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# Facile and Large-Scale Fabrication of Porous Carbon Sheet Supported Sub-3 nm PtNi Nanoparticles: A Bifunctional Material for HER and Hydrogenation

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#### Dedication ((optional))

Abstract: Facile and large-scale preparation of materials with uniform distribution of ultra-fine particles is a challenging work for catalysis, and it is even more difficult that the catalyst is excellent in both hydrogen evolution reaction (HER) and hydrogenation, which are corresponding merge and split procedure of hydrogen, respectively. Here, we report the fabrication of ultra-fine bimetallic PtNi nanoparticles embedded in the carbon nanaosheets by means of insitu self-polymerization and annealing. It is a bifunctional catalyst possessing excellent performance in HER and hydrogenation of p-Nitrophenol. Remarkably, the low-loading PtNi bimetallic catalyst (PtNi<sub>2</sub>@CNS-600, 0.074 wt% Pt) exhibited outstanding HER activity with an overpotential as low as 68 mV at a current density of 10 mA cm<sup>-2</sup> when platinum loading was only 0.612 µg Pt/cm<sup>2</sup> and Tafel slope of 35.27 mV decade<sup>-1</sup> in a 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution, which is comparable to those values for the 20% Pt/C catalyst (31 mV decade<sup>-1</sup>). Meanwhile, it also shows the more excellent long-term electrochemical durability for at least 30 h with negligible degradation than 20% Pt/C. In addition, the material with increased loading (mPtNi<sub>2</sub>@CNS-600, 2.88% Pt) displayed robust catalytic activity for hydrogenation of *p*-Nitrophenol in ambient pressure and temperature. The catalytic activity towards the split of hydrogen give a circumstantial evidence that agrees the path of Volmer-Tafel reaction in HER in turn.

#### Introduction

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The serious energy crisis and environmental issues caused by the consumption of fossil fuels have prompted numerous efforts to explore sustainable energy source,<sup>[1]</sup> such as solar energy, wind power, electro/photochemical water splitting, etc.<sup>[2]</sup> Hydrogen, a zero emission energy source and the most promising durable energy carrier, has been deemed as a perfect substitute to the traditional fossil fuel-based energy on account of its high gravimetric energy density, carbon footprints and environmentalfriendly properties.<sup>[3]</sup> Differ from the water gas shift reaction that consumes carbon resource, the electro production of hydrogen concern, and it is primarily produced by chloro-alkali industry or water splitting.<sup>[4]</sup> The hydrogen evolution reaction (HER), as an important half-reaction involved in electrochemical water electrolysis process,<sup>[5]</sup> has been emerging as a promising approach for hydrogen production among various routes of hydrogen supply owing to its low cost, high efficiency and environment benign.<sup>[6]</sup> It is generally accepted that the catalytic mechanism of HER in acid media includes the Volmer reaction  $(H_3O + e^- \rightarrow H_{ad} + OH^-)$ , the Heyrovsky reaction  $(H^+ + H_{ad} + e^-)$  $\rightarrow$ H<sub>2</sub>) and the Tafel reaction (2H<sub>ad</sub>  $\rightarrow$  H<sub>2</sub>).<sup>[7]</sup> However, hydrogen evolution reaction (HER) is thermodynamically impeditive for the hydrogen binding energy.<sup>[8]</sup> Therefore, academic researchers have been trying to explore the efficient and sustainable HER catalysts,<sup>[9]</sup> which is designed and prepared to reduce overpotential  $(\eta)$  value and increase the reaction rate for more economical utilization of energy in the sustainable hydrogen generation.[10]

