Pd heterointerfaces in a clearer way (Figure 1e). The lattice spacings of 0.225 nm and 0.225 nm from different regions indexed to the (111) plane of Pt and Pd, respectively (Figures. 1e and 2a). Furthermore, the average spacing of the (111) planes of both Pt and Pd is 2.25 Å as shown in the inset of Figure. 1e. In addition, as shown in the energy dispersive X-ray spectroscopy (EDX) images, Pt and Pd elements are uniformly distributed on the metallene, further confirming the presence of Pt and Pd elements (Figure. 2b). The atomic ratio of Pt/Pd is estimated to be about 3/20 (Figure. S3). When no Pd metallene was added to the synthesis system,
the obtained Pt NPs suffered from violent agglomeration due to the lack of Pd metallene substrate (Figure. S4).

Figure 3. (a) XRD patterns of the Pd metallene and Pt/Pd hetero-metallene. (b) XPS survey spectrum of the Pt/Pd hetero-metallene. (c) Pt 4f XPS spectra of the Pt/Pd hetero-metallene. (d) Pd 3d XPS spectra of Pt/Pd hetero-metallene and Pd metallene. (e) Bader charge of the Pt/Pd hetero-metallene. Negative and positive charge are indicated by red and blue balls, respectively. (f) Electron density difference on the Pt/Pd hetero-metallene. (g, h and i) main side view, side view and Top-view of electron density difference on the Pt/Pd hetero-metallene, respectively. The charge accumulation and depletion are indicated by cyan and yellow area, respectively. The isosurface level is 0.007 e Å⁻³.

The crystal structure of Pt/Pd hetero-metallene was studied by X-ray diffraction (XRD). As shown in Figure. 3a, the XRD pattern shows four distinct diffraction peaks of the metal fcc structure, confirming the polycrystalline structure of Pt/Pd hetero-metallene. In addition, compared with Pd metallene, it is found that the XRD diffraction peak width increases after Pt NPs deposition, and the peak position does not shift significantly. The elemental composition and valence distribution of Pd
metallene and Pt/Pd hetero-metallene were further investigated by X-ray photoelectron spectroscopy (XPS). The XPS spectra of Pt/Pd hetero-metallene showed obvious Pt 4f orbital peaks and Pd 3d orbital peaks, which confirmed the existence of Pt and Pd elements (Figure 3b). In the XPS spectrum of Pt 4f in Pt/Pd hetero-metallene, two strong peaks can be observed at 74.4 and 71.1 eV, which can be attributed to Pt 4f_{5/2} and Pt 4f_{7/2} (Figure 3c). Furthermore, two small peaks are present at 75.4 and 71.9 eV, which can be attributed to Pt(II). In the XPS spectrum of Pd 3d in Pt/Pd hetero-metallene, two significant peaks located at 340.7 and 335.4 eV can be assigned to Pd(0) 3d_{3/2} and Pd(0) 3d_{5/2}, respectively (Figure 3d). The small peaks at 341.8 and 336.3 eV can be assigned to Pd(II), the existence of Pd(II) may be due to the oxidation of Pt/Pd hetero-metallene in air. It is worth noting that the peak position of Pt/Pd hetero-metallene is shifted 0.2 eV to the lower binding energy direction compared to the Pd 3d peak position of Pd metallene, which indicates the transfer of electrons from Pd to Pt.

Bader charge analysis was performed to further investigate the charge transfer at the Pt/Pd heterointerface. The total net charge of -0.23 eV for Pt and 0.23 eV for Pd was obtained by Bader charge analysis, thus confirming the transfer of electrons from Pd atoms to Pt atoms (Figures. 3e and S5). The charge transfer forms the generation of built-in electric field at the Pt/Pd heterointerface, which modulates the electronic configuration between the Pt and Pd atoms, and further promotes the adsorption and activation of the reactants. The charge density difference plots further indicate that the positive charge is accumulated in the Pt/Pd heterointerface, which is more likely to accept the lone pair electrons of the reactant molecules, thereby facilitating the adsorption of reactant molecules (Figures 3f-3i).

