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Easily-prepared dinickel phosphide (Ni_2P) nanoparticles as an efficient and robust electrocatalyst for hydrogen evolution

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Chemicals and Reagents

$NiCl_2 \cdot 6H_2O$ (Reagent plus) were purchased from Aldrich and stored under nitrogen. NaH_2PO_2 (analysis grade) were purchased from Acros and stored under nitrogen. Unless noted, all other reagents were purchased from commercial sources and used without further purification. It should be noted that all solutions in our work were prepared using Millipore-MiliQ water (resistivity : $\rho \geq 18$ MΩ cm^{-1}) and the reagents used were analytical-grade.

Preparation of Ni_2P nanoparticles

A solid mixture of 0.66 g NaH_2PO_2 and 0.3 g $NiCl_2 \cdot 6H_2O$ was mechanically grounded using a mortar and pestle in the glove box (to prevent deliquescence; not absolutely necessary). After that, the solid mixture was transferred to a quartz tube, where it was heated to 250 °C in a tubular oven and kept for 1 h in a flowing 30 mL/min N_2. Following cooling to room temperature in a continuous N_2 flow, the Ni_2P particles were passivated in a 1.0 mol% O_2/N_2 mixture at 20 mL/min for 1 h. Finally, the products were washed with water and dried at room temperature. The synthesis is similar to that reported in Catalysis Communications, 2011, 12, 1157, except that NaH_2PO_2 rather than NaH_2PO_3 is used. The latter is not available to us.

Physical methods

Energy Dispersive X-Ray Spectroscopy (EDX) was taken in a Phillips (FEI) XLF-30 FEG scanning electron microscope. XRD measurements were carried out on a X'Pert Philips diffractometer in Bragg-Brentano geometry with Cu $K_{\alpha 1}$ radiation and a fast Si-PIN multi-strip detector (0.1540 nm). TEM images were taken on a Philips (FEI) CM12 transmission electron microscope with a LaB6 source operated at 120 kV accelerating voltage. The Scherrer equation was used for crystal size calculation: $d=K\lambda/\beta\cos(\theta)$. K is the shape factor with a typical value of about 0.9, λ is the X-ray wavelength, i.e., 1.54056 Å here, β is the full width at half maximum (FWHM) in radians, and θ is the Bragg angle, d is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size.

The Inductively Coupled Plasma Mass spectrometry (ICP-MS) ICP-MS instrument used in this work was the Finnigan™ Element2 High Performance High Resolution ICP-MS, which consists of a double focusing reverse geometry mass spectrometer. The sensitivity was better than

$1.2x10^5$ cps/ppb of ^{115}In at a mass resolution of 4000, which corresponds to $1.2x10^6$ cps/ppb at low resolution mode of 500. Measurement repeatability expressed in terms of RSD was better than 5%, depending on the element. The accuracy of the method was tested using certified riverine water reference materials SLRS-3. Accuracy was better than 5%. The detection limits obtained for trace metals in the Medium resolution mode (R=4000) without the influence of signal interferences were in routine mode less than 0.2 ng l^{-1} for all elements. Calibration standards were prepared through successive dilutions in cleaned Teflon bottles, of 1g l^{-1} ICPMS stock solutions (Bernd Kraft). Suprapur® grade nitric acid (65% Merck) was used for the dilution of samples and for the preparation of standards (2+1000). Ultrapure water was produced using Milli-Q® Ultrapure Water System (Millipore, Bedford, USA). The mass resolution was set to 4000 in order to use the ability of the high resolution technique to resolve most spectral interferences from the analyte ions observed for Ni. The high resolution mode is also useful for samples having unexpected or unknown interferences, because the quantification is obtained by integrating only the area of the analyte peak, without the influence of an unexpected interference peak.