To date, platinum (Pt) and Pt-based materials,<sup>[11]</sup> exhibiting the high-performance (activity and durability) as the 'Holy Grail' of HER electro-catalysts, are considered the most efficient HER catalysts with a near-zero overpotential in acid solution, a small Tafel slope and excellent long-term stability. However, their widespread implementation are hindered greatly by their scarcity and high cost.<sup>[12]</sup> Recent trends in nanomaterial catalysts have proposed the use of bimetallic NPs, which comprise two distinct metal atoms in various configurations.<sup>[13]</sup> The bimetallic alloy NPs can provide more potent electrocatalytic activity and superior stability than their monometallic counterparts owing to the synergistic effects that arise from the interaction of two distinct metals,<sup>[14]</sup> as well as allow one to minimize the use of expensive noble metals.<sup>[15]</sup> Thus the incorporation of functional non-noble 3d transition metals (TMs) (e.g., Co, Fe, Ni, Cu, etc.) is an effective strategy to improve the electrocatalytic activity.<sup>[16]</sup> At present, Ptbased binary alloys: PtNi-Ni,<sup>[17]</sup> PtNi,<sup>[18]</sup> PtNi nanocage,<sup>[19]</sup> PtCo,<sup>[20]</sup> Pt<sub>3</sub>Co,<sup>[21]</sup> PtPd,<sup>[22]</sup> and ternary alloys: Pt-Ni-Co,<sup>[23]</sup> CNTs-PdAu/Pt,<sup>[24]</sup> Pt-Cu-Ni,<sup>[25]</sup> Pt-Ni-Cu<sup>[26]</sup> have been widely designed

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electrochemistry academics for research. Those by electrocatalysts have wonderful HER performance, such as: low overpotential, small Tafel plot and long-time stability, etc. Among such efficient catalysts, the 3-D transition metal-Ni is commonly utilized and especially prominent due to its low price, high abundance, good corrosion resistance and excellent electrical conductivity. This results are cheering, however, in the meanwhile, most of them are not satisfactory as a result of the complex processes for catalyst preparation, extremely low yield and lavish loading of Pt. Therefore, designing a highly active HER electrocatalyst with environment-friendlies, facile and large-scale preparation as well as low cost is desperately desired but still remains a key challenge.

Following these demands and basing on our interest in advanced material,<sup>[11c, 27]</sup> we designed a catalyst with the ultrafine sub-3 nm PtNi bimetallic nanoparticles embedded on porous carbon materials and ultralow Pt content (0.074 wt%) confirmed by ICP-MS via in situ polymerization and annealing in Ar, which modified the previously reported procedures.<sup>[28]</sup> As expected, ultralow noble Pt content, easiness and high production of catalyst preparation, the low overpotential and excellent stability of HER were combined in our material. It is worth mentioning that the material with increasing Pt loading (2.88 wt%) also presented robust catalytic activity for hydrogenation of *p*-Nitrophenol in ambient pressure and temperature, which evidences the path of Volmer-Tafel reaction in HER in turn.

#### **Results and Discussion**

The synthesis route of the electrocatalyst involves mainly four steps as shown in Scheme 1. A certain amount of Hacac, Pt(acac)<sub>2</sub> and Ni(acac)<sub>2</sub> were polymerized and subsequently converted to PtNix@3DP nanocomposites under normal temperature and alkaline conditions. Hereafter, the polymer was carbonized in the tube furnace with Ar atmosphere. The mechanism of the reaction are systematically descript in the Scheme S1 and Scheme S2. In the process of synthesizing the precursor, a C-C bond is formed by simple Aldol condensation and the small molecules are uniformly connected into a carbon framework in the presence of NaOH. The carbon anion intermediate first formed from Hacac immediately attacked the nearby carbonyl carbon atoms of Hacac, Pt(acac)<sub>2</sub> and Ni(acac)<sub>2</sub>, which contribute to continuous dehydration of the monomer and cross-linking. Finally, Pt and Ni nanaoparticals are uniformly supported on the carbon skeleton in the carbonization process.



Scheme 1. Schematic representation for the preparation process of PtNix@CNS-600 electrocatalyst.

TGA measurement is conducted to study the thermal decomposition behavior of the precursor:  $PtNi_2@3DP$ , which is shown in Figure 1. The characteristic thermal response of precursor shows three obvious mass loss processes: (I) the removal of the surface adsorbed and internal water molecule takes place from room temperature to 100 °C (20% weight loss), (II) the loss of some small organic molecules, combined water and most oxygen-containing functional groups occurs in the range from 210 °C to 500 °C with a sharp decrease starting from 245 °C, and (III) the decomposition of the precursor arise from 500 °C to 1000 °C. Therefore, we decide to adopt a calcined temperature ranges from 400 °C to 800 °C to prepare carbon-based catalysts.



Figure 1. TGA curve of the PtNi<sub>2</sub>@3DP.

The morphology and microstructure of PtNi<sub>2</sub>@CNS-600 nanocatalyst are described by scanning electron microscopy (SEM), HAADF-STEM and HRTEM measurements. The SEM images (Figure 2a–c) of PtNi<sub>2</sub>@CNS-600 indicate that the structure of this composite is flaky.