Pt/Pd hetero-metallene was investigated as an electrocatalyst for CH₃OH-assisted H₂ evolution due to its ultrathin nanosheet structure and the interfacial effect between Pt and Pd atoms, which facilitates the adsorption and activation of reactant molecules. CH₃OH-assisted H₂ evolution was evaluated by a two-electrode system in 1 M KOH. Firstly, the MOR and HER properties of Pt/Pd hetero-metallene were investigated. The catalytic performance of Pt/Pd hetero-metallene was evaluated by comparison with pure Pd metallene and commercial Pt/C as benchmarks. The electrochemically active surface area (ECSA) of the catalyst was calculated by using CO stripping experiments. Based on the adsorption and desorption area of CO, the ECSA of Pt/Pd
hetero-metallene was obtained as 66.3 m$^2$ g$^{-1}$, which is much larger than that of pure Pd metallene (56.8 m$^2$ g$^{-1}$) and Pt/C (45.3 m$^2$ g$^{-1}$) (Figure. S6). The results indicate that Pt/Pd hetero-metallene with ultrathin nanosheet structures and abundant Pt/Pd heterointerfaces can provide more catalytically active sites. The MOR performance testing of Pt/Pd hetero-metallene was performed at a scan rate of 50 mV s$^{-1}$ in N$_2$ saturated 1 M CH$_3$OH + 1 M KOH. The current normalized by the noble metal mass (NM) represents the mass activity (MA). As shown in Figure. 4a, the MA of Pt/Pd hetero-metallene is 1.82 mA μg$^{-1}$NM, which is higher than that of Pd metallene (1.11 mA μg$^{-1}$NM) and Pt/C (0.48 mA μg$^{-1}$NM). The current normalized by ECSA represents specific activity (SA). The Pt/Pd hetero-metallene has the highest specific activity (2.76 mA cm$^{-2}$), which is much higher than that of Pd metallene (1.97 mA cm$^{-2}$) and Pt/C (1.05 mA cm$^{-2}$) (Figures. 4b and 4c). Furthermore, the MOR activity of Pt/Pd hetero-metallene was superior to that of the recently reported catalysts (Table S1). Pt/Pd hetero-metallene has lower onset potential compared to Pd metallene and Pt/C, suggesting that the formation of Pt/Pd heterointerfaces optimizes the intermetallic electronic configuration and results in better reaction kinetic activity (Figure. S7).
order to evaluate the stability of Pt/Pd hetero-metallene, the chronoamperometry curves of each sample were tested. The current densities of Pt/Pd hetero-metallene were higher than those of Pd metallene and Pt/C throughout the measurement process, indicating the excellent catalytic stability of Pt/Pd hetero-metallene in MOR (Figure 4d).

![Figure 5.](image)

**Figure 5.** (a) HER polarization curves for various catalysts in 1 M KOH and (b) the comparison of overpotentials at 10 mA cm\(^{-2}\). (C) Tafel slope plots for various catalysts. (d) HER polarization curves for the Pt/Pd hetero-metallene in 1 M KOH with and without 1 M CH\(_3\)OH. (e) HER polarization curves for the Pt/Pd hetero-metallene before and after 5000 cycles in 1 M KOH. (f) Chronopotentiometry curves for the Pt/Pd hetero-metallene at a constant cathodic current density of 10 mA cm\(^{-2}\) in 1 M KOH for 15 h.

