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Confinement and synergy effects of supported-confined bimetal catalysts with superior stability and catalytic activity

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abstract

Bimetallic nanocrystals have attracted considerable attention because of their complicated systems, which are far superior to those of their individual constituents. A TiO₂-confined PtMnP bimetallic catalyst (PtMnP@TiO₂) was prepared using an ultrasonic-assisted coincident strategy, which demonstrated exceptional catalytic activity in the universal hydrogen evolution reaction (HER). Owing to the bimetallic synergistic effect and TiO₂ confinement, PtMnP@TiO_x showed ultrasmall metal nanoparticles (NPs), a higher active Pt⁰ content, adequate activation at the porous surface, and abundant acid sites. Simulations were performed to visualize the strain properties of Mn and Pt during the bending process and demonstrate the high activity of Pt. The Pt-Mn bimetallic catalysts were enriched with Pt NPs, con-voyed by electron transfer from Mn to Pt. Briefly, PtMnP@TiO₂ showed robust evolution reaction activi-ties (an overpotential of 220 mV at a current density of 10 mA cm⁻² and a Tafel slope of 186 mV dec⁻¹) and the ability to contrast stated catalysts without ultrasonication-plasma. This protocol revealed that the geometrical and electronic effects of Pt and P surrounding the Mn species in PtMnP@TiO₂ were crucial for increasing the catalytic activity (99%) and durability (over 20 cycles), which were far superior to those of other reported catalysts.

1. Introduction

Nitro compounds are widely used as raw materials in the prepa-ration of amino paracetamol, dyes, clofibrate, pesticides, agro-chemicals, and other industrial products [1]. The reduction of nitro-compounds using supported nanoparticle catalysts has been documented as a well-organized and environmentally friendly treatment to yield amino compounds [1,2]. However, inevitable by-products such as azo- and nitroso-components, as well as the severe operating conditions (high temperature and pressure), pose challenges in the recovery of catalysts from chemical products

[3–5]. The one-step preparation of 4-aminophenol (4-AP) from 4-nitrophenol (4-NP) using different multimetal nanoparticles (NPs) has attracted significant attention. This reduction process displays simple selectivity problems, such as the reduction of phenylhydroxylamine to amino groups, because the one-step reac-tion includes the hydrogenation of nitro-compounds, such as nitrobenzene, to phenylhydroxylamine and their rearrangement into p-aminophenol.

The development of supported Pt-based nanocatalysts for the reduction of nitro-compounds to amino compounds has been com-prehensively studied because Pt-based nanocatalysts demonstrate high performance in the hydrogenation of nitro groups (–NO₂) [6–11]. However, poor durability and the lack of valuable metals hinder the extensive application of Pt-based nanocatalysts. Thus, numerous conventional multi-step approaches (e.g., impregnation or deposition–precipitation) have been developed in previous

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reports to decrease the concentration of Pt while improving or even maintaining the performance and selectivity and preventing aggregation and sintering upon calcination of the catalyst, such as core-shell or interfacially embedded nanostructure [12–15]. Different transition metals (e.g., Pd, Au, and Ag) is advantageous for the formation of trimetallic or bimetallic catalysts, which can concurrently reduce the use of Pt and enhance its surface electronic structure. Particularly, Pt-Mn-based alloys have been used instead of Pt to enhance the selectivity for C–H activation for the oxidation of propane at high temperature at 550 °C [15–17]. However, to date, there are no reports regarding their utilization in the reduction of 4-NP to 4-AP. Moreover, it remains challenging to realize the roles of Pt and Mn compounds and the intrinsic catalytic mechanisms for the reduction of 4-NP to 4-AP; further, nanocatalysts with an optimal electronic structure and highly active sites that can realize both high catalytic performance and selectivity remain to be proposed.

Herein, we fabricated PtMnP@TiO₂ catalysts with an average particle size of 2.5 ± 0.2 nm using simple strategy. Advanced characterizations of bimetallic catalyst established the alloy formation of these bimetallic nanoparticles. Notably, the high activity and durability test revealed no significant performance decay after 20 cycles, highlighting the promising stability of this ultrasmall PtMnP@TiO₂.

2. Materials and methods

2.1. Materials

Mn(NO₃)₂, H₂PtCl₆ · 6H₂O, KOH, K₃PO₄, glycerin (C₃H₈O₃), NaBH₄, 4-NP, and other nitro-compounds were purchased from Sigma-Aldrich and used as received.

