Supporting Information for

A super-efficient cobalt catalyst for electrochemical hydrogen production from neutral water with 80 mV overpotential

Lin Chen,^a Mei Wang,^{*a} Kai Han,^a Peili Zhang,^a Frederic Gloaguen,^b and Licheng Sun^{*a,c}

^aState Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), Dalian 116024, China ^bUMR 6521, CNRS, Universit éde Bretagne Occidentale, CS 93387, 29238 Brest, France ^cDepartment of Chemistry, KTH Royal Institute of Technology, Stockholm 10044, Sweden

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Materials and instruments

Materials. Compounds $[M(NH_4)_2](SO_4)_2$ (M = Fe, Co), CoSO₄, CoX₂, (X = Cl, OAc), $[P(CH_2OH)_4]_2SO_4$, $[P(CH_2OH)_4]X$, $(NH_4)_2SO_4$, and $(NH_4)X$ were purchased from local suppliers and used without further purification. Mercury (99.999%) was purchased from Aladdin and deionized water was used as solvent in all experiments.

Instruments. UV-Vis absorption measurements were carried out on an Agilent 8453 spectrophotometer. Proton and ³¹P NMR spectra were collected with a varian INOVA 400 NMR spectrometer. XPS profiles of CoP_4N_2 were obtained on a Thermo ESCALAB250 instrument with a monochromatized AlKa line source (200 W). The EPR spectrum of the CoP_4N_2 solid was collected under nitrogen atmosphere with a Bruker A200-9.5/12 electron-spin resonance spectrometer. Elemental analyses were performed with a Thermoquest-Flash EA 1112 elemental analyzer. Inductively coupled plasma mass spectrometric analysis (ICP) was recorded on an Optima 2000 DV spectrometer (Perkin Elmer Inc.). SEM images and EDX spectra were recorded with a FEG-SEM (FEI NOVA NANOSEM 450) operating at 3 kV and equipped with an OXFORD X-max EDX system operating at 20 kV.

Preparation of catalysts

In situ-generation of MP₄N₂ (M = Fe, Co) catalysts. Complex FeP₄N₂ was generated in situ by a convenient metal-templated method according to the literature procedure,^[1] either with [Fe(NH₄)₂](SO₄)₂ and [P(CH₂OH)₄]₂SO₄ or with FeSO₄, (NH₄)₂SO₄, and [P(CH₂OH)₄]₂SO₄ as starting reagents in aqueous solution at pH 4.5–5.0. The solutions obtained display the same UV-vis and ³¹P NMR spectra as those reported for FeP₄N₂ in the literature.

An essentially identical procedure for preparation of FeP_4N_2 was adopted with $[Co(NH_4)_2](SO_4)_2$ or $CoSO_4$ as reactant. The salt $[P(CH_2OH)_4]_2SO_4$ (1.07 g, aqueous solution, 75.5% wt/wt, 2.0 mmol) was added to the solution of $[Co(NH_4)_2](SO_4)_2 \cdot 6H_2O$ (0.40 g, 1.0 mmol) or to the solution of $CoSO_4 \cdot 6H_2O$ (0.26 g, 1.0 mmol) and $(NH_4)_2SO_4$ (0.13 g, 1.0 mmol) in water (50 mL), immediately followed by slow

addition of 2.0 M NaOH solution to the mixture to maintain the pH value in the range of 4.5 to 5.0. Addition of NaOH was stopped when the pH value did not change any more. The solution turned to orange-red and the reaction was stopped (~2 h) when the intensity of new absorptions at 270 and 440 nm did not grow further in the UV-vis spectrum and the ³¹P NMR signal of $[P(CH_2OH)_4]^+$ was completely disappeared.

These in situ-generated FeP_4N_2 and CoP_4N_2 aqueous solutions were directly used for electrochemical experiments by assuming that MP_4N_2 was formed by 100%.