The HER performance of Pt/Pd hetero-metallene was then investigated in 1 M KOH, where the current density was normalized to the geometric area of the glassy carbon electrode. As shown in the linear sweep voltammetry (LSV) curves of each sample, to reach a current density of @-10 mA cm\(^{-2}\), the Pt/Pd hetero-metallene requires an overpotential of 35 mV, which is lower than that of the Pd metallene (283 mV) and Pt/C (46 mV) (Figures 5a and 5b). Notably, the Pt/Pd hetero-metallene also exhibited superior HER activity at 1 M KOH compared with recently reported catalysts (Table S2). The ultrathin nanosheet structure of Pt/Pd hetero-metallene provides sufficient active sites, while the abundant Pt/Pd heterointerface enhances the adsorption and dissociation of H\(_2\)O. In addition, the HER reaction kinetics of each
sample was further investigated by the Tafel slope plot. The Pt/Pd hetero-metallene (49 mV dec$^{-1}$) has the lowest Tafel slope value compared to the Pd metallene (279 mV dec$^{-1}$) and Pt/C (62 mV dec$^{-1}$), indicating that the Pt/Pd hetero-metallene has excellent HER kinetics (Figure. 5c). For the next step of CH$_3$OH reforming for H$_2$ evolution, the effect of CH$_3$OH on the HER performance was investigated. In 1 M CH$_3$OH + 1 M KOH, Pt/Pd hetero-metallene exhibited HER activity comparable to that exhibited in 1 M KOH (Figure. 5d). Next, the charge transfer rate of the catalyst was investigated by electrochemical impedance spectroscopy. Compared with Pd metallene, Pt/Pd hetero-metallene exhibit smaller charge transfer resistance in both HER and MOR (Figure. S8). This suggests that Pt/Pd hetero-metallene has a superior charge transfer rate, which can be attributed to the built-in electric field spontaneously constructed by the abundant heterointerfaces, enriching a large amount of positive charges in the interface region. The HER stability of Pt/Pd hetero-metallene was further investigated by CV cycle test and chronopotentiometry test. After 5000 CV cycles, the polarization curves of Pt/Pd hetero-metallene showed almost no decay compared with the initial curves (Figure. 5e). Meanwhile, the overpotential hardly decreased when tested at a current density of @-10 mA cm$^{-2}$ for 15 h, indicating the excellent HER stability of Pt/Pd hetero-metallene (Figure. 5f).

**Figure 6.** (a) Schematic illustration for two-electrode CH$_3$OH-assisted water splitting system. (b) LSV curves of the Pt/Pd hetero-metallene as anode and cathode in 1 M KOH with and without 1 M CH$_3$OH. (c) LSV curves of various catalysts in 1 M KOH + 1 M CH$_3$OH in a two-electrode system. (d) LSV curves of Pt/Pd hetero-metallene||Pt/Pd hetero-metallene in 1 M KOH with different CH$_3$OH concentrations
and (e) corresponding voltages at 100 mA cm\(^{-2}\). (f) Chronopotentiometry curves of Pt/Pd hetero-metallene||Pt/Pd hetero-metallene at a constant current density of 10 mA cm\(^{-2}\) in 1 M KOH + 1 M CH\(_3\)OH for 25 h.

Based on the excellent activity and stability of Pt/Pd hetero-metallene in MOR and HER, Pt/Pd hetero-metallene ink drops were dropped onto the surface of carbon paper as the electrodes for anodic MOR and cathodic HER (Pt/Pd hetero-metallene/CP || Pt/Pd hetero-metallene/CP) to construct a two-electrode system (Figure. 6a). The performance of Pt/Pd hetero-metallene for CH\(_3\)OH assisted H\(_2\) evolution was evaluated by comparing with (Pd metallene/CP || Pd metallene/CP) and (Pt/C/CP || RuO\(_2\) /CP) two-electrode systems. The LSV of Pt/Pd hetero-metallene/CP at 1 M CH\(_3\)OH + 1 M KOH and 1 M KOH as shown in Figure. 6b. When reaching a current density of 100 mA cm\(^{-2}\), with the assistance of 1 M CH\(_3\)OH was 0.83 V lower than without the addition of CH\(_3\)OH. This fully proves that the introduction of small-molecule CH\(_3\)OH can greatly reduce the overpotential required for H\(_2\) evolution, thus achieving energy-saving and efficient H\(_2\) evolution. Further at a current density of 100 mA cm\(^{-2}\), the obtained potential is similarly much smaller than that of Pd metallene/CP || Pd metallene/CP and Pt/C/CP || RuO\(_2\) /CP (Figure. 6c). In addition, the voltage required for Pt/Pd hetero-metallene in CH\(_3\)OH-assisted H\(_2\) evolution is also better than that of the reported small molecule-assisted H\(_2\) evolution catalysts (Table S3). The LSV curves of Pt/Pd hetero-metallene in 1 M KOH with different concentrations of CH\(_3\)OH were significantly better than those obtained in 1 M KOH without CH\(_3\)OH (Figure. 6d). The results show that the concentration of CH\(_3\)OH has little effect on the catalytic activity (Figure. 6e). Stability is an important indicator for evaluating catalysts, and the current density changes are negligible by long-time chronopotentiometry (V-t) measurement in 1 M CH\(_3\)OH + 1 M KOH for 25 h, indicating that Pt/Pd hetero-metallene have excellent stability in the CH\(_3\)OH assisted H\(_2\) evolution (Figure. 6f). In addition, the morphology and structure of Pt/Pd hetero-metallene did not significantly change after a long-time V-t measurement (Figure. S9).

