1. Introduction

Water splitting by electrolysis or photocatalysis is attracting attention as a prospective sustainable source of hydrogen for energy storage applications. The hydrogen evolution reaction (HER) is the cathode half reaction:

\[ \text{H}^+(\text{aq}) \rightarrow \frac{1}{2}\text{H}_2(\text{g}) \]

The most active and stable catalysts in acid environments for HER are currently based on precious metals. At low over-potentials, HER from Pt(111) is dominated by the Volmer–Tafel mechanism which can be written as:

\[ \text{H}^+(\text{aq}) \rightarrow \text{H}^*(1) \]
\[ 2\text{H}^* \rightarrow \text{H}_2(\text{g}) \]

This requires two H atoms to be adsorbed in proximity for fast diffusion and recombination. Alternatively the reaction may take place via a Volmer step (1), followed by the Heyrovski step:

\[ \text{H}^+(\text{aq}) + \text{H}^* + e^- \rightarrow \text{H}_2(\text{g}) \]

Reaction (3) is considered to be relevant at high over-potentials only.

In the last decade, several classes of non-precious materials have been found to be active catalysts for the HER. MoS\(_2\) was proven as a promising non-precious HER catalyst material, which is stable in a wide pH range. However MoS\(_2\) catalysts are not as active as platinum and they are only active at under-coordinated edge sites. Hydrodesulfurization (HDS) catalysts such as Mo\(_2\)C and MoB have recently attracted attention as hydrogen evolution catalysts with good stability in both acid and alkaline solution. Ni\(_2\)P has also previously been subjected to experimental and theoretical studies for the catalysis of hydrodesulfurisation water-gas-shift, and more recently for hydrogen evolution in acid. The active sites and the details of the mechanism remain unknown for several of the newly discovered HER catalysts including Ni\(_2\)P. The observed Tafel slopes of the Ni\(_2\)P catalysts are similar to what is observed for MoS\(_2\) edges, and the specific activity is one of the highest of the non-precious catalysts. Further experimental and theoretical studies can yield new insights for further design of electro-catalysts, which is the motivation of this study. In this paper, density functional theory (DFT) calculations are combined with experiments on high aspect ratio crystalline Ni\(_2\)P nanowires to understand the mechanism of HER from Ni\(_2\)P.

The trends in hydrogen evolution activity over various transition metals, and various metal- and non-metal combinations have been investigated using DFT. The free energy of hydrogen...
The slabs were relaxed using the Broyden–Fletcher–Goldfarb–Shanno LineSearch algorithm within ASE until the forces were below 0.01 eV Å⁻¹. A recalculation was later carried out with double the k-point sampling and a grid spacing of 0.12 Å for the most interesting slabs and adsorbate configurations. The resulting differences in adsorption energies did not exceed 0.02 eV, which is below the accuracy usually attributed to DFT.

The choice of facets and surface termination were based on calculations of the minimum energy configuration of all different ways to cut the crystal into the lowest index planes. Several STM and LEED studies³⁷–⁴⁰ show that the Ni₂P surfaces can have a stable phosphor termination, but under the hydro-thermal treatment before testing, it is expected that they lose the phosphor layer and expose active metal sites, as on the structures investigated in our calculations. The chosen structures are (10̅10), (11̅20), (11̅21) and the Ni₂P terminated (0001), as shown in Fig. 1 along with their (hkjl) indices from a top view.

The free adsorption energies are found from calculated potential energies by correcting for the gas phase entropy ΔS = −S₀(H₂) and the difference in zero point energy ΔZPE using the equation

$$ΔG = ΔE - TΔS + ΔZPE$$

where E denotes the ground state energy at 0 K obtained from DFT. The correction for ZPE and entropy makes an addition of 0.24 eV to the adsorption energy of a hydrogen atom.²⁴,⁴¹

The calculation of adsorption free energies and adsorbate coverages was carried out using the self consistent scheme as in the work reported by Skulason et al. The integral adsorption energy Gₓₓ(n) is

$$G_{\text{int}} = (G(N,n) - G(N,0) - nμ_H), \quad μ_H = 1/2G_{H_2} - eU$$

where $G(N,n)$ is the free energy of a surface which includes N nickel atoms in the top layer and n adsorbed hydrogen atoms. Thus we use a definition of the coverage $θ = n/N$, where n is the number of hydrogen adsorbates and N is the number of Ni.
atoms on the surface. The configuration which is relevant at a given chemical potential of protons and electrons is the one with the minimum integral adsorption energy ($G_{\text{int}}(n)$). Using the computational hydrogen electrode approach with self-consistent coverage and adsorption free energies, the adsorption phase diagram was calculated for every facet. The required over-potential to favor an intermediate step is given through the differential binding energy, which is given by:

$$\Delta G_{\text{ads}}(n) = \left( G_{\text{int}}(n) - G_{\text{int}}((n - 1)) \right)$$

We apply $\eta = \Delta G_{\text{ads}}(n)/e$ to find the minimum required over-potential to adsorb the intermediate, which enables a surface recombination reaction (the Tafel step). The barriers were calculated using the nudged elastic band (NEB) method with a climbing image.

2. Experimental methods

Materials

The commercially available materials were used as received: nickel acetylacetonate (Ni(acac)$_2$, for synthesis, VWR), oleic acid (suitable for cell culture, BioReagent, Aldrich), oleylamine (OA approximate C18-content 80–90%, Acros), trietylphosphine (TOP 90%, technical grade, AcroSeal®, Acros), ethanol (absolute alcohol without additive ≥ 99.8%, Aldrich), n-hexane (HiPerSolv CHROMANORM® for HPLC 97%, VWR), sulfuric acid (H$_2$SO$_4$ volumetric 1 M, Aldrich), and Nafion® (117 solution, Aldrich). Water was first purified using a Millipore Milli-Q® Integral water purification system (18.2 MΩ cm resistivity). All syntheses were performed under strict air-free conditions using glove-box and Schlenk line techniques unless stated otherwise.

Synthesis of nickel phosphide nanowires

The synthesis was performed following a previous report. A stock solution containing 0.75 mmol of Ni(acac)$_2$, 1.8 mmol of oleic acid and 10 mL of OA was heated at 120 °C. Then the stock solution was very slowly injected (0.05 mL min$^{-1}$) using a syringe pump into a stirred mixture containing 5 mL of OA and 2.4 mmol of TOP heated at 320 °C under reflux. The reaction mixture was kept at 320 °C under reflux until the stock solution was used up. Over the course of the reaction, the mixture color changed from transparent to dark yellow, orange and finally black. After cooling to room temperature, the products were washed using a mixture of hexane and ethanol, and separated by centrifugation. The supernatant was discarded and the washing step was repeated two more times. After the supernatant was discarded the nanowires were collected on a watch glass and dried in an oven at 50 °C overnight.

Physical characterization

X-ray diffraction (XRD) was carried out on a X’Pert Philips diffractometer in Bragg–Brentano geometry with Cu K$_{\alpha1}$ radiation ($\lambda = 0.1540$ nm) and a fast Si–PIN multi-strip detector. The tube source was operated at 45 kV and 40 mA. The Scherrer equation was used to calculate the average crystallite size of the powder.

The diffraction pattern was analyzed and compared with references in the international center of diffraction data (ICDD). Transmission electron microscope (TEM) images were taken on a Philips (FEI) CM12 with a LaB$_6$ source operated at 120 kV accelerating voltage. Specimens were prepared by ultrasonic dispersion of the samples in ethanol. The suspension was mixed with a micropipette by several suction-release cycles to ensure a representative and reproducible TEM sample is obtained. A few drops of the mixed suspension were deposited onto the carbon-coated grid.

Electrochemical measurements

Electrochemical measurements were recorded using a Gamry Instruments Reference 3000™ potentiostat. A traditional three-electrode configuration was used. For polarization and electrolysis measurements, a platinum wire was used as the auxiliary electrode and a double-junction Ag/AgCl (KCl saturated) electrode was used as the reference electrode. Both counter and reference electrodes were rinsed with distilled water and dried with compressed air prior to measurements. Potentials were referenced to a reversible hydrogen electrode (RHE) by adding a value of (0.2 + 0.059 × pH) V. The current was normalised over the geometric surface area of the electrode. Ohmic drop was corrected using the current interrupt method. A total electrolyte volume of ~50 mL was used to fill the glass cell. All potentials were converted and referred to the RHE unless stated otherwise. The electrolyte used throughout all electrochemical experiments was a 1 M H$_2$SO$_4$ solution. During electrochemical experiments, the electrolyte was agitated using a magnetic stirrer rotating at 300 rpm. For all electrochemical experiments a glassy carbon electrode (~0.071 cm$^2$) was used as the working electrode. The cyclic voltammetry (CV) experiments were conducted in 1 M H$_2$SO$_4$ at 25 °C using a scan-rate of 5 mV s$^{-1}$ across a potential window of ~0.3 to +0.1 V vs. RHE.

Pretreatment of the working electrode

Prior to loading of the catalyst, the working electrode was pretreated to achieve a better performance. First, the electrode was manually polished using alpha alumina powder (CH Instruments, Inc.) with decreasing grain sizes (typically 0.3 and 0.05 μm) on a 73 mm diameter nylon polishing pad (MasterTex, Buehler). Between each polishing step the electrode was rinsed with deionized water and ultrasonicated in distilled water for 10 seconds. Then the electrode was dried using compressed air. This ultrasonication and drying cycle was repeated two more times: once in absolute ethanol and a second time with distilled water. This polishing process resulted in a shiny mirror finish. The bare working electrode was subjected to a constant potential of 2 V vs. RHE in 1 M H$_2$SO$_4$ under vigorous stirring at 25 °C over 1 hour. Then, the pretreated electrode was rinsed with absolute ethanol and dried with compressed air prior to catalyst deposition.