#### Figure 2. SEM images of PtNi<sub>2</sub>@CNS-600.

The deeper understanding for catalyst structure is realized via HAADF-STEM (Figure 3a-c) and HRTEM (Figure 3d-e) characterization. As in Figure 3a-c, the microscopic appearance of PtNi<sub>2</sub>@CNS-600 is composed of extremely thin carbon sheets and ultra-small nanoparticles, which is in line with SEM results. From the Figure 3c, we can conclude that the ultra-fine PtNi bimetal alloy nanoparticals with the average size of 3 nm exist in this material. Besides, we can observe that massive porous structure in the carbon substrate, which can further improve electrocatalytic performance via increasing the quantity of active sites and accelerating the transfer of mass.<sup>[29]</sup> Figure 3d highlights a typical PtNi alloy nanoparticle with crystal lattice of 0.215 nm,

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which is between single metal Pt (111) of 0.2256 nm and single metal Ni (111) of 0.2034 nm, indicating the formation of alloy.<sup>[30]</sup> Besides, the selective area electron diffraction (SAED) pattern inserted in Figure 3d shows the crystal lattice of 0.2123 nm, which is almost identical to the above result, the crystal lattice of 0.1832 nm, which is between single metal Pt (200) of 0.1962 nm and single metal Ni (200) of 0.1762 nm, and the crystal lattice of 0.1114 nm, which is between single metal Pt (311) of 0.1183 nm and single metal Ni (311) of 0.1062 nm (Pt PDF#04-0802, Ni PDF#04-0850), suggesting the polycrystalline characteristic of the prepared PtNi<sub>2</sub>@CNS-600. In addition, the element mapping in Figure 3e point out that the ultrafine PtNi alloy nanoparticles are uniformly distributed in the nanosheets. Combined with the lattice fringe, SAED and EDS results, we consider that Pt and Ni existed as alloy in the electrocatalyst.



Figure 3. (a-c) HAADF-STEM, (d) HRTEM images and (e) EDS mapping of
PtNi2@CNS-600. The corresponding SAED pattern is inserted in Figure 3d



Figure 4. XPS spectra of PtNi<sub>2</sub>@CNS-600. (a) Survey, (b) Pt 4f, (c) Ni 2p and (d) C 1s

The X-ray photoelectron spectroscopy (XPS) was further conducted to analyze the surface chemical composition of the

PtNi<sub>2</sub>@CNS-600. The survey XP spectrum (Figure 4a) confirms that the existent elements of catalyst contained platinum, nickel, carbon and oxygen. The two main binding energies of 71.4 eV and 74.9 eV corresponds to Pt 4f<sup>7/2</sup> and 4f<sup>5/2</sup> of metallic state (Figure 4b). The chemical states of Ni and C were also presented in Fig 4(c-d). As shown in Figure 4c, the BEs at 852.1 eV and 869.2 eV were attributed to Ni 2p<sup>3/2</sup> and Ni 2p<sup>1/2</sup>, confirming the presence of Ni<sup>0</sup>. However, the 855.1 eV XPS peaks of Ni in Figure 4c illustrates that the some component of Ni was probably in the way of the oxidized state in the surface.<sup>[31]</sup> Figure 4d, the carbon spectrum embodies C1s (284.8 eV) and COOR (289.2 eV). The negative shift occurred for Ni 2p<sup>3/2</sup>(~0.5 eV) and the positive shift appeared for Pt 4f<sup>7/2</sup>(~0.4 eV) compared with their benchmark values, which indicates the electron transfer process and alloy formation.



Figure 5. (a) X-ray diffraction pattern, (b) Raman spectra of  $\mathsf{PtNi}_2@\mathsf{CNS}\text{-}600$  nanocatalyst

The XRD pattern of the PtNi2@CNS-600 catalyst shows three main peaks in Figure 5a, which are assigned to the typical (111), (200) and (220) facets of the face centered cubic phase of the PtNi alloy. That indicates the high crystallinity of the as-synthetic PtNi2@CNS-600. Additionally, the structural information about the carbon substrate of the acquired material is obtained by Raman spectroscopic measurement. Apparently, the Raman spectra of the catalyst in Fig 5b presents two characteristic absorption bands, which were assigned to D band ( $\sim$ 1345 cm<sup>-1</sup>) and G band ( $\sim$ 1595 cm<sup>-1</sup>) respectively. The D band is attributed to the existence of substantial defects or structural disorder in the composite,[32] whereas the G band refers to the ordered graphitic structure,<sup>[33]</sup> which is associated with the (002) diffraction peak of the XRD pattern. ID/ IG, the ratio of the D peak intensity to the G peak intensity,<sup>[34]</sup> is usually employed as an indicator for evaluating the graphitization degree of the synthesized carbon materials. From the Raman spectra, the calculated ID/IG ratio for PtNi2@CNS-600 catalyst is as high as 0.8577, which combines with a broad D peak and a sharp G peak suggests the strong electronic conduction and corrosion resistance contributed by the interaction between Pt, Ni and carbon during carbonization process. This result was in accordance with the above discussions on EDS and HRTEM data, suggesting that PtNi2@CNS-600 catalyst has a high degree of graphitization and considerable conductivity.

The N<sub>2</sub> adsorption-desorption isotherms of PtNi<sub>2</sub>@CNS-600 and CNS-600 (Figure 6) can be divided into IV-type with a H<sub>3</sub> hysteresis loop according to IUPAC's classification, which are attributed to the crevice formed by the accumulation of nanosheets. The pore distribution curve of PtNi<sub>2</sub>@CNS-600 in

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Figure 6a indicates that the existence of micro pores, confirmed by the apparently vertical rise of quantity adsorbed at the relative low pressure of  $p/p^0 < 0.05$ . The specific surface area from the adsorption isotherms of PtNi<sub>2</sub>@CNS-600 was calculated to be 99.65 m<sup>2</sup> g<sup>-1</sup>, which were lower than that of CNS-600 (118.14 m<sup>2</sup> g<sup>-1</sup>) as shown in Figure 6b. For this phenomenon, we consider that the alloy particles may block a part of the pores. Thus, with high surface area and pore volume, the electrocatalyst will be favorable for the accessibility of electrolyte and provide more tunnels as well as sufficient active sites for hydrogen evolution.<sup>[35]</sup>



Figure 6.  $N_2$  adsorption-desorption isotherms of (a) PtNi<sub>2</sub>@CNS-600, (b) CNS-600. The inset is their corresponding pore size distribution.



Figure 7. (a) HER polarization curves of PtNi<sub>1</sub>@CNS-600, PtNi<sub>2</sub>@CNS-600, PtNi<sub>3</sub>@CNS-600, PtNi<sub>1.5</sub>@CNS-600, mPtNi<sub>2</sub>@CNS-600, Pt@CNS-600, Ni@CNS-600 and CNS-600, carbonized under Ar, acquired with 5 mVs<sup>-1</sup> in N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25 °C.

In order to investigate the electrocatalytic performances of PtNi<sub>2</sub>@CNS-600, HER experiment of the as-prepared samples were conducted in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution (Figure 7a-c). As expected, the polarization curves in Figure 7a show that the overpotential of PtNi<sub>2</sub>@CNS-600 was only 68 mV at the current density of 10 mA-cm<sup>-2</sup> comparable to 20% Pt/C (40 mV),<sup>[36]</sup> which is much lower than that of PtNi<sub>1</sub>@CNS-600 (113 mV), PtNi<sub>1.5</sub>@CNS-600 (95 mV), PtNi<sub>3</sub>@CNS-600 (115 mV) and other Pt-based HER electrocatalysts (Table S1). The results indicated that when the proportion of Pt to Ni reach to 2, the electrocatalytic