In order to better analyze the product distribution of MOR, nuclear magnetic resonance (NMR) was performed on the electrolyte solution before and after the test. According to the 1H and 1C spectra, obvious peaks of carbonate and formate appeared after the test, thus indicating that the products of MOR are carbonate and formate (Figure. S10).

4. Discussion
When using small-molecule CH$_3$OH-assisted H$_2$ evolution, the voltage required for Pt/Pd hetero-metallene is much lower than that required for conventional water electrolysis, indicating that small molecule assisted H$_2$ evolution is indeed an energy-saving strategy. Benefiting from the advantages of structural engineering and surface-interface engineering, Pt/Pd hetero-metallene exhibit excellent performance in CH$_3$OH-assisted H$_2$ evolution. The ultrathin nanosheet structure of Pt/Pd hetero-metallene can expose more active atoms, thereby facilitating charge transfer.$^{54-57}$ In addition, Pt/Pd hetero-metallene has a large number of Pt/Pd heterointerfaces, and the built-in electric field constructed spontaneously at the interface can adjust the electronic structure of Pt and Pd atoms, thereby enhancing the adsorption and activation of reactant molecules.$^{58,59}$

5. Conclusions

In conclusion, ultrasmall Pt NPs are uniformly anchored on Pd metallene by interface engineering, resulting in the formation of abundant Pt/Pd heterointerfaces. The Pt/Pd hetero-metallene has an ultrathin wrinkled nanosheet structure, exhibiting an extremely large specific surface area, exposing more catalytically active sites. In addition, the constructed Pt/Pd heterointerface modulates the electronic configuration between metal atoms, which could amplify the metal/metal interface effect interaction, thereby optimizing the adsorption and activation of reaction intermediates to further accelerate the reaction kinetics. The Pt/Pd hetero-metallene in a two-electrode system for CH$_3$OH-assisted H$_2$ evolution can exhibit excellent H$_2$ evolution activity and stability at a low voltage of 0.83 V at @100 mA cm$^{-2}$, which is far superior to traditional electrochemical water splitting. This study not only provides an effective strategy for the preparation of high-efficiency small molecule-assisted H$_2$ evolution electrocatalysts, but also provides a reference for interface engineering to construct hetero-metallene.

6. Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No. 21972126, 21978264, 21905250, 22101254, 22278369), Natural Science Foundation of Zhejiang Province (No. LQ22B030012) and China Postdoctoral Science Foundation (2021M702889).
Additional results for material characterizations and electrochemical measurements, and Table S1-S3 comparisons of the performance.

8. Conflict of interest

The authors declare no conflict of interest.

9. Author contributions

Hongjing Wang and Liang Wang supervised the project. Songliang Liu conceived the idea and designed the experiments. Songliang Liu and Shuli Yin wrote the manuscript. Shuli Yin, Lin Cui, Hongjie Yu, Kai Deng, Ziqiang Wang, and You Xu discussed the experiment results. All authors have given approval to the final version of the paper.