Electrode preparation

Before being deposited on the working electrode, the nanowires were annealed at 450 °C for 4 hours under 5% H$_2$/N$_2$ gas in order to remove any surfactant present on the nanowire surface.
The catalyst was loaded on a pretreated working electrode via drop-casting of 10 μL of the catalyst ink, equivalent to a loading of 1.42 mg cm⁻². The catalyst suspension was a 500 μL solution consisting of 5 mg of the catalyst, 400 μL of distilled water, and 100 μL of absolute ethanol. The slurry was ultrasonicated for 5 hours and mixed with a micropipette by several suction-release cycles prior to deposition to ensure that a representative and reproducible catalyst sample is obtained. The temperature of the ultrasonic bath was kept below 45 °C at all times to avoid any undesired heating effect. The nanowires are ultra-sonicated for 5 h to minimize aggregation. Once the catalyst was deposited, the electrode was dried in an oven at 50 °C for 10 minutes. 5 μL of 0.2% Nafton® solution in absolute ethanol was then drop-cast on the glassy carbon surface and the electrode was dried in air for 5 minutes prior to electrochemical measurements.

3. Results and discussion

XRD measurements were conducted on the annealed Ni₃P nanowires (Fig. 2). According to Scherrer’s equation, the average crystallite size of the nanowires is 11 nm. Ni₃P is the predominant species in the sample, while small amounts of Ni₃P₅ and NiO are also present. Recently, Zhang et al. reported that pure Ni₁₂P₅ has a similar activity to that of Ni₂P for HER in acid.⁴⁵ We showed earlier that NiO is less active than Ni₂P; furthermore, NiO tends to dissolve at a reductive potential in acid. Thus, the HER activity of the nanowires (see below) can be mostly attributed to Ni₂P.

The transmission electron microscope (TEM) image and selected area electron diffraction (SAED) patterns of the nanowires are shown in Fig. 2a-d. The nanowires are rather uniform and the width of the nanowires observed by TEM is in agreement with the crystallite size calculated from the XRD pattern.

Fig. 2 (a) Representative TEM image of the annealed Ni₃P nanowires. (b) Focused SAED of nanowire crystallites indexed using JEMS© software. (c) and (d) Unfocused SAED patterns whose complementary information served to identify the growth direction of the nanowires.

The focused SAED pattern (Fig. 2b) was indexed using the JEMS software program (P. Stadelmann, JEMS, EPFL). The line linking the (000n) spots is the (0001) direction. The nanowire can be observed on the SAED pattern when the focus is reduced (Fig. 2c and d). Comparison between the indexed (Fig. 2b) and unfocused SAED patterns (Fig. 2c and d) allows the determination of the growth direction. The results indicate that the nanowires grow along the c-axis, i.e., the (0001) direction.

Thus, the nanowires do not expose many (0001) facets, since the (000n) planes exist only in their cross section (see Fig. 3). The low index facets ±(1120) and (1010) are assumed to be widely available on the samples. These morphologies would be expected to exhibit a less than optimal performance if the ensemble on the Ni₃P terminated (0001) facet was the only active site.

Fig. 4 shows the HER activity of the Ni₃P nanowires in 1 M H₂SO₄. The nanowires are excellent HER catalysts. This result combined with the calculations (see below) does not indicate that the (0001) ensemble is the only active site of HER from Ni₃P, although it is not possible to separate contributions from the various facets and sites in the experiments. The overpotential to drive a current density of 10 mA cm⁻² is 133 mV (Fig. 4a). Two Tafel slopes are observed. At η < 125 mV, the Tafel slope is about 60 mV dec⁻¹, while at η ≈ 125–275 mV, the Tafel slope is 126 mV dec⁻¹ (Fig. 4b). Despite the difference in sample preparation and morphology, the catalytic activity of the Ni₃P nanowires is very similar to the activity of hollow and multfaceted Ni₃P nanoparticles reported by Schaak et al.,¹⁹ that of polydispersed Ni₃P nanoparticles reported by our group,²⁰ and that of high surface area Ni₃P nanoflakes reported by Han et al.²⁹ This suggests that widely available facets or sites of Ni₃P are active. This is contrary to MoS₂, where only specific morphologies are efficient because the edge sites need to be exposed.⁸ The facets with (ab − (a + b) 0) indices are propagating along the growth direction of the nanowires (see Fig. 3), and are thus expected to be abundant in the sample.