Fabrication of working electrodes

Ni_2P particles were dispersed by sonication of a 1mL ethanol solution containing 50 μL Nafion solution (5 wt%, Aldrich Co. USA). 10 μL of the above solution was pipetted and spread on a mirror-finished glassy carbon electrode. The glassy carbon electrode was polished with alumina slurry (0.5 and 0.03 μm) successively before use. The modified electrode was dried at room temperature for 30 min. The apparent surface area of the glassy carbon electrode was 0.07 cm^2. The Nickel electrode with a surface area of 0.03 cm^2 was used for comparison. Nickel hydroxide electrode was prepared by electrodeposition method in a 0.1 M $Ni(NO_3)_2$ solution using glassy carbon electrode as the working electrode. The reduction current was 1 mA cm^{-2} and the deposition was carried out for 60 s. The measurements were carried out at room temperature in 1 M H_2SO_4 or 1 M KOH solution with a scan rate of 5 mV s^{-1}.

For the study of the dissolution of Ni_2P, a large pellet disk electrode was used. 0.25 g of powdered Ni_2P was mixed with 0.150 g of Teflon powder (1μm). The mixture was pressed in a conventional KBr pelletizer under 10 Tons to produce a 12 mm diameter pellet. A copper wire

contact was glued to one side of the pellet using silver conductive epoxy glue (CircuitWorks CW2400 - Chemtronics). A 5 mm hole mask was glued to the other side of the electrode to limit the surface area. With the exception of the active area, the whole body of the electrode was insulated with molten polypropylene.

Electrochemical measurements

Electrochemical measurements were recorded by a Gamry Instruments Reference 600 potentiostat. A traditional three-electrode configuration was used. For polarization and electrolysis measurements, a platinum wire was used as the auxiliary electrode and an Ag/AgCl (KCl saturated) electrode was used as the reference electrode. Potentials were referenced to a reversible hydrogen electrode (RHE) by adding a value of (0.197 + 0.059pH) V. Ohmic drop correction was performed using the current interrupt method. A total liquid volume of 50 mL was used to fill the cell. The platinum counter electrode was separated from the solution through a porous glass frit (porosity 3) and this whole assembly inserted into one side of the H cell. The modified working electrode was inserted in the other side of the cell, together with a magnetic stirring bar and a Luggin capillary.

For the ICP-MS measurement of dissolution of Ni_2P, 1 mL of the electrolyte solution under electrolysis was sampled at different hours and stored in the refrigerator before test.

Hydrogen production yield

The yield of hydrogen is determined using our previously established procedure (e.g. Chem. Sci. 2011, 2, 1262). Two small inlets were present in the cell allowing the connection to the pressure monitoring device and the other kept closed by a septum for sampling of the gas phase. The whole cell apparatus is gas-tight and the pressure increase is proportional to the gases generated ($H_2 + O_2$). Prior to each experiment, the assembled cell was calibrated by injecting known amounts of air into the closed system and recording the pressure change. Pressure measurements during electrolysis were performed using a SensorTechnics DSDX0500D4R differential pressure transducer. Pressure data was recorded using an A/D Labjack U12 interface with a sampling interval of 1 point per second. The electrolysis was conducted at fixed potential and the solution was stirred with a magnetic stir bar during test.

After the calibration the cell was purged with nitrogen for 20 minutes and the measurements were performed. The Faradaic yield was calculated as follow:

The total amount of charge (Q) passed through the cell was obtained from the current-potential curve. The total amount of hydrogen produced (x) was measured using the pressure sensor. Assuming 2 electrons are needed to make one H_2 from two protons. Faradaic yield for H_2 = Q/2xF.

Table S1. Comparison of non-precious HER catalysts. Note that the specific surface of the different catalysts was not controlled for and thus, the estimates are quite crude and may not be reflective of the differences in specific activity.

catalysts	**Condition**	**Loading**	**Overpotential @ 20 mA cm^{-2}**	**Tafel slope (mV/dec)**	**Reference**
Ni_2P nanoparticles	1 M H_2SO_4	0.38 mg/cm^2	0.14 V	87	This work
MoS_2/RGO	0.5 M H_2SO_4	0.28 mg/cm^2	0.17 V	41	[1]
Ni_2P hollow particles	0.5 M H_2SO_4	1 mg/cm^2	0.13V	81 (η > 125)	[2]
MoS_2/SWCNTs	0.5 M H_2SO_4	0.136 mg/cm^2	0.2 V	44.4	[3]
MoS_2	0.5 M H_2SO_4	0.136 mg/cm^2	0.23 V	56.4	[3]
MoS_{2+x}	1 M H_2SO_4	0.2 mg/cm^2	0.17V	40	[4]
MoS_2	0.5 M H_2SO_4	0.06 mg/cm^2	0.23V@10mA cm^{-2}	50	[5]
NiMoN	0.1 M $HClO_4$	0.25 mg/cm^2	0.23V@5mA cm^{-2}	35	[6]
MoB	1 M H_2SO_4	2.5 mg/cm^2	0.23 V	55	[7]
Mo_2C/CNT	0.1 M $HClO_4$	2 mg/cm^2	0.15V@10mA cm^{-2}	55.2	[8]
Mo_2C	1 M H_2SO_4	1.4 mg/cm^2	0.23 V	56	[7]
WS_2 nanosheet	0.5 M H_2SO_4	0.1–0.2 μg /cm^2	0.3 V	60	[9]
WS_2 nanosheet	0.5 M H_2SO_4	0.285 mg/cm^2	0.17 V	72	[10]
MoB	1 M KOH	2.3 mg/cm^2	0.24 V	59	[7]
Mo_2C	1 M KOH	0.8 mg/cm^2	0.21 V	54	[7]
NiZn	1 M NaOH	--	0.25 V	119	[11]
NiZr	6 M KOH	--	0.30 V	110	[12]
Porous Ni_3Al	6 M KOH	--	0.25 V	--	[13]
NiTi	1 M NaOH	--	0.17 V	283	[14]
Ni_2P nanoparticles	1 M KOH	0.38 mg/cm^2	0.25 V	100	This wrok

-- not reported in the literature

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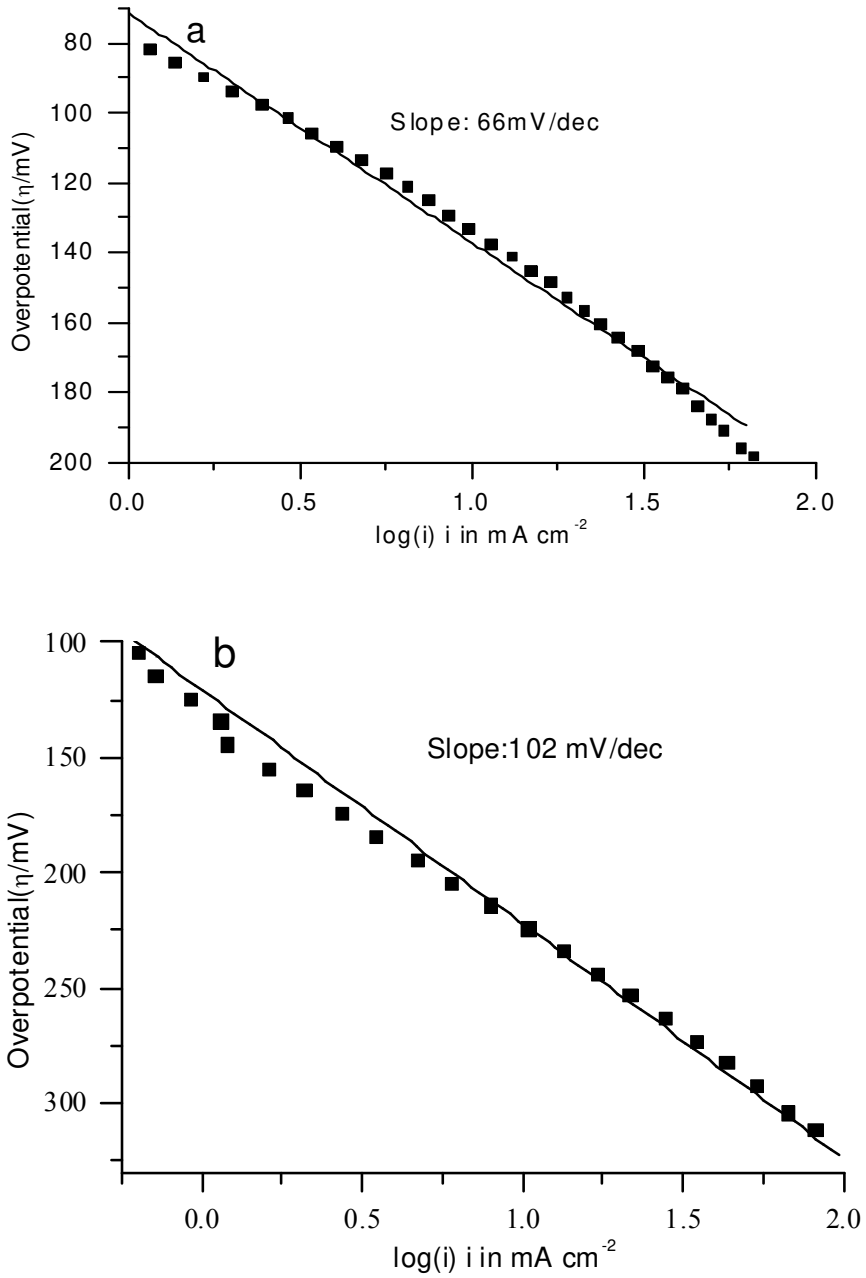