activity was optimal. The accurate composition of Pt and Ni in PtNi2@CNS-600 catalyst verified by the inductively coupled plasma mass spectrometry (ICP-MS) analysis are only 0.074% and 0.043%, which are closely to theoretical value of 0.068% and 0.038%, indicating that there is no lossing of active metal in the preparation process. Besides, the accurate composition of Pt and Ni in PtNi1@CNS-600, PtNi15@CNS-600, PtNi3@CNS-600 and mPtNi<sub>2</sub>@CNS-600 catalyst verified by the ICP-MS analysis are 0.069% and 0.019%, 0.072% and 0.030%, 0.070% and 0.057%, 2.88% and 1.57% ,which are closely to theoretical value of 0.068% and 0.019%, 0.068% and 0.028%, 0.067% and 0.056%, 2.72% and 1.52% respectively. The high overpotentials of Pt@CNS-600 (348 mV) and Ni@CNS-600 (816 mV) were caused by the ultralow single metal content and less active sites. The more excellent HER activity of bimetallic catalyst than singlemetals' could be attributed to the synergistic effect of the addition of a non-noble metal Ni into the noble metal Pt, namely the enhanced charge transfer efficiency as well as modified electronic structure, and both of which can reduce the energy barrier and accelerates the reaction kinetics.[37] In order to research the dominant reaction mechanism in the HER process, the Tafel plots, as another fundamental criterion, were obtained from the Linear scan curve (LSV). In general, the catalytic mechanism of HER including the Volmer reaction, the Heyrovsky reaction and the Tafel reaction, and the Tafel slope are 120 mV dec<sup>-1</sup>, 40 mV dec<sup>-1</sup> and 30 mV dec<sup>-1</sup>, respectively.<sup>[38]</sup> As shown in Fig 7b, the outstanding electrocatalytic activity of PtNi2@CNS-600 and mPtNi2@CNS-600 electrocatalyst could also be confirmed by a small Tafel slope of 35.27 mV dec<sup>-1</sup> and 29.00 mV dec<sup>-1</sup>, which was close to the Tafel slope of commercial 20% Pt/C (31 mV dec-<sup>1</sup>)<sup>[36]</sup> but much lower than the PtNi<sub>1</sub>@CNS-600(60.19 mV dec<sup>-1</sup>), PtNi1.5@CNS-600 (45.06 mV dec<sup>-1</sup>), PtNi3@CNS-600 (47.71 mV dec<sup>-1</sup>), Pt@CNS-600 (72.25 mV dec<sup>-1</sup>), Ni@CNS-600 (146.82 mV dec<sup>-1</sup>) and CNS-600 (158.90 mV dec<sup>-1</sup>), respectively. The comparisons with other representative Pt-based HER electrocatalysts recently reported were shown in Table S1, suggesting that the PtNi2@CNS-600 electrocatalyst with lowest Pt content (0.074 wt%) had smaller overpotential and Tafel plot. The exceedingly small Tafel plot of PtNi2@CNS-600 shows that HER is possibly controlled by Volmer-Tafel mechanism, where recombination of absorbed H is the rate-limiting step<sup>[39]</sup>, implying more favorable kinetics and faster reaction rate, which is highly corresponding to the above results and proved by Nyquist plot. The Nyquist plots of the control samples with iR correction were researched at 0.238 V (vs. RHE) (Figure S1). Similarly, the comparison of impedance value show the same trend as the result of Tafel slop: the smaller Tafel slope and impedance indicat smaller kinetic hindrance and faster electron transfer, making the reaction kinetics more favorable and the reaction rate faster.

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Figure 8. (a) HER polarization curves (b) Tafel plots in 0.5 M H<sub>2</sub>SO<sub>4</sub> for the PtNi<sub>2</sub>@3DP annealed at different temperature under Ar atmosphere.(c) Data histogram obtained from (a) and (b) for convenient comparison.

From the Figure 8a-c, we can observe that the HER activity of the electrocatalysts along with the carbonization temperature showed the Volcanic type. The most excellent HER activity was achieved for the sample annealed under 600 °C, which could presumably be attributed to the balance of electrical conductivity, active site and porosity.<sup>[40]</sup> The activity of the electrocatalyst enhanced with the increase of annealing temperature below 600 °C, and reduced with the increase of annealing temperature above 600 °C. The trend in overpotential were as the following: PtNi2@CNS-600 (68 mV) < PtNi2@CNS-700 (297 mV) < PtNi2@CNS-800 (423 mV) < PtNi<sub>2</sub>@CNS-500 (512 mV) < PtNi<sub>2</sub>@CNS-400 (867 mV) in Figure 8a. This phenomenon was analyzed as follows: the degree of charring was insufficient and the metals were not completely reduced at lower temperatures, however, when the temperature was too high, the alloy might be aggregated, which can also be proved by Figure S1 (Nyquist plots). Therefore, the optimum HER activity was obtained when keep the annealing temperature at 600 °C and the molar ratio of Pt to Ni was 2, as shown in Figure 7 and 8.