The DFT calculations show that the most strongly binding sites tend to be nickel bridge sites or nickel 3-fold hollow sites. The nickel bridge sites are found in continuous rows on the (1010) and (1̅120) facets and adjacent to nickel hollow sites on the (1121) facet. (see ESI† for geometries and adsorption
energies.) Adsorption on Ni–P sites and on top P atoms was generally 0.2 eV to 0.4 eV less stable than the metal sites. Thus, adsorption on Ni–P sites and on top P atoms would require a higher over-potential.

It takes a high over-potential to favor a high coverage of atomic hydrogen on all the facets. Thus, Ni$_2$P is on the weak binding side of the Sabatier volcano. Adsorbates on Ni$_2$P interact strongly leading to a steeper increase in binding energy with increasing coverage (see ESI† for the surface phase diagrams), compared to most transition metals including platinum.

The (0001) facet has the hollow site occupied at equilibrium, but as shown in Fig. 6, it requires a large over-potential of 0.41 V to stabilize the initial Ni–P bridge state for the Tafel step. It is also improbable that adsorbates from separate hollow sites on (0001) can combine since they are not neighbouring. This was confirmed by calculating the diffusion barriers on the (0001) and the (1010) facets (see ESI†). The (1010), (1120) and (1121) facets only require an over-potential of 0.0 V, 0.06 V and 0.19 V, respectively, to stabilise neighbouring H* or H**, which are mobile in the row of nickel atoms. These results suggest that H* in Ni hollow sites on the (0001) facet do not contribute to the HER rate at low over-potentials. To investigate further, the barriers for the Tafel step were calculated as described in the following.

Previous calculations on Pt(111) suggest that the Tafel pathway is faster than the Heyrovski pathway at low over-potentials. If proton transfer is faster to H*[Ni$_2$P] than to H*[Pt(111)], it is possible that isolated metal hollow sites on the (0001) facet play a role. In the following, it is assumed that the surface coverage is in equilibrium with protons in solution, which means that the Tafel step is rate limiting. Calculation of the barrier for proton transfer (Volmer or Heyrovski step) is out of the scope of this paper, since it requires very precise information on the interfacial structure.46

As shown in Fig. 5, the rate limiting HER barrier is $G_{TS}$, where $G_{TS}$ is the energy of the transition state relative to the $2(H^+ + e^-)/C_0$ state. The initial states were the most stable configurations at the lowest possible over-potential according to the surface phase diagrams. As shown from calculations presented in Fig. 5, $G_{TS}$ can be lowered by further increasing the over-potential until the free energy of protons in solution are at the Tafel transition state level. This agrees well with the exchange current density being a good indication for the activity at higher over-potentials.

The results for a Tafel pathway are summarized in Fig. 6, with comparison between the studied facets. The adsorption energies, which are easy to calculate, are usually a good descriptor, since they are expected to scale with the transition state energies. In the case of a Tafel pathway, it is more accurate to use calculated $G_{TS}$ to compare the activity from the different facets, since it is the highest barrier in the reaction pathway, which limits the rate.

Observing the calculated $G_{TS}$ in Fig. 6 for the Tafel steps, it is clear that the (1120) facet and the (1121) facet should have the highest exchange current density and thus be the most active facets. The reason why these sites have the lowest combination barrier may be found in the geometry of the Ni atom binding...
the transition state. The transition states for (1120) and (1121) are presented in the insets in Fig. 6. The atomic hydrogen moves from stable bridge sites on top of the nickel atom, which on these two facets is coordinated to six nickel atoms and two or three phosphor atoms. It is possible to imagine that a few defect sites, not investigated here, could be participating in the catalysis. However, the most active sites investigated in this study have binding energies very close to the optimal value and they are calculated to be very active. Other sites such as corners or kinks would only be relevant if they have a much higher activity than the low index facets. Furthermore, we expect that sites with lower coordination will bind too strongly, thus being less active according to the Sabatier principle.

4. Conclusion

In summary, the DFT calculations have shown that phosphor stabilized Ni-bridge sites found on several available facets of Ni₂P nanowires provide moderate binding to hydrogen atoms. The sites with highest exchange current density estimated from the Tafel transition state energy appear to be the Nickel bridge sites on either the (1120) facet or the (1121) facet. The high activity measured from nanowires grown along the (0001) direction suggests that the active site of Ni₂P is unlikely the (0001) facets as previously speculated. Thus the experiments support the calculations, although contributions from various sites or facets cannot be completely isolated in the electrochemical measurements.

This work shows that Ni₂P has many very active sites for HER, which explains the good performance. An interesting outlook is the calculation of other metal phosphor compounds, to look for sites with slightly stronger hydrogen binding energies or less adsorbate repulsion, which could be promising candidates for new catalyst materials.

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