Figure S1. Tafel slopes of HER catalyzed by Ni_2P obtained from polarization curves in (a) 1 M H_2SO_4; (b) 1 M KOH.

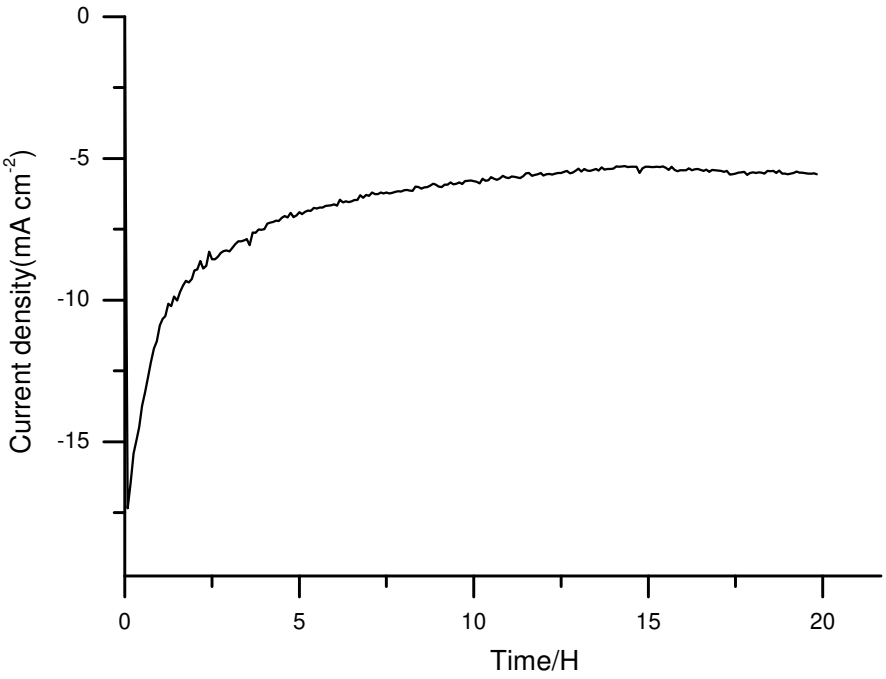

Figure S2. Time dependence of the catalytic current for a Ni_2P/Ti foil electrode during potentiostatic electrolysis over 20 hours at -0.15 V in 1 M H_2SO_4. Loading: 0.25 mg/cm^2.