Figure 9. (a) Durability test for PtNi<sub>2</sub>@CNS-600 in 0.5 M H<sub>2</sub>SO<sub>4</sub> before and after 2000 cycle (b) The current-time curve of PtNi<sub>2</sub>@CNS-600 for 30 h. The exploitation of high-performance electrocatalysts are critical for efficient and economical production of hydrogen from water, which is designed to drive fast HER reaction with lower

overpotential.<sup>[41]</sup> In addition to the catalytic activity, another significant criterion for evaluating a HER catalyst is the long-term stability and durability in practical applications. In order to assess the stability of PtNi<sub>2</sub>@CNS-600 catalyst in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, long-term cyclic voltammetry (CV) cycles was carried out between -0.1 and 0.1 V (vs RHE) at a scan rate of 100 mV s<sup>-1</sup>. As shown in Figure 9a, the linear scanning voltammetry (LSV) curves showed negligible shift after 2,000 cycles, exhibiting the outstanding stability of PtNi2@CNS-600 catalyst in acidic media. Subsequently, the chronoamperometric experiment was also conducted to evaluate the long-term durability of PtNi2@CNS-600 catalyst at a constant potential in 0.5 M H<sub>2</sub>SO<sub>4</sub>, as shown in Figure 9b. The i-t curve showed that the current density maintained 10 mA cm<sup>-2</sup> and almost unchanged during 30 h test, displaying the more robust stability of the PtNi2@CNS-600 catalyst than 20% Pt/C<sup>[42]</sup>, which was in good agreement with the above results.

The number of active sites was measured via electrochemical active surface area (ECSA),<sup>[43]</sup> which could be calculated from the double-layer capacitance (Cdl) corresponding to the catalytic surfaces by means of the following equation.<sup>[44]</sup>

$$ECSA = \frac{C_{dl} (mF \ cm^{-2})}{1.7mF \ cm^{-2} \ per \ cm^{2} \ ecsa}$$

The excellent electrocatalytic performance of PtNi2@CNS-600 was attributed to ultra-fine sub-3 nm PtNi nanoparticles embedded in porous carbon sheet, which provides a large surface area for electrochemical reactions. As we can observe, the appearance of the Cdl presented a regular rectangle, which is the nature of carbon (Figure 10a-c). The value of Cdl of PtNi2@CNS-600 (4.16 mF cm<sup>-2</sup>) was bigger than those of Pt@CNS-600 (0.49 mF cm<sup>-2</sup>) and Ni@CNS-600 (0.34 mF cm<sup>-2</sup>) shown in Figure 10d, suggesting the more active sites on the surface owing to the synergism of bimetal. The Cdl of PtNi<sub>1</sub>@CNS-600 (1.38 mF cm<sup>-2</sup>), PtNi1.5@CNS-600 (1.41 mF cm<sup>-2</sup>), PtNi2@CNS-600(4.16 mF cm<sup>-2</sup>), and PtNi<sub>3</sub>@CNS-600(1.34 mF cm<sup>-2</sup>) were represented in Figure S2, which also proved that the proportion of Pt to Ni was 2 can achieve the optimum HER activity with the ultralow Pt loading. Therefore, such high Cdl suggests that PtNi2@CNS-600 exhibited more exposed surface reactive sites and potential site than others,<sup>[38]</sup> which contributes to excellent HER electrocatalytic performance.

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Figure 10. The CV curves at different scan rates of (a) PtNi2@CNS-600, (b) Pt@CNS-600, (c) Ni@CNS-600. (d) Cdl values of the nanocatalysts. Reduction of *p*-Nitrophenol:



**Figure 11.** a) Reaction equation for the reduction of *p*-Nitrophenol to *p*-Aminophenol. b) The reactive extent tests with time of mPtNi<sub>2</sub>@CNS-600 nanaocatalyst for the hydrogenation of *p*-Nitrophenol.

We prepared the high content PtNi electrocatalyst (named as mPtNi<sub>2</sub>@CNS-600) following the same procedure except that the additive amount of Ni(acac)<sub>2</sub> and Pt(acac)<sub>2</sub> were 266.4 mg and 200 mg respectively. The microscopic appearance of mPtNi<sub>2</sub>@CNS-600 is showed in Figure S3. As shown in Figure 11a, 1 mmol of *p*-Nitrophenol, 40 mg of catalyst were add to 3 mL of isopropanol in a 25 mL round bottom flask. The reaction proceeded under normal pressure hydrogen without heating. Evidently, the color of the reaction solution changed from yellow to colorless and transparent after 5.5 h, illustrating that the hydrogenation of *p*-Nitrophenol was completed. The completion of reaction was also verified by HPLC. The plot of *p*-Nitrophenol conversion with time is shown in Figure 11b. With the reaction proceeded, the reactant concentration descended rapidly while

the product increased sharply, and the yield of p-Aminophenol is > 99% after 5.5 h of monitor.

This reaction did not only prove that the mPtNi<sub>2</sub>@CNS-600 had excellent catalytic activity, but also confirmed that H<sub>2</sub> could be dissociated to H<sub>ad</sub> (Hydrogen adsorption) under the presence of catalyst, which would further reduce the nitro compound to an amino compound. This was the first proof to reveal that the electrocatalyst underwent a chemical desorption to generate H<sub>ad</sub> through the Volmer-Tafel pathway in the process of electrolyzing water by adopting such a method.

## Conclusions

In conclusion, we have successfully developed a facile approach to synthesize the sub-3 nm PtNi bimetallic embedded on porous carbon nanosheet in large-scale, which as a bifunctional catalyst precede in HER and hydrogenation. The PtNi bimetallic material with ultra-low Pt content (0.074 wt%), which was verified by ICP-MS, possesses high number of exposed active sites and superior intrinsic activities for HER. Remarkably, the electrocatalyst exhibited excellent HER activity with an overpotential as low as 68 mV at a current density of 10 mA cm<sup>-2</sup> and extremely small Tafel slope of 35.27 mV decade<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution, which is comparable to those values for the 20% Pt/C catalyst (31 mV decade<sup>-1</sup>). It is worth noting that the PtNi bimetallic alloy shows splendid long-term electrochemical stability and durability for 2000 CVs and at least 30 h with negligible degradation. Last but not the least, the mPtNi bimetallic catalyst (2.88% Pt) also displayed the catalytic activity for hydrogenation of p-Nitrophenol in ambient pressure and temperature, which was employed to prove the Volmer-Tafel path in HER for the first time, by the way, the electrocatalyst has robust catalytic hydrogenation activity. The excellent bifunction and the low content of noble metals render the material a good prospect for practical application.

## **Experimental Section**

#### Synthesis of the precursors PtNi<sub>2</sub>@3DP (3D Polymer)

First and the foremost, 66.6 mg Ni(acac)<sub>2</sub> and 50 mg Pt(acac)<sub>2</sub> were completely dissolved in 40 mL Hacac under the ultrasonic condition, 16 g NaOH was then added rapidly under vigorous magnetic stirring. After stirred for 50 min, the compound was converted to a pastry, then put at room temperature without further treatment to grow up with a long chain. After 6 days, the blends turned into a dry, granular and fluffy polymeric compound. The PtNi<sub>1</sub>@3DP, PtNi<sub>1.5</sub>@3DP and PtNi<sub>3</sub>@3DP were synthesized via similar procedures for the PtNi<sub>2</sub>@3DP but with 33.3, 50 and 97.8 mg Ni(acac)<sub>2</sub> in the first step, respectively. The 3DP was synthesized with the same procedures as PtNi<sub>2</sub>@3DP, except for the adding Pt(acac)<sub>2</sub> and Ni(acac)<sub>2</sub>.

#### Synthesis of the PtNi<sub>2</sub>@CNS

The as-prepared polymer precursor of PtNi<sub>2</sub>@3DP sample were annealed at various temperatures (400 °C, 500 °C, 600 °C, 700 °C, 800 °C) and held at the setting temperature for 3 h with a heating rate of 2 °C min<sup>-1</sup>

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under Ar atmosphere to obtain the ultimate carbon-supported bimetal catalyst: bimetallic PtNi<sub>2</sub> carbon nanosheets (PtNi<sub>2</sub>@CNS-400, 500, 600 or others). After cooling to room temperature, the products were washed with ethanol and deionized water until pH=7. Ultimately, the nanocomposites were filtrated under reduced pressure and dried at 120 °C overnight. 3DP, PtNi<sub>1</sub>@3DP, PtNi<sub>1.5</sub>@3DP, PtNi<sub>3</sub>@3DP were also dealt with the same procedures as PtNi<sub>2</sub>@3DP to obtain CNS, PtNi<sub>1</sub>@CNS, PtNi<sub>1.5</sub>@CNS, PtNi<sub>3</sub>@CNS, respectively.