Isolation of MP₄N₂ catalysts. The condensation reaction of $[Fe(NH_4)_2](SO_4)_2 \cdot 6H_2O$ (0.39 g, 1.0 mmol) with $[P(CH_2OH)_4]_2SO_4$ (1.07 g, aqueous solution, 75.5% wt/wt, 2.0 mmol) was made in the modified procedure. To separate the product, the base Ba(OH)₂ (0.95 g, 3.0 mmol) was added slowly in very small portions to the solution (~3 h) to control the pH in the range of 4.5–5. When the reaction ended (stirred overnight), the BaSO₄ solid was removed by filtration. The filtrate (~50 mL) was concentrated by rotatory evaporation and decanted into methanol (100 mL) with vigorous stirring. The red precipitate was isolated in 85% yield after it was washed with ether for three times and dried in vacuum. ¹H NMR (400 MHz, D₂O): δ 4.62, 4.55 (q, *J* = 13.4 Hz, 8H, P(CH₂OH)₂), 4.35 (s, 4H, P(CH₂OH)), 3.66 (s, 4H, CH₂N), 3.15, 3.09 (q, *J* = 14.6 Hz, 8H, CH₂N); ³¹P{¹H} NMR: δ 20.1 (t, 2P, *J*(PP) = 53.2 Hz), -1.5 (t, 2P, *J*(PP) = 53.4); UV-vis (H₂O): λ_{max} 477 nm; analysis (calcd., found for C₁₂H₃₄N₂O₁₂P₄SFe·4H₂O): C (21.12, 20.98), H (6.20, 6.31), N (4.11, 4.02). The UV-vis, ¹H and ³¹P NMR spectra of the isolated complex FeP₄N₂ are identical with those reported for FeP₄N₂ in the literature.^[1]

The condensation reaction of $[Co(NH_4)_2](SO_4)_2$ with $[P(CH_2OH)_4]_2SO_4$ was made in the same way as the afore-mentioned method, but Ba(OH)₂ was used as base to control the pH of the medium. The CoP₄N₂ was isolated as orange-yellow solid in 80% yield with an essentially identical protocol for isolation of FeP₄N₂. The product was characterized by UV-vis, EPR, and XPS spectroscopy, and the composition of the product was determined by ICP and elementary analyses. The NMR spectra of CoP₄N₂ do not give any useful structural information due to its paramagnetic property. UV-vis (H₂O): λ_{max} 270 and 420 nm; analysis (calcd., found for C₁₂H₃₄N₂O₁₂P₄SCo·2CH₃OH): C (24.82, 25.01), H (6.25, 6.01), N (4.14, 4.21). The ICP analysis gives a result of Co 8.32% and P 17.51%, corresponding to a 1:4 Co/P ratio. The EPR spectrum of the CoP₄N₂ solid measured at room temperature shows a broad signal with g value at 2.147 (Fig. S14). The binding energy peaks in XPS centered at 779.6 eV (Co, $2p_{3/2}$), 794.9 eV (Co, $2p_{1/2}$), 398.9 eV (N 1*s*), and 132.0 eV (P 2*p*) (Fig. S15).

Electrocatalytic experiments

Electrochemical measurements. Electrochemical measurements were recorded in a three-electrode cell under argon atmosphere using a CHI 630D potentiostat. A mercury pool (3.1 cm²), an amalgamated copper plate (1.0 cm^2) and an amalgamated copper rod (surface area 1.1 cm^2), as well as a glassy carbon disc (diameter, 3 mm, 0.07 cm^2) and a platinum disc (0.2 cm^2) were used as working electrodes. Electrical contact to the mercury pool was achieved through a platinum wire that remained completely immersed in the mercury. The amalgamated copper electrode was made by immersing a copper plate or a rod in mercury for 60–120 min. The glassy carbon and platinum disks were successively polished with 3 and 1 µm diamond pastes and sonicated in ion-free water for 10 min before use. The auxiliary electrode was a platinum gauze (ca. