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High-dispersion Ultrafine Shell-like Nano-Pt with Efficient Hydrogen Evolution Evolved via Metal Boron Organic Polymers

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Hydrogen is considered the most promising sustainable and economical energy source that can be used on a large scale as an alternative to fossil fuels, but its production requires additional catalysts. As the outstanding catalyst in hydrogen evolution reaction, increasing the surface atomic ratio of Pt clusters can further improve its catalytic performance for hydrogen evolution reaction. Here, using metal boron organic polymers (MBOPs) as bifunctional precursors (both reducing and self-supporting properties), a new approach to rapidly large-scale preparation of supported Pt-based catalysts (Pt/MBOPs) with hydrogen evolution activity and stability is presented. First, the Pt nanoparticles in Pt/MBOPs with high dispersion and small particle size showed excellent catalytic performance in electrochemical hydrogen evolution reaction (E-HER), with the overpotential as low as 22.8 mV (at 10 mA cm⁻²) and the Tafel slope only 56 mV dec⁻¹. In addition, Pt/MBOPs also shows extraordinary performance in the decomposition of ammonia borane (a hydrogen storage chemical), and the TOF from ammonia borane to H₂ is as high as 1654.9 mol_{H2} mol_{Pt}⁻¹ min⁻¹. It is worth noting that Pt/MBOPs shows outstanding stability in electrochemical water splitting to hydrogen and ammonia borane hydrolysis, and is an efficient catalyst in industrial production or the immediate hydrogen production field.

Introduction

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With the depletion of fossil energy and the deterioration of the global environment, human beings are constantly trying to obtain hydrogen, a green energy source that can replace fossil fuels, which has high calorific value, zero environmental pollution and renewable advantages.^{1, 2} At present, hydrogen mass production is achieved by steam reforming natural gas, which inevitably consumes a large amount of energy from fossil fuels and releases a large amount of CO2 into the environment.^{3, 4} In order to achieve the green economic production of hydrogen, it is of great significance to develop new ways to produce hydrogen by electricity-driven water splitting or decomposition of readily available hydrogen storage chemicals (ammonia borane, H content up to 19.6 wt%).⁵⁻¹⁰ Although these methods give people the option to avoid using fossil fuels, additional catalyst input also faces severe challenges. Pt-based catalysts show irreplaceable superiority in either hydrogen production from

electrochemical water splitting or hydrogen production from ammonia borane hydrolysis.¹¹⁻¹⁵ However, the scarcity of Ptbased catalysts and the stability of nanotopography limit their large-scale use. Further improving the anchoring state (such as nanoparticle dispersibility and particle size levels) of Pt in the carrier is the key point to enhancing its catalytic activity and reducing costs.

Single Pt metal catalysts often exhibit low atomic surface exposure ratio and tend to aggregate, which leads to poor catalytic activity. The development of supported Pt-based catalysts is the mainstream and effective solution in current research.¹⁶⁻¹⁸ Conventional methods of synthesizing Pt-based catalysts, includes impregnating metal salts in suspensions containing carriers, and then adding a strong reducing agent $NaBH_4$ or high-temperature calcination to convert Pt^{n+} to Pt^0 and attach to the catalyst surface.¹⁵ This approach is considered unintelligent because it is based entirely on physical mixing. Pt often shows large size and unevenly dispersed aggregate state on the surface of the carrier, which greatly reduces the surface exposure of Pt. Although Pt-based catalysts with monoatomic Pt dispersion make the surface exposure of Pt atoms close to 100%, in the state of monoatomic dispersion, Pt atom is usually accompanied by extremely high surface free energy.¹⁹ This leads to spontaneous aggregation of most Pt monatomic catalysts during preparation (or placement) and catalytic processes, especially at high Pt content.^{20, 21} Therefore, the monoatomic Pt content in the catalyst presented in this way must be controlled below 2 wt%, which is a deviation from the actual application.^{19, 22, 23} To our knowledge, there have been few

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reports of modifying reducing substances into framework materials through chemical bonding, and then embedding nano-metals into carriers.