#### Electrochemical study

The electrochemical measurement was conducted at room temperature  $(25 \pm 1 \ ^{\circ}C)$  with a standard three-electrode system controlled by a CHI660E Electrochemical Workstation (Shanghai CH Instrument, China). A modified glassy carbon electrode (GCE, 3 mm in diameter) using Pt-Ni2@CNS-600 was used as the working electrode (WE), a saturated calomel electrode (SCE) was used as the reference electrode (RE), and a graphite rod was used as the counter electrode (CE). homogeneous catalyst ink was prepared by mixing catalyst powder (10 mg) with 40  $\mu L$  of 5 wt% Nafion solution (Alfa Aesar) , 500  $\mu L$  of ethanol and 460  $\mu$ L of deionized water, following by a strong ultrasonic treatment 30 min. For preparation of the working electrode, the GCE was polished with 1.0, 0.3 and 0.05  $\mu m$  Alpha Alumina Powder in sequence to obtain a mirror-like surface, subsequently rinsed with deionized water, and then the catalyst ink (7  $\mu$ L) was dripped onto a glassy carbon disk electrode. Hence the loadings of Pt on the electrode were about 0.612 µg cm-2 for PtNi2@CNS-600. The catalyst layer was allowed to dry under ambient conditions before an electrochemical measurement. All the polarization curves were iR-corrected as well as the presented potentials in our work were converted to a commonly used reversible hydrogen electrode (ERHE) with Nernst equation using 0.5 M H<sub>2</sub>SO<sub>4</sub> as the electrolyte solution. The conversion formula for the SCE reference electrodes as follows:  $E_{RHE} = E$  (SCE) + 0.2412 + 0.0594 \* pH. For the HER test, the Linear scanning curves were measured between 0 V and -0.6 V (vs. RHE) at a scan rate of 5 mV s<sup>-1</sup> in a 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> aqueous solution. The Tafel plot is assigned to the equation  $\eta = b \log (j) + a$  (where  $\eta$  is the overpotential, b represents the Tafel slope, and j refers to the current density). The double-layer capacitance (Cdl) was determined by cyclic voltammetry in the voltage ranged between -0.1 and 0.1 V vs. RHE and the i-t curves were measured at a constant potential of 0.3 V (vs. RHE). EIS was conducted by SP-150, Bio-Logic SAS.

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#### DECLARATION OF INTERESTS

The authors declare no competing interests.

**Keywords:** Ultra-fine bimetallic PtNi nanoparticles • Ultra-low Pt content • Excellent HER and hydrogenation performance • Facile and large-scale fabrication

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# ARTICLE

#### Entry for the Table of Contents (Please choose one layout)

Layout 1:

# ARTICLE

A facile method of fabricating carbon nanosheet supported sub-3nm bimetallic PtNi nanoparticles in largescale was developed.

This bifunctional material preceded in both hydrogen split and combination.

Ultra-low content of Pt (0.074 wt%) based electrocatalyst with excellent HER activity was obtained.

Excellent stability, durability and low power consumption were confirmed.

Layout 2:

## ARTICLE

Jifan Li<sup>1,21</sup>, Lei Liu<sup>11</sup>, Yongjian Ai<sup>2</sup>, Zenan Hu<sup>1</sup>, Liping Xie<sup>3</sup>, Hongjie Bao<sup>1</sup>, Jiajing Wu<sup>1</sup>, Haimeng Tian<sup>1</sup>, Rongxiu Guo<sup>1</sup>, Shucheng Ren<sup>1</sup>, Wenjuan Xu<sup>1</sup>, Hongbin Sun<sup>1,\*</sup>, Gang Zhang<sup>1,\*</sup> and Qionglin Liang<sup>2,\*</sup>.

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Facile and Large-Scale Fabrication of Porous Carbon Sheet Supported Sub-3 nm PtNi Nanoparticles: A Bifunctional Material for HER and Hydrogenation

Author(s), Corresponding Author(s)\*

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Text for Table of Contents



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