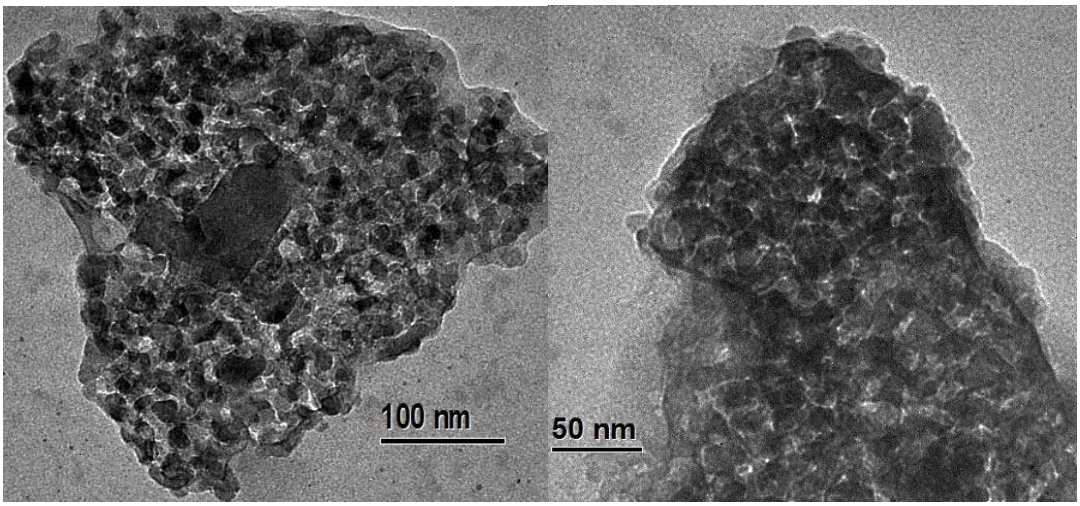

Figure S3a. TEM imgaines of Ni_2P particles after electrolysis for 48 hours elecrolysis at 13 mA cm^{-2}. The particles were removed from the electrode before analysis.

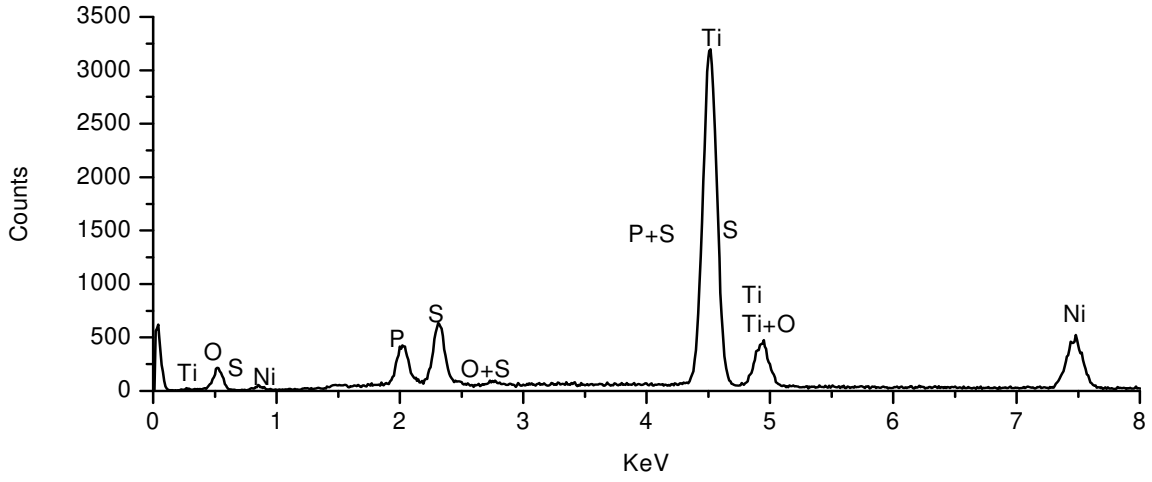

Figure S3b. EDX spectrum of Ni_2P particles after electrolysis for 48 hours elecrolysis at 13 mA cm^{-2}. The particles were removed from the electrode before analysis. Atomic ratio: Ni/P=1.94. S is from the H_2SO_4 and Ti is from the support where EDX is done.

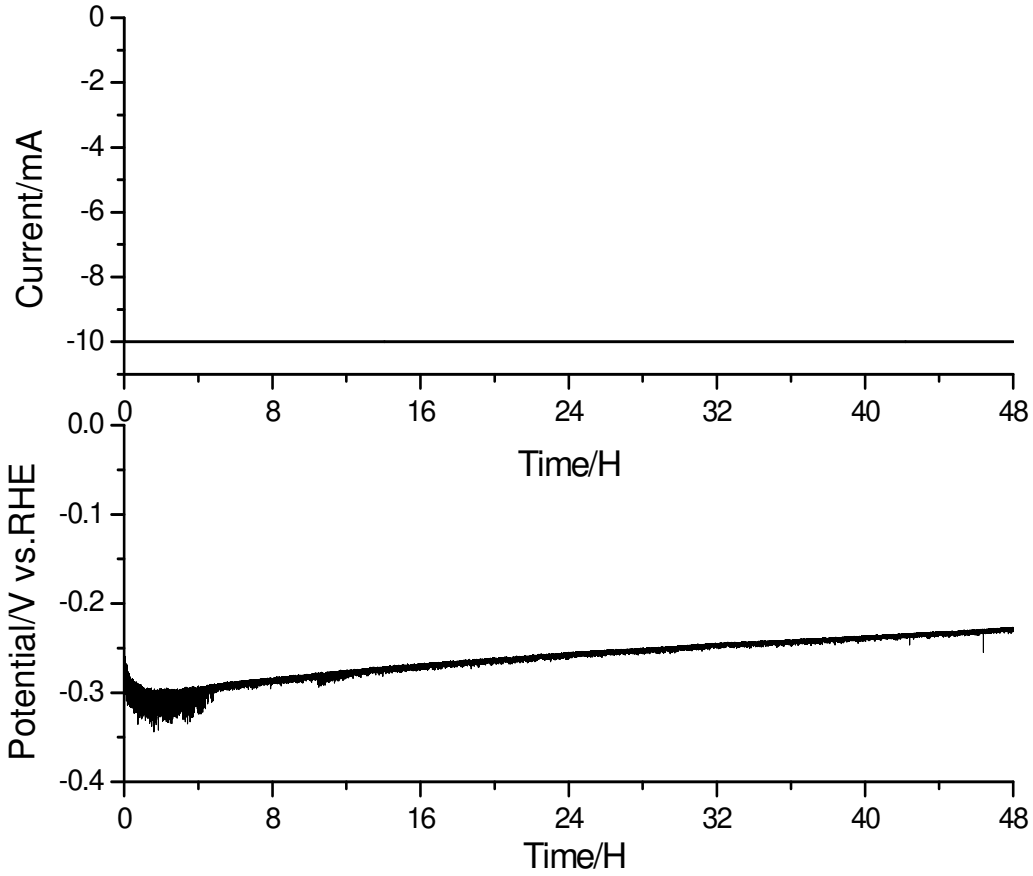

Figure S4. Accelerated stability test for Ni_2P particles on a glassy carbon electrode. Loading: 0.38 mg/cm^2. Top: Galvanostatic electrolysis at 140 mA/cm^2 for 48 hours. Bottom: the dependence of potential during this process. The small decrease of potential over time might be due to some electrochemical conditioning.

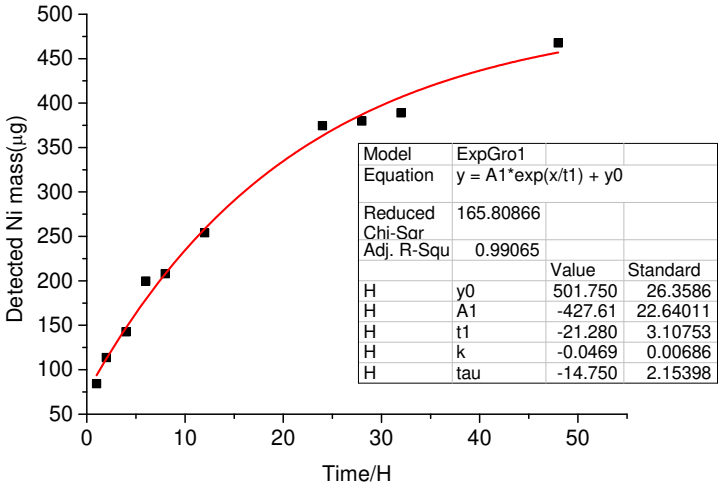

Figure S5. The amount of Ni detected in the electrolyte solution during electrolysis at 10 mA/cm^2. The electrode is a Ni_2P pellet with 250 mg Ni_2P (ca. 200 mg Ni). The data is fitted with an exponential growth function.