Here, the in-situ preparation of highly dispersed ultra-fine nano Pt-dispersed shell-like hydrogen evolution catalysts using the weak reduction (we have reported that $closo-[B_{12}H_{12}]^{2^{-}}$ is a reducing agent with weak reducibility^{10, 15, 24-26}. See "Supporting information" for further introduction) and selfsupporting characteristics of ternary metal organic polymers is reported. The confined effect of the carrier and the chemisorption characteristic of *closo*- $[B_{12}H_{12}]^{2-}$ on Pt make the Pt in the carrier maintain high dispersion and small particle size state under high load. In electrochemical water splitting to H₂, under the action of Pt/MBOPs, the overpotential at a current density of 10 mV cm⁻² is as low as 22.8 mV, and the Tafel slope is only 56 mV dec⁻¹. In the hydrolysis of ammonia borane to H₂, the high catalytic activity of Pt/MBOPs makes TOF as high as 1654.9 mol_{H2} mol_{Pt}^{-1} min⁻¹. In addition to the high catalytic activity of hydrogen evolution reaction, Pt/MBOPs also exhibited long-term stable performance. Compared to most of the supported Pt-based catalysts reported, Pt/MBOPs will be a performance-grade sustainable catalyst suitable for industrial production and the immediate hydrogen production field.

Experimental

Chemicals and materials

 $Cs_2[B_{12}H_{12}]$ (98 wt%) was purchased from Strem Chemicals. Carbon paper (CP) was purchased from Shanghai Hesen Electric Co., Ltd. for the E-HER experiments. Ultrapure water (18 M Ω cm⁻¹) was used throughout the research. Unless otherwise stated, all reagents were purchased from Aladdin Chemical Reagent Co., Ltd. and used as is.

Materials preparation

Synthesis of metal boron organic polymers (MBOPs) was following our previously reported procedures.²⁴ 0.8148 g of $Cs_2[B_{12}H_{12}]$ and 0.5816 g of Ni(NO₃)₂·6H₂O were dissolved in 50 mL of water and then slowly added to 50 mL of an acidic solution containing 0.1321 g of 1,10-*o*-phenanthroline ($C_{12}H_8N_2$ ·H₂O). The mixed system immediately formed a large amount of pink solid suspension. After stirring for 30 min, the filter cake was collected by filtration and washed with ethanol and water three times alternately, and then dried under vacuum at 60 °C for 2 h, which is MBOPs.

0.8600 g of MBOPs (containing 1 mmol of $[B_{12}H_{12}]^{2-}$) was dispersed again in 100 mL of water and sonicated for 10 min to form a homogeneous suspension, and then 5.9 mL H_2PtCl_6 solution (33.9 mmol L⁻¹) was slowly added. Subsequently, the temperature was raised to 80 °C and the reaction was continued for 2 h. The gray-black solid was collected by filtration, washed with water/ethanol alternately three times, and dried under vacuum at 60 °C for 2 h to obtain Pt/M-BOP (Figure 1a).

Materials characterization

Fourier transform infrared (FT-IR) spectroscopy was used for qualitative analysis of materials. Powder X-ray diffraction (PXRD) was used for qualitative analysis of phase structure of materials. X-ray photoelectron spectroscopy (XPS) was used to determine the valence state of elements in materials. Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) were used to observe the microscopic morphology of materials. High-resolution transmission electron microscope (HRTEM) was used for capturing lattice fringes in materials. Electronic dispersion spectroscopy (EDS) was used for the qualitative detection of elements in materials and gives the element mapping in the material. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to accurately determine the content of Pt in Pt/MBOPs.

Electrochemical measurements

At room temperature (25 $^{\circ}$ C), the H-Cell equipped with a three-electrode system was used to evaluate the catalytic performance of Pt/MBOPs on the electrochemical splitting to H₂ of water, and the results were collected by an electrochemical workstation (Wuhan Corrtest Instruments Corp., Ltd.). Working electrode was prepared as follows: 1) 3.0 mg Pt/MBOPs were dispersed in 600 uL isopropanol solution containing 0.1 wt% Nafion, and then ultrasonicated for 1 h to promote dispersion to form a uniform ink; 2) 10 uL of ink was evenly coated on carbon paper in the area of 0.5 cm × 0.5 cm,



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the load of Pt/MBOPs on carbon paper is about 0.12 mg cm⁻². The reference electrode is Hg/HgO electrode with 1 M KOH filling solution, and its accurate potential is 0.098 V (by standard hydrogen calibration). Counter electrode is graphite rod (purity 99.999 wt%) and electrolyte is 1 M KOH aqueous solution. Before the electrochemical test, 20 cycles of cyclic voltammetry (sweep speed: 100 mV s-1) were performed to activate and stabilize the working electrode. The linear sweep voltammetry (LSV) curve was obtained under the condition of 3 mV s⁻¹. All potentials were reported relative to the reversible hydrogen electrode and no iR compensation, $E_{REH} = E_{Hg/HgO} + 0.059$ pH + 0.098.

Ammonia borane hydrolysis measurements

The hydrolysis of ammonium borane was carried out in a twonecked flask with constant temperature water bath system (with a temperature error within \pm 0.5 °C). One neck of the flask was sealed with a rubber stopper and the other neck was connected to a gas collection bottle. In the experiment, 4.0 mg of Pt/MBOPs catalyst was placed in a flask in advance, and then an aqueous solution of ammonia borane was injected into the flask from a rubber stopper with a syringe, and the amount of generated gas was immediately recorded. Three parallel experiments were performed under each condition to obtain the average value.

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Results and discussion

DOI: 10.1039/D0TA02110E The single crystal structure of the metal boron organic polymers (MBOPs) precursor has been reported in our previous work (ref.²⁴), and we have redisplayed its cell structure in "Supporting information" (Figure S1). The single crystal of MBOPs shows that one Ni²⁺ binds to three 1,10-ophenanthroline (via N coordination), and $closo-[B_{12}H_{12}]^2$ balances the positive charge of Ni²⁺ while form supramolecular interaction (special hydrogen bond^{24, 27, 28}) with 1,10-ophenanthroline. In order to maintain the interlocking state between Ni^{2+} , *closo*- $[B_{12}H_{12}]^{2-}$ and 1,10-*o*-phenanthroline ternary substances, the input amount of H₂PtCl₆ is only 1/5 of *closo*- $[B_{12}H_{12}]^{2}$ in MBOPs. In FT-IR spectrum (Figure 1b), the weakened intensity of the B-H stretching vibration peak attributable to the consumption of $closo-[B_{12}H_{12}]^{2-}$ during the conversion from MBOPs to Pt/MBOPs. In PXRD (Figure 1c), the peak shape of 10° to 35° further indicates that the crystal form of MBOPs still exists after the synthesis of Pt/MBOPs, and the new peaks at 39.3°, 45.6°, 66.6° and 80.1° correspond to (111), (200), (220) and (311) crystal planes of Pt0 (JCPDS card, no.88-2343). XPS energy spectrum (Figure 1d-e) shows that nickel in Pt/MBOPs exists in the form of +2 valence, consistent with the state in MBOPs, while Pt all exists in Pt/MBOPs in the form of zero valence.

In FE-SEM images (Figure 2a-b), it can be clearly observed that Pt/MBOPs exhibit a thin shell-like structure with shell



Figure 2. a) and b) are FE-SEM images of Pt/MBOPs; c) and d) are TEM images of Pt/MBOPs; e) HRTEM images of Pt/MBOPs; f) EDS results of Pt/MBOPs and g) Element mapping of each element in Pt/MBOPs.

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thickness of about 15 nm. The morphology of Pt/MBOPs in TEM images (Figure 2c-d) is consistent with the results of FE-SEM, all of which are thin shell-like structures. Based on the imaging principle of TEM, the dark black spots in TEM images can be well identified as Pt nanoparticles, which exhibit the characteristics of high dispersion and small particle size (~ 3.5 nm). Further, the HRTEM images (Figure 2e) show that the lattice spacing of dark black spots is about 0.22 nm, which corresponds to the (111) lattice spacing of PtO. The apparent Pt signal in the EDS test results (Figure 2f) proved the correctness of the PXRD, XPS and HRTEM results. In addition to the results of TEM images, element mapping images (Figure 2g) more intuitively show the uniform distribution state of each element in Pt/MBOPs. Furthermore, the accurate loading of Pt in Pt/MBOPs obtained by ICP-OES test is 5.1 wt%.

The most intuitive way to evaluate the performance of E-HER catalysts is to compare them with commercial Pt/C. Figure 3a shows the LSV test results of Pt/MBOPs and commercial Pt/C as catalysts, both of which show excellent hydrogen evolution performance. However, as the object of attention, a current density of 10 mA cm⁻² can be achieved by applying only 22.8 mV of overpotential under the action of Pt/MBOPs, whereas 36.1 mV is required for commercial Pt/C. After converting the LSV curve to a log[j] - overpotential relationship, the slope of the linear portion when Pt/MBOPs is applied is only 56 mV dec⁻¹, while the slope of the linear portion when commercial Pt/C is applied is 67 mV (Figure 3b). It is worth noting that MBOPs exhibit extremely poor E-HER performance under the same conditions (Figure S2, a current density of 10 mA cm⁻² requires an overpotential of up to 478 mV). Therefore, the excellent E-HER performance comes from the contribution of active centre nano-meter Pt instead of Ni²⁺ in Pt/MBOPs (Ni²⁺ is bound to 1,10-o-phenanthroline in a hexacoordination form, and its empty orbit is completely occupied). Based on the Tafel slope value, it can be determined that under the action of Pt/MBOPs, the E-HER process is most likely to follow the "electrochemical desorption mechanism (Heyrovsky mechanism)", that is, "the electrochemical discharge step: M + H^{+} + e = M-H_{ads}, and the electrochemical desorption steps: M- $H_{ads} + H^{+} + e = M + H_{2}^{"}$, where the former is a fast step and the latter is a slow step. In addition, the stability of Pt/MBOPs in E-HER is an important factor in evaluating their performance. After 10,000 times cycling, Pt/MBOPs still maintains high catalytic activity, and its overpotential is almost the same as the initial value (at 10 mA cm⁻²), showing excellent catalytic stability (Figure 3c). In addition, it can be seen from i-t curve (Figure 3e) that Pt/MBOPs have good tolerance when working for a long time, and *i*-t curve has only slight fluctuations. According to *i*-t test, the amount hydrogen evolved is about 205μ mol h⁻¹ cm⁻², and the Faraday efficiency is greater than 98%. Figure 3d illustrates Nyquist plots of Pt/MBOPs composites. The Nyquist plots semicircle diameter of the Pt/MBOPs composite material showed a lower value, and the calculated R_{ct} under the action of Pt/MBOPs was 15.9 Ω (R_s is 5.92 Ω , and the N value of CPE was 0.997). This shows that Pt/MBOPs has a low HER charge transfer resistance and therefore exhibits a fast HER kinetics. In order to more easily



Figure 3. a) E-HER polarization curves (LSV) and b) Tafel plots for Pt/MBOPs and 20 wt% commercial Pt/C; c) LSV curves of Pt/MBOPs and 20 wt% commercial Pt/C in 1M KOH before and after 10000 cycles; d) Nyquist plot of Pt/MBOPs composites; e) Tolerance test of Pt/MBOPs in E-HER and f) Overpotentials of Pt/MBOPs with other recently reported Pt-based E-HER catalysts in 1M KOH.

show the superiority of Pt/MBOPs in basic E-HER, its performance was compared with the basic E-HER Pt-based catalysts reported in recent years (Figure 3e and Table S1).

On the other hand, the catalytic performance of Pt/MBOPs in the hydrolysis hydrogen evolution of ammonia borane hydrogen storage chemicals was evaluated in detail. Under the action of the catalyst, ammonia borane can be rapidly hydrolyzed to hydrogen, and Pt-based catalysts have been considered as the best catalysts to promote the hydrolysis of ammonia borane. At room temperature (25 °C), Pt/MBOPs can promote the rapid hydrolysis of ammonia borane. It takes only 120 s (2 min) for Pt/MBOPs to promote the completion of ammonia borane hydrolysis, while it takes about 180 s (3 min) for commercial Pt/C to promote the completion of the same amount of ammonia borane hydrolysis (Figure 4a). It should be noted that the amount of Pt/MBOPs and commercial Pt/C is 4.0 mg, and the content of Pt in Pt/C is 20 wt%, but the loading of Pt in Pt/MBOPs is only 5.1 wt%. Based on this, the catalytic performance of Pt/MBOPs in ammonia borane hydrolysis was