2.2. Preparation of the PtMnP@TiO₂ catalyst

The PtMnP@TiO₂ catalyst was prepared using an incipient ultrasonic-assisted coincident electro-oxidation-reduction-precipitation (U-ORP) strategy. The titanium alloy (99.8% purity) was obtained from Sejin Titanium (South Korea). The PtMnP@TiO₂ catalyst was synthesized by submerging a titanium plate (10 mm × 10 mm × 2.5 mm), which was used as the working electrode, in an electrolyte solution (10 g L⁻¹ K₃PO₄, 5 g L⁻¹ KOH, and 20 g L⁻¹ C₃H₈O₃ in 2000 mL of water) and processed for 300 s under a 20 kW AC with a frequency of 60 Hz. Approach is an assisting system to produce plasma discharges more simply in a better method in the following working mode (more details in Ref. [17]).

2.3. Catalytic activity and electrochemical measurements

Details are provided in [Supporting Materials](#) and Ref. [18].

3. Results and discussion

We prepared titania-supported PtMnP NPs via a one-step U-ORP strategy using a highly dispersed metal precursor with high electronegativity, such as Pt, which was reduced by C₃H₈O₃ during reaction process. Meanwhile, the Ti metal plate oxidized to form a porous metal oxide owing to the high-voltage discharge on the Ti surface during U-ORP. In the following heat-treatment strategy (at low temperature, 0 °C), TiO₂ precipitated simultaneously, and PtMnP NPs gradually diffused into the porous surface of TiO₂ under ultrasonic irradiation (Fig. 1a–f).

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), high-resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), and energy-

dispersive spectroscopy mapping (EDS mapping) were used to analyze and confirm the formation of microscopic morphology, crystal structure, well-dispersed, narrowly distributed, and nanosized particles (2.0 ± 0.3 nm) on and within the surface of TiO₂ support. As shown in Fig. 1(g–j), the results of EDS-mapping showed that the PtMnP NPs were homogeneously mixed in each NP loaded on the TiO₂ surface. In addition, the XRD spectrum (Fig. S1) of the PtMnP NPs did not display any diffraction peaks, which can be attributed to the amorphous state of the U-ORP-TiO₂ films and the uniform dispersion of small PtMnP NPs [18]. HR-TEM images were obtained to examine the PtMnP NPs. As shown in Fig. 1(e and f), PtMnP NPs show a single-phase solid-solution structure and a lattice fringe spacing of 0.218 nm of PtMnP NPs along the [011] zone axis, suggesting that PtMnP NPs have a (111) base plane. The U-ORP strategy and the control experiment prove that when P atoms are used as the seed, the mixing of transition elements can be enhanced, which can be assigned to the small ΔH_{mix} of atom pairs between Pt and Mn [19].

X-ray photoelectron spectroscopy (XPS) was used to analyze the structure of PtMnP@TiO₂ catalysts (Fig. 2). The presence of two peaks at 72.4 eV (Pt 4f_{7/2}) and higher binding energy at 75.15 eV (Pt 4f_{5/2}) are attributed to the Pt 4f peaks, demonstrating the presence of the dominant metallic Pt⁰ state and trace Pt^{II} at lower and higher energy, respectively. The distinctive Mn 2p was fitted to two peaks at 652.96 and 645.86 eV, corresponding to Mn 2p_{1/2} and Mn 2p_{3/2} (Fig. 2b), respectively. In addition, the peaks at 132 eV in the P 2p XPS spectra was ascribed to elemental P⁰ (Fig. S2). This result confirms the presence of the Mn⁰ state [20]. The XPS peaks of Pt 4f in the PtMnP@TiO₂ catalyst displayed a positive shift compared to those of the Pt⁰ state in Pt@TiO₂. This electron shift is due to transfer of electron from Mn to Pt. This positive shift in binding energy was produced by electron transfer from the Mn atom to the Pt atom, which confirmed the successful fabrication of the PtMnP@TiO₂ catalyst. The Ti 2p two peaks agreeing to Ti 2p_{1/2} and Ti 2p_{3/2} at 457.98 and 463.74 eV, respectively. The peaks are positioned at lower binding energy associated to the anatase TiO₂ [459.6 eV; 465.3 eV] [20,21]. This not only confirms the NP-support interaction but also the origin of oxygen vacancies and the formation of Ti³⁺ ions [22,23]. Similarly, the O 1s spectrum in the support TiO₂ displays only two peaks at the binding energies of 529.42 and 530.53 eV, which could be attributed to TiO₂ and surface-adsorbed OH groups, respectively [24].