10. References

[1] Z. Zhao, H. Liu, W. Gao, W. Xue, Z. Liu, J. Huang, X. Pan, Y. Huang, J. Am. Chem. Soc., 2018, 140, 9046.
[2] Y. Li, C. K. Peng, H. Hu, S. Y. Chen, J. H. Choi, Y. G. Lin, J. Lee, M. Nat. Commun., 2022, 13, 1143.
[3] Z. L. Wang, K. Sun, J. Henzie, X. Hao, C. Li, T. Takei, Y. M. Kang, Y. Yamauchi, Angew. Chem. Int. Ed., 2018, 57, 5848.
[4] K. Wang, B. Huang, F. Lin, F. Lv, M. Luo, P. Zhou, Q. Liu, W. Zhang, C. Yang, Y. Tang, Y. Yang, W. Wang, H. Wang, S. Guo, Adv. Energy Mater., 2018, 8, 1801891.
[5] Y. Guo, J. Tang, Z. Wang, Y.-M. Kang, Y. Bando, Y. Yamauchi, Nano Energy, 2018, 47, 494.
[6] X. Wu, J. Li, Y. Li, Z. Wen, Chem. Eng. J., 2021, 409, 128161.
[7] M. Zhang, J. Chen, H. Li, P. Cai, Y. Li, Z. Wen, Nano Energy, 2019, 61, 576.
[8] Y. Xu, X. Chai, T. Ren, S. Yu, H. Yu, Z. Wang, X. Li, L. Wang, H. Wang, Chem. Commun., 2020, 56, 2151.
[9] S. Fang, X. Zhu, X. Liu, J. Gu, W. Liu, D. Wang, W. Zhang, Y. Lin, J. Lu, S. Wei, Y. Li, T. Yao, Nat. Commun., 2020, 11, 1029.
[10] A. Ali, P. K. Shen, Carbon Energy 2019, 2, 99.
[11] Q. Mao, K. Deng, W. Wang, P. Wang, Y. Xu, Z. Wang, X. Li, L. Wang, H. Wang, J. Mater. Chem. A, 2022, 10, 8364.
[12] W. Zhang, B. Huang, K. Wang, W. Yang, F. Lv, N. Li, Y. Chao, P. Zhou, Y.
Yang, Y. Li, J. Zhou, W. Zhang, Y. Du, D. Su, S. Guo, *Adv. Energy Mater.*, 2020, 11, 2003192.

[13] J. Xu, I. Amorim, Y. Li, J. Li, Z. Yu, B. Zhang, A. Araujo, N. Zhang, L. Liu, *Carbon Energy*, 2020, 2, 646.

[14] H. Huang, Y. Zhao, Y. Bai, F. Li, Y. Zhang, Y. Chen, *Adv. Sci.*, 2020, 7, 2000012.

[15] G. Zhou, M. Li, Y. Li, H. Dong, D. Sun, X. Liu, L. Xu, Z. Tian, Y. Tang, *Adv. Funct. Mater.*, 2019, 30, 1905252.

[16] W. Song, M. Li, C. Wang, X. Lu, *Carbon Energy*, 2020, 3, 101.

[17] K. Kani, H. Lim, A. E. Whitten, K. Wood, A. J. E.Yago, M. S. A. Hossain, J. Henzie, J. Na, Y. Yamauchi, *J. Mater. Chem. A*, 2021, 9, 2754.

[18] W. Zhou, T. Jia, D. Zhang, Z. Zheng, W. Hong, X. Chen, *Appl. Catal. B: Environ.*, 2019, 259, 118067.

[19] L. Chen, J. Shi, *J. Mater. Chem. A*, 2018, 6, 13538.

[20] K. Deng, Q. Mao, W. Wang, P. Wang, Z. Wang, Y. Xu, X. Li, H. Wang, L. Wang, *Appl. Catal. B: Environ.*, 2022, 310, 121338.

[21] Y. Xu, M. Liu, S. Wang, K. Ren, M. Wang, Z. Wang, X. Li, L. Wang, H. Wang, *Appl. Catal. B: Environ.*, 2021, 298, 120493.

[22] J. Y. Zhang, H. Wang, Y. Tian, Y. Yan, Q. Xue, T. He, H. Liu, C. Wang, Y. Chen, B. Y. Xia, *Angew. Chem. Int. Ed.*, 2018, 57, 7649.

[23] C. Lin, P. Zhang, S. Wang, Q. Zhou, B. Na, H. Li, J. Tian, Y. Zhang, C. Deng, L. Meng, J. Wu, C. Liu, J. Hu, L. Zhang, *Journal of Alloys and Compounds*, 2020, 823, 153784.