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evaluated in detail. Under the same conditions, with the increase of temperature, the time required for Pt/MBOPs to promote the completion of ammonia borane gradually decreases (Figure 4b). From 283.15 K to 343.15 K, the completion time of ammonia borane hydrolysis was shortened from 500 s to about 10 s, indicating that this is a temperaturedependent process. According to the Arrhenius formula (Figure 4c), the activation energy for the hydrolysis of ammonia borane to hydrogen under the action of Pt/MBOPs is only 41.4 KJ mol⁻¹. After 8 cycles of utilization, the catalytic performance of Pt/MBOPs in ammonia borane hydrolysis remained at the same level as the initial value (Figure 4d), indicating that Pt/MBOPs maintained high stability during the catalytic reaction, thus no nano-Pt was lost from the carrier. Through kinetic isotope experiments, the rate-determining step in the hydrolysis of ammonia borane can be determined, and it is also the most sensitive method to judge the O-H bond cleavage.^{15, 29-33} The value of the kinetic isotope effect (KIE) is calculated by the ratio of the rate constants of H₂O and D₂O as the reactants, that is, KIE = kH/kD. Figure 4e shows that when D_2O is used instead of H_2O as the reactant, the hydrogen release rate of ammonia borane is significantly slower, and the KIE value obtained is as high as 5.54. This strongly suggests that the activation of water during the hydrolysis of ammonia borane is a speed-determining step, and the introduction of Pt/MBOPs can effectively activate H₂O molecules.^{32, 34, 35} Because Pt/MBOPs catalyzes 1 mol of ammonia borane to release about 3 mol of gas, and H₂O is an essential reactant for hydrolysis, the hydrolysis of ammonia borane in this study was performed according to the following formula: H₃NBH₃ + 4H₂O = NH_4^+ + B(OH)₄ + 3H₂. On the whole, the high catalytic activity and stability of Pt/MBOPs in the hydrolysis of ammonia borane is more advantageous than the reported Pt-based catalysts (Figure 4f and Table S2), and it is a promising hydrogen evolution catalyst. In addition, the physical and chemical stability tests of Pt/MBOPs catalysts (including XPS spectrum, PXRD, SEM image and TEM image) were listed in the "Supporting information" (Figure S3, Figure S4 and Figure S5), which are similar to the original state. In the hydrogen evolution reaction, Pt/MBOPs showed excellent catalytic activity and stability, which may be closely related to the composition of Pt/MBOPs catalysts. On the one hand, the dispersion of highly dispersed ultrafine nano-Pt on the shelllike structure makes Pt/MBOPs have a large surface area and an active site exposure rate, which allows the reactants to fully contact the catalytic sites. On the other hand, our previous research proved that $closo-[B_{12}H_{12}]^{2-}$ can be attached to the surface of Pt nanocrystals in the form of chemisorption,³⁶ so the excellent catalytic activity of Pt/MBOPs in the hydrogen evolution reaction may be related to the following two aspects. 1) Closo-[B₁₂H₁₂]²⁻ The inherent negative charge of it represents that it can promote the transfer of electrons in the catalyst; 2) Pt in Pt/MBOPs is in a large amount of remaining $closo-[B_{12}H_{12}]^{2-}$ atmosphere, $closo-[B_{12}H_{12}]^{2-}$ can make Pt enter an electron-rich state (the XPS test results prove this), which not only improves the catalytic activity of Pt/MBOPs, but also stabilizes nano-Pt.



Figure 4. a) Catalytic performance of Pt/MBOPs and 20 wt% commercial Pt/C in ammonia borane hydrolysis to hydrogen (at 25 °C); b) Hydrogen productivity vs time plots from hydrolysis of ammonia borane at different temperatures under Pt/MBOPs catalysis; c) Arrhenius plots fit by the kinetic data (b); d) Stability tests of Pt/MBOPs (in 6 runs); e) hydrolysis to hydrogen of ammonia borane in H₂O and D₂O catalyzed by Pt/MBOPs (for obtain KIE value); f) TOF value of Pt/MBOPs with other recently reported Pt-based catalysts in hydrolysis hydrogen evolution of ammonia borane.

Conclusions

Here, using the reductivity (*closo*-[B₁₂H₁₂]²⁻) and selfsupporting characteristics of the functional metal boron organic polymer, a two-step method was used to rapidly and large-scale synthesize shell-like Pt/MBOPs catalyst with highly dispersed ultrafine Pt particles for hydrogen evolution reaction. In alkaline electrolyte, Pt/MBOPs can effectively promote the electrochemical splitting of water into hydrogen, and the current density can reach 10 mA cm⁻² only by providing overpotential of 22.8 mV, while the tafel slope is as low as 56 mV dec⁻¹. During the hydrolysis of the hydrogen storage chemical ammonia borane, Pt/MBOPs exhibited excellent catalytic performance, and the TOF for the hydrolysis of ammonia borane to hydrogen was as high as 1654.9 mol_{H2} mol_{Pt}⁻¹ min⁻¹. In addition, the domain limiting effect of the MBOPs carrier and the characteristics of *closo*-[B₁₂H₁₂]²⁻ chemosorption Pt not only enable the Pt nanoparticles to maintain high dispersion and small particle size state under high load, but also ensure long-term stability of Pt/MBOPs in catalytic process. Compared to most of the supported Pt-based catalysts reported, Pt/MBOPs are a performance-grade sustainable economy catalyst suitable for industrial production and the immediate hydrogen production field.

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Conflicts of interest

There are no conflicts to declare.

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