To predict the experimental properties of PtMnP NPs, a simulation of the bending process was performed using Abaqus software, where the Pt and Mn plates were bent by a round metal object with a total displacement of 4 mm for a total time of 4 s. The output of this simulation was visualized using the value of shear stress (Fig. 3) for three different time frames: 0, 1, and 2 s. Fig. 3 shows the time frames that clearly show the difference in terms of stress between Pt and Mn. According to the bending simulations, the mechanical (flexural) properties of Pt and Mn changed with time. Pt changed its properties faster during the formation of PtMnP NPs than Mn, based on the change in the stress component, especially S12 (shearing type of stress).

3.1. Catalytic performance of PtMnP@TiO_x for 4-nitrophenol reduction

The performance of PtMnP@TiO₂ was assessed in the reduction of 4-NP, which was selected as the model reaction, using NaBH₄. There are two different reaction reduction routes for 4-NP. In the first route, 4-NP is hydrogenated and dehydrated to 4-nitrosophenol, which is further reduced to hydroxylamine, and finally to 4-AP. In the second route, the condensation reaction includes the chemical reaction of 4-(hydroxyamino)phenol and 4-NP to yield azoxyphenol, which is then successively reduced to azophenol, hydrazophenol, and 4-AP. As shown in Fig. 4(a and b),

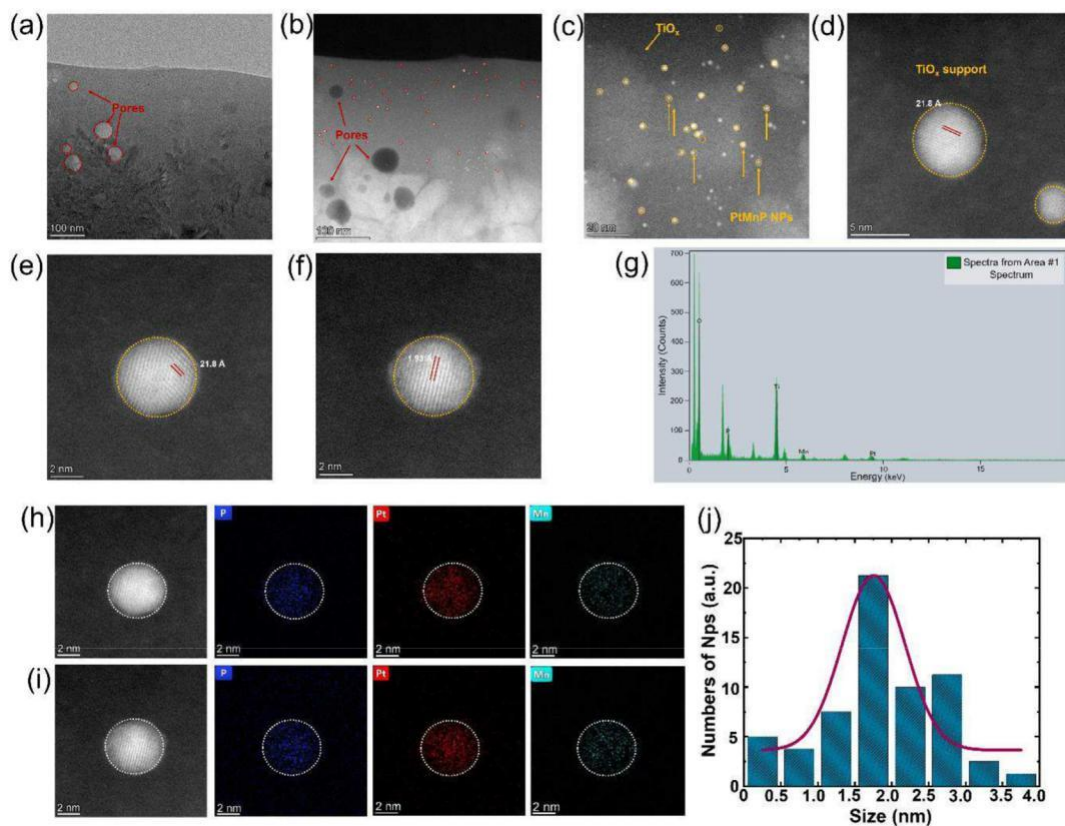


Fig. 1. Coordination of atomically dispersed PtMnP to TiO_x. (a–f) HAADF-STEM images schematic illustration of PtMnP@TiO_x structures. (g) EDS composition result of PtMnP@TiO_x catalyst. (h and i) EDS elements mappings of P, Pt and Mn in the PtMnP@TiO_x catalyst. The elements are color coded as follows: blue, P; red, Pt; aqua, Mn. (j) Size distribution of the NPs.

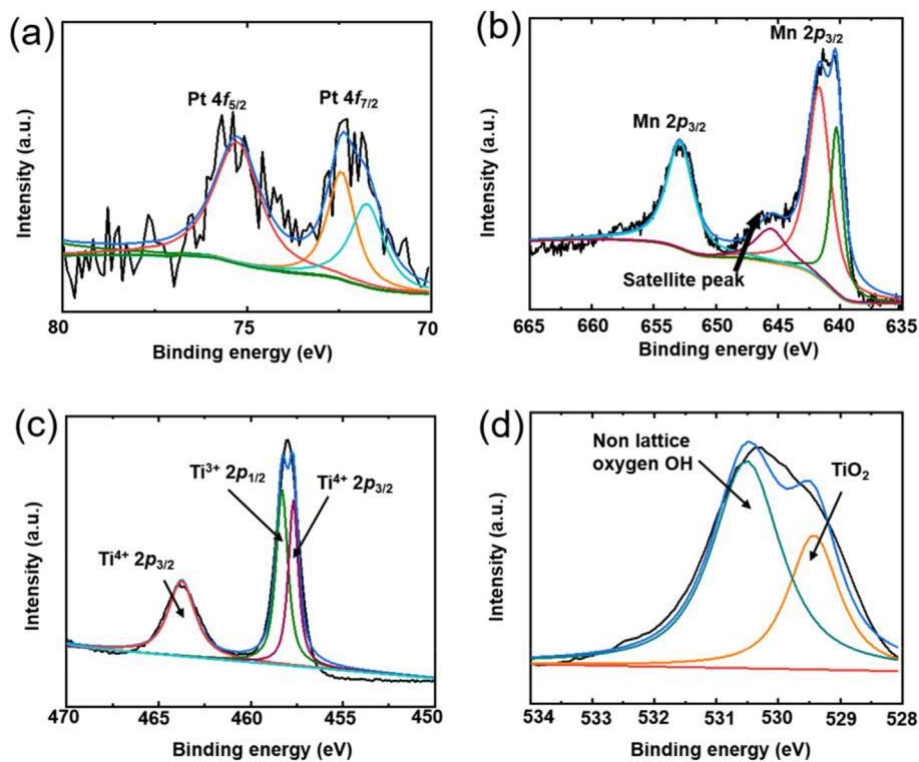


Fig. 2. XPS patterns of (a) Pt 4f, (b) Mn 2p, (c) Ti 2p, and (d) O 2s of PtMnP@TiO₂.

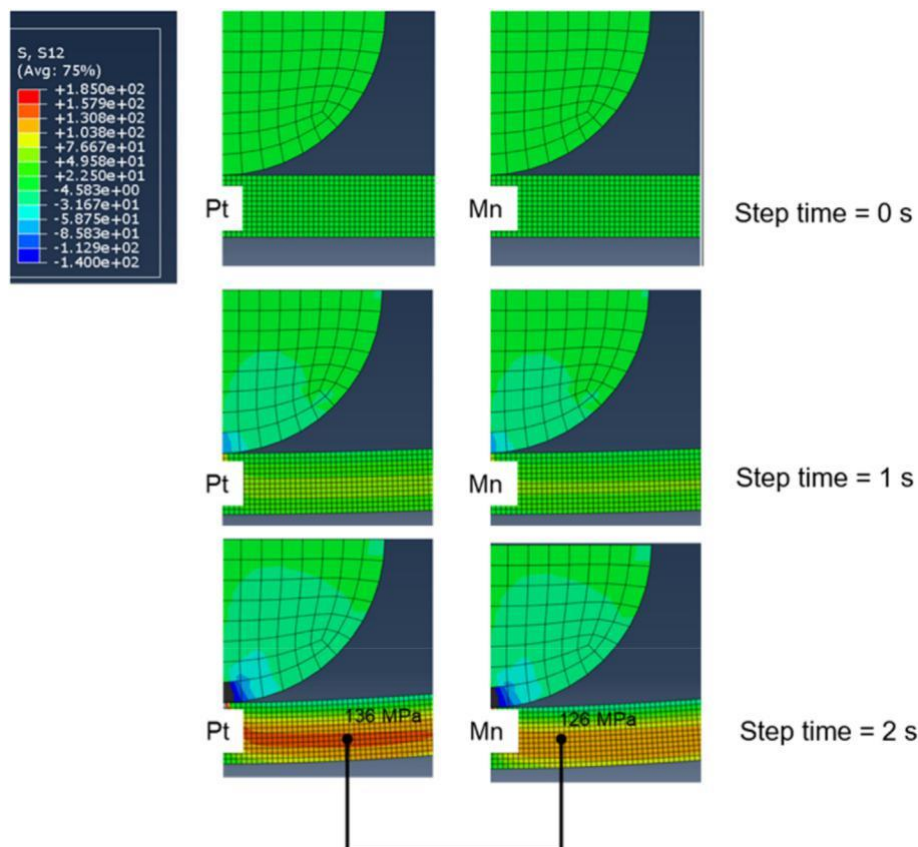


Fig. 3. Simulation for both Pt and Mn based on the strain distributions.

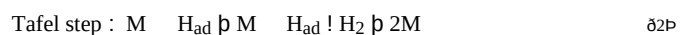
in the first step, 4-NP was hydrogenated to nitrosophenol. During the reduction reaction, nitrosophenol was produced, which then suddenly decreased. Although chloroform and tetrahydrofuran were found to be benign solvents for 4-NP hydrogenation using the PtMnP@TiO_x catalyst, no conversion of 4-NP was observed when tetrahydrofuran or chloroform was used (Fig. 4c) with PtMnP@TiO₂ as the catalyst. However, when H₂O was used as the solvent, PtMnP@TiO_x showed strong catalytic activity with larger amounts of 4-AP detected (Fig. 4b); the conversion was as high as 100%, which was nearly 1.5 times higher than that for the TiO_x-supported PtP and MnP NPs. As the final product of the catalytic reactions, the 4-AP content continuously increased. In addition to the previous results, trace amounts of azoxybenzene were observed, probably resulting from the decomposition of nitrosophenol or the presence of condensation chemical reactions (Fig. 4d and e).

In addition to catalytic activity, cycling experiments were completed to assess the stability of the PtMnP@TiO_x catalyst. As expected, there was a negligible decrease in the PtMnP@TiO_x in 4-AP production even after 20 consecutive cycles, representing the outstanding durability of the PtMnP@TiO_x catalyst. The PtMnP@TiO_x catalyst after 20 cycles of the catalytic reaction was confirmed using STEM to describe the size change of the PtMnP NPs after cycling. As shown in Fig. 4(f–h), no significant agglomeration and leaching were exhibited in the STEM images of NPs. This suggests a structural advantage of porous TiO_x as a support.

3.2. Electrochemical performance of PtMnP@TiO_x

A conventional three-electrode system with 0.5 M H₂SO₄ electrolytes was employed to evaluate the HER activity of PtMnP@TiO_x compared with MnP@TiO_x and PtP@TiO_x at 25 °C, which were

assessed under similar conditions at a current density of 10 mA cm⁻². As shown in Fig. 5(a), PtMnP@TiO_x possesses an overpotential of 549 mV, which is lower than those of MnP@TiO_x (791 mV) and PtP@TiO_x (598 mV). Furthermore, PtMnP@TiO_x exhibits the smallest Tafel slope value of 123 mV dec⁻¹ (Fig. 5b), compared with those of MnP@TiO_x (253 mV dec⁻¹) and PtP@TiO_x (225 mV dec⁻¹) according to the LSV curves. The Tafel slope, which indicates the kinetic behavior of the catalyst, also reveals the reaction mechanism, following the steps described by Volmer and Tafel [25].



where M represents the number of active sites in the PtMnP@TiO_x catalyst and H_{ad} indicates the adsorption sites. This process is initiated by the attachment of an H⁺ ion to the H_{ad} site, followed by the subsequent attachment of two adsorbed H_{ad} molecules to the active site, resulting in the formation of a single H₂ molecule. Consequently, the adsorption onto these active sites is the rate-limiting step in this reaction pathway. The double-layer capacitance (C_{dl}) values can be used to quantify the electrochemically active sites. In this study, C_{dl} values were determined via cyclic voltammetry (CV) measurements conducted over a range of voltages spanning 0.05–0.15 V (versus reversible hydrogen electrode; RHE), employing various scan rates (refer to Fig. 5c–e). Plotting the difference between anodic and cathodic current densities (Δj) against the corresponding scan rates completed the determination of C_{dl} [26], with values of 0.73, 0.76, and 0.78 mF cm⁻² for MnP@TiO_x, PtP@TiO_x, and PtMnP@TiO_x, respectively, which indicates that PtMnP@TiO_x possesses a higher number of active sites for catalysis behavior. Therefore, PtMnP@TiO_x facilitated faster diffusion of H⁺ to the active sites for catalytic reactions than the other synthesized materials.

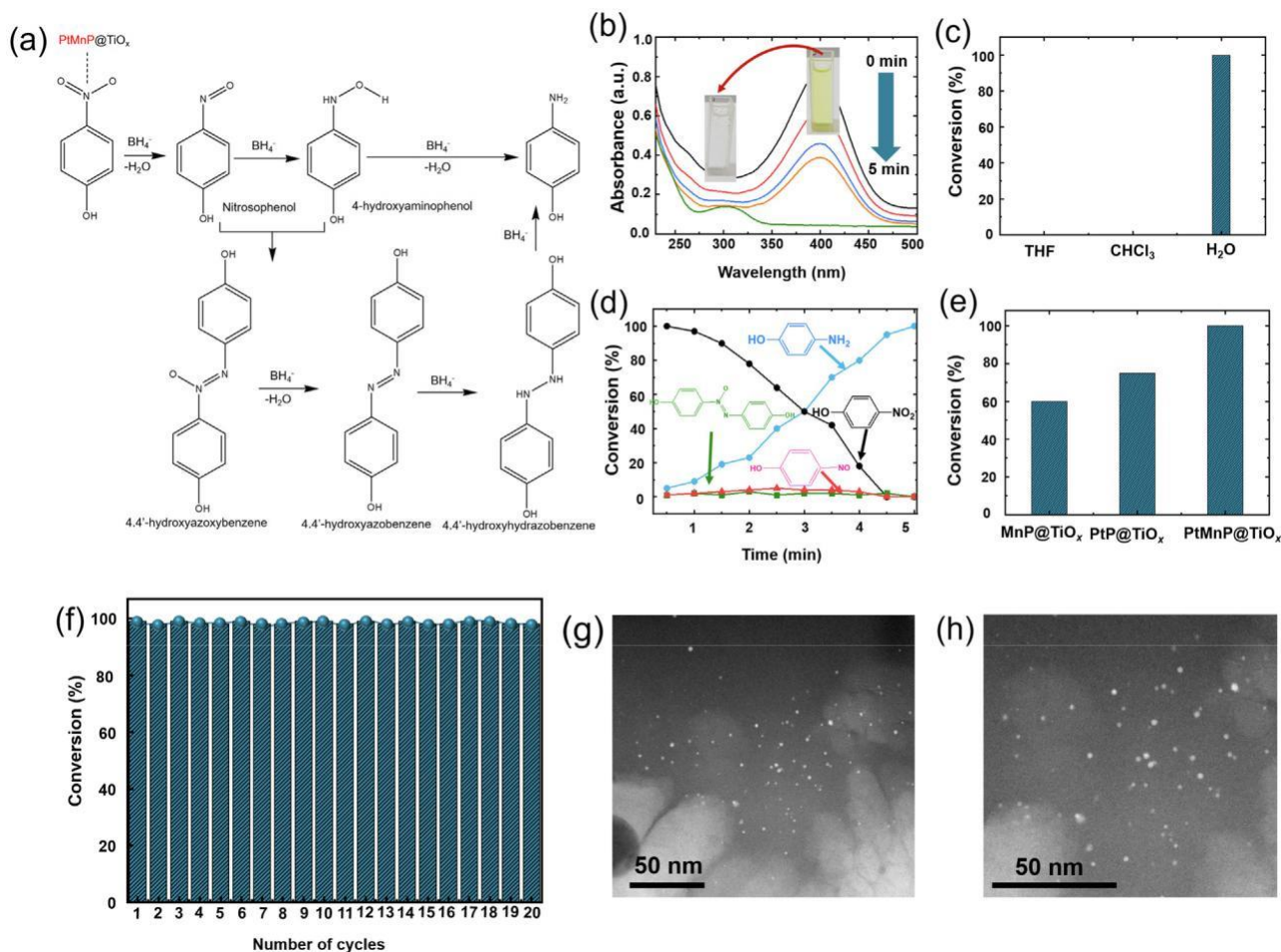


Fig. 4. (a) Possible reduction reaction of 4-NP. (b) PtMnP@TiO_x-catalyzed reduction of 4-NP by NaBH₄. (c) Products for the reduction of 4-NP by NaBH₄ with different solvents. (d) Distribution of products during the reduction reaction of 4-NP. (e) Product distribution for the reduction of 4-NP on different catalysts such as MnP@TiO_x, PtP@TiO_x, and PtMnP@TiO_x. (f) Stability tests of the PtMnP@TiO_x in the 4-NP reduction reaction. (g and h) STEM images of PtMnP@TiO_x after 20 cycles 4-NP.

In addition, the electrochemical surface area (ECSA) serves as a common metric for evaluating the number of active sites, directly correlating with the density of the electroactive sites involved in the reaction [27,28].

The ECSA is determined by using the following equation [29]:

$$\text{ECSA} = \frac{C_{dl}}{C_s} \approx \frac{C_{dl}}{0.04 \text{ mF cm}^{-2}} \text{ per cm}^2$$

where C_{dl} and C_s are the double-layer and specific capacitances, respectively. The C_s of a flat surface was considered as 0.04 mF cm^{-2} [30].

ECSA is a crucial parameter for the assessment of electrocatalysts. The ECSA values for MnP@TiO_x, PtP@TiO_x, and PtMnP@TiO_x are 18.25, 19, and 19.5 m^2 , respectively (Fig. 5g). The higher ECSA of PtMnP@TiO_x than those of MnP@TiO_x and PtP@TiO_x is due to several factors: the preferential formation of Pt over Mn, the larger number of active sites on the surface, and the synergistic effects of various factors, including a high degree of alloying, a significant number of accessible active sites, high miscibility, and robust electronic interactions between Mn and Pt atoms [31]. Electrochemical impedance spectroscopy (EIS) was conducted on all the samples using Nyquist plots (Fig. 5h). The PtMnP@TiO_x composite exhibited the lowest charge transfer resistance compared with the other samples, indicating efficient charge transfer during the electrocatalytic HER. Furthermore, Fig. 5(i) presents a chronopotentiometric

stability analysis for the PtMnP@TiO_x sample at -10 mA cm^{-2} , demonstrating excellent stability over 16 h, with the initial 1.5 h being an activation phase for reaching a stable potential (Fig. S3). Consequently, the synergistic electronic effect between Pt and Mn in the presence of P atoms shifts the energy of the d-band center. This modification in the composition of single NPs containing Pt, Mn, and P can reduce the hydrogen binding energy and is thus beneficial for H* desorption and subsequent H₂ formation reactions [30–35].

4. Conclusions

Supported PtMnP NPs catalysts with dissimilar chemical compositions were prepared using a controlled ultrasonic irradiation-assisted coincident oxidation–reduction–precipitation strategy and confirmed by characterization under reaction conditions, which allowed for the evaluation of HER reaction and its catalytic properties. With the same well-ordered NPs, PtMnP NPs, instead of Pt or Mn NPs, significantly improved the HER activity in acidic electrolytes. These results revealed that the PtMnP NPs catalysts were enriched with Pt, accompanied by electron transfer from Mn to Pt. PtMnP@TiO_x presented ultra-small PtMnP NPs, a higher active Pt⁰ content, adequate activation at the porous inorganic surface, and abundant active sites. This strategy can be tuned via the well-ordered synthesis of PtMnP NPs with atomically accurate inter-