[24] K. Xiang, D. Wu, X. Deng, M. Li, S. Chen, P. Hao, X. Guo, J. L. Luo, X. Z. Fu, *Adv. Funct. Mater.*, 2020, 30, 1909610.

[25] G. Ma, X. Zhang, G. Zhou, X. Wang, *Chem. Eng. J.*, 2021, 411, 128292.

[26] S. Yin, S. Liu, Z. Wang, Y. Xu, X. Li, H. Wang, L. Wang, *Chem. Eng. J.*, 2022, 435, 134711.

[27] Y. Shi, Z. R. Ma, Y. Y. Xiao, Y. C. Yin, W. M. Huang, Z. C. Huang, Y. Z. Zheng, F. Y. Mu, R. Huang, G. Y. Shi, Y. Y. Sun, X. H. Xia, W. Chen, *Nat. Commun.*, 2021, 12, 3021.

[28] J. Chen, M. Qin, S. Ma, R. Fan, X. Zheng, S. Mao, C. Chen, Y. Wang, *Appl. Catal. B: Environ.*, 2021, 299, 120640.

[29] H.-S. Chen, T. M. Benedetti, J. Lian, S. Cheong, P. B. O’Mara, K. O. Sulaiman, C. H. W. Kelly, R. W. J. Scott, J. J. Gooding, R. D. Tilley, *ACS Catal.*, 2021, 11, 2235.
[30] Z. Zhang, J. Liu, J. Wang, Q. Wang, Y. Wang, K. Wang, Z. Wang, M. Gu, Z. Tang, J. Lim, T. Zhao, F. Ciucci, Nat. Commun., 2021, 12, 5235.

[31] Q. Yang, H. Liu, P. Yuan, Y. Jia, L. Zhuang, H. Zhang, X. Yan, G. Liu, Y. Zhao, J. Liu, S. Wei, L. Song, Q. Wu, B. Ge, L. Zhang, K. Wang, X. Wang, C. R. Chang, X. Yao, J. Am. Chem. Soc., 2022, 144, 2171.

[32] H. Wang, S. Yin, Y. Xu, X. Li, A. A. Alshehri, Y. Yamauchi, H. Xue, Y. V. Kaneti, L. Wang, J. Mater. Chem. A, 2018, 6, 8662.

[33] T. J. Wang, Y. C. Jiang, J. W. He, F. M. Li, Y. Ding, P. Chen, Y. Chen, Carbon Energy, 2022, 4, 283.

[34] X. Zhao, X. Li, D. Xiao, M. Gong, L. An, P. Gao, J. Yang, D. Wang, Appl. Catal. B: Environ. 2021, 295, 120280.

[35] J. Fan, J. Wu, X. Cui, L. Gu, Q. Zhang, F. Meng, B. H. Lei, D. J. Singh, W. Zheng, J. Am. Chem. Soc., 2020, 142, 3645.

[36] K. Zhu, J. Ma, L. Chen, F. Wu, X. Xu, M. Xu, W. Ye, Y. Wang, P. Gao, Y. Xiong, ACS Catal., 2022, 4840.

[37] J. Liang, S. Li, Y. Chen, X. Liu, T. Wang, J. Han, S. Jiao, R. Cao, Q. Li, J. Mater. Chem. A, 2020, 8, 15665.

[38] J. Zhang, F. Lv, Z. Li, G. Jiang, M. Tan, M. Yuan, Q. Zhang, Y. Cao, H. Zheng, L. Zhang, C. Tang, W. Fu, C. Liu, K. Liu, L. Gu, J. Jiang, G. Zhang, S. Guo, Adv. Mater., 2022, 34, e2105276.

[39] X. Mu, J. Gu, F. Feng, Z. Xiao, C. Chen, S. Liu, S. Mu, Adv. Sci., 2021, 8, 2002341.

[40] Q. Mao, P. Wang, Z. Wang, Y. Xu, X. Li, L. Wang, H. Wang, Appl. Mater. Today, 2022, 26, 101400.

[41] C. Cao, Q. Xu, Q.-L. Zhu, Chem Catal., 2022, 2, 693.

[42] C. Tang, S.-Z. Qiao, Matter, 2019, 1, 1454.

[43] F. Lv, B. Huang, J. Feng, W. Zhang, K. Wang, N. Li, J. Zhou, P. Zhou, W. Yang, Y. Du, D. Su, S. Guo, Natl. Sci. Rev., 2021, 8, nwab019.

[44] M. Luo, Z. Zhao, Y. Zhang, Y. Sun, Y. Xing, F. Lv, Y. Yang, X. Zhang, S. Wang, Y. Qin, J. Y. Ma, F. Lin, D. Su, G. Lu, S. Guo, Nature, 2019, 574, 81.

[45] Q. Yun, Q. Lu, C. Li, B. Chen, Q. Zhang, Q. He, Z. Hu, Z. Zhang, Y. Ge, N. Yang, J. Ge, Y. B. He, L. Gu, H. Zhang, ACS Nano, 2019, 13, 14329.

[46] L. Y. Zhang, F. Wang, S. Wang, H. Huang, X. Meng, Y. Ouyang, W. Yuan, C. X. Guo, C. M. Li, Adv. Funct. Mater., 2020, 30, 2003933.

[47] L. Shi, Q. Wang, Q. Ren, Q. Yang, D. Zhao, Y. Feng, H. Chen, Y. Wang, Small, 2022, 18, e2103665.

[48] B. Zhang, G. Zhao, B. Zhang, L. Xia, Y. Jiang, T. Ma, M. Gao, W. Sun, H. Pan, Manuscript
Adv. Mater., 2021, 33, e2105400.

[49] Y. Yan, H. Shan, G. Li, F. Xiao, Y. Jiang, Y. Yan, C. Jin, H. Zhang, J. Wu, D. Yang, Nano Lett., 2016, 16, 7999.

[50] Z. Zhang, Y. Liu, B. Chen, Y. Gong, L. Gu, Z. Fan, N. Yang, Z. Lai, Y. Chen, J. Wang, Y. Huang, M. Sindoro, W. Niu, B. Li, Y. Zong, Y. Yang, X. Huang, F. Huo, W. Huang, H. Zhang, Adv. Mater., 2016, 28, 10282.

[51] H. Yu, T. Zhou, Z. Wang, Y. Xu, X. Li, L. Wang, H. Wang, Angew. Chem. Int. Ed. 2021, 60, 12027.

[52] R. Wu, Y. Li, W. Gong, P. K. Shen, ACS Sustainable Chem. Eng., 2019, 7, 8419.

[53] H. Wang, S. Jiao, S. Liu, S. Wang, T. Zhou, Y. Xu, X. Li, Z. Wang, L. Wang, ACS Appl. Mater. Interfaces, 2021, 13, 30479.

[54] M. Farsadrooh, J. Torrero, L. Pascual, M. A. Peña, M. Retuerto, S. Rojas, Appl. Catal. B: Environ., 2018, 237, 866.

[55] K. Deng, T. Zhou, Q. Mao, S. Wang, Z. Wang, Y. Xu, X. Li, H. Wang, L. Wang, Adv. Mater., 2022, e2110680.

[56] B. Jiang, Y. Guo, J. Kim, A. E. Whitten, K. Wood, K. Kani, A. E. Rowan, J. Henzie, Y. Yamauchi, J. Am. Chem. Soc., 2018, 140, 12434.

[57] C. Tang, N. Zhang, Y. Ji, Q. Shao, Y. Li, X. Xiao, X. Huang, Nano Lett., 2019, 19, 1336.

[58] L. Zhai, X. She, L. Zhuang, Y. Li, R. Ding, X. Guo, Y. Zhang, Y. Zhu, K. Xu, H. J. Fan, S. P. Lau, Angew. Chem. Int. Ed., 2022, 61, e202116057.

[59] Z. Li, Y. Pei, R. Ma, Y. Wang, Y. Zhu, M. Yang, J. Wang, J. Mater. Chem. A, 2021, 9, 13109.
The Pt/Pd hetero-metallene with abundant heterointerfaces and employed as electrocatalysts for methanol-assisted hydrogen evolution.