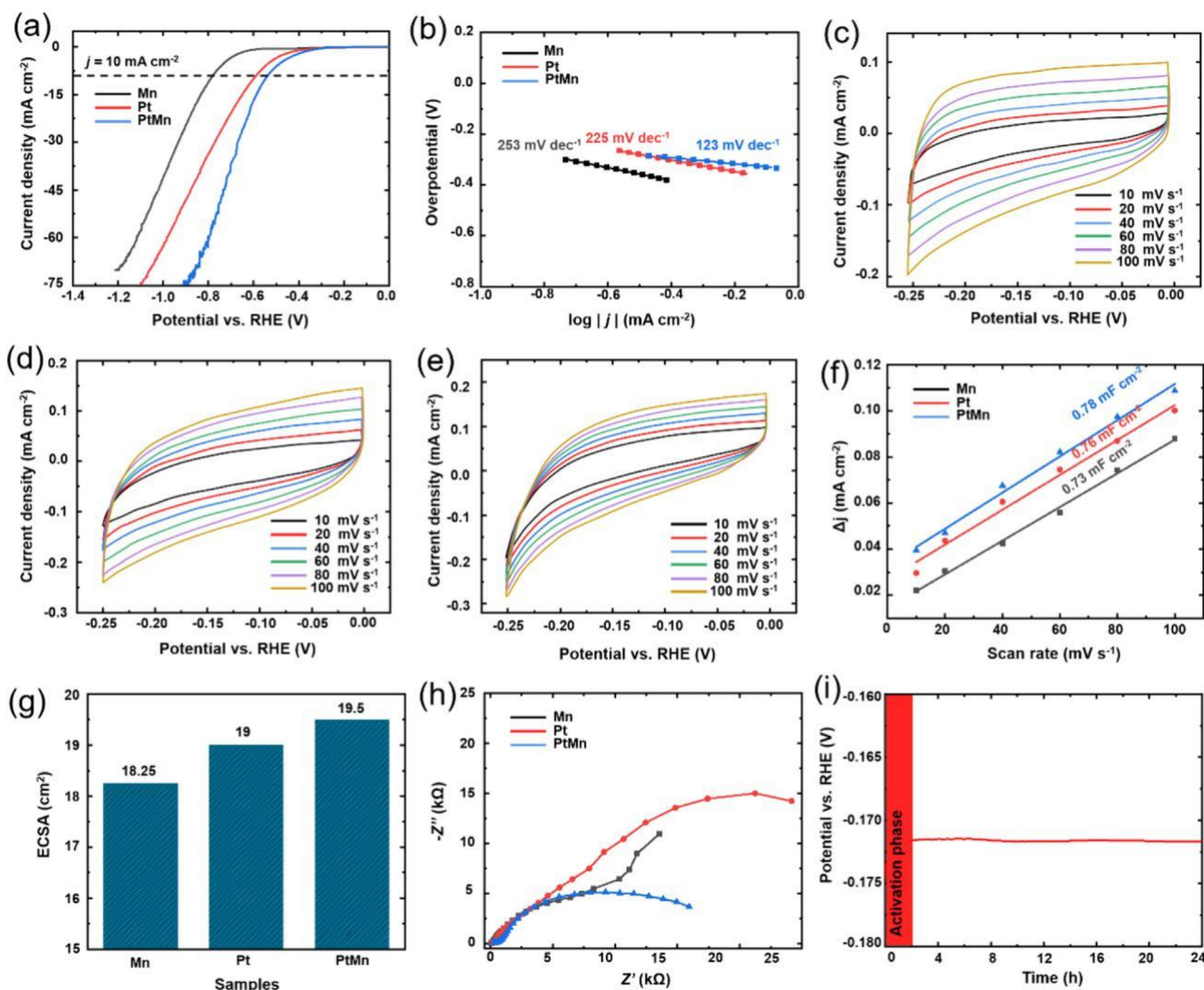


Fig. 5. Electrocatalytic results of HER experiment using 0.5 M H_2SO_4 solution: (a) Linear sweep voltammetry (LSV); (b) Tafel plots; cyclic voltammetry (CV) results of (c) MnP@TiO_x , (d) PtP@TiO_x , and (e) PtMnP@TiO_x ; (f) Cal values. (g) Electrochemical surface areas (ECSA), (h) electrochemical impedance spectroscopy (EIS), and (i) chrono-potentiometric stability analysis of PtMnP@TiO_x in double layer regions.

metallic phases, promising a wide composition range for multipurpose catalyst designs targeting dissimilar catalytic processes. The PtMnP@TiO_2 catalyst achieved outstanding HER activity efficiency in acidic media, which was higher than that of the most commonly used catalysts. This simple method offers a new approach for designing strong repellent elements.

CRediT authorship contribution statement

Yujun Sheng: Conceptualization, Methodology, Investigation, Visualization, Writing – original draft. Farah Hazmatulhaq: Data curation, Investigation, Visualization, Writing – original draft. Abdullah Al Mahmud: Data curation. Mostafa S. Sayed: Visualization, Investigation. Iftikhar Hussain: Data curation. Stefano Leoni: Visualization. Wail Al Zoubi: Investigation, Visualization, Writing – review & editing, Writing – original draft, Supervision. Young Gun Ko: Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jechem.2024.07.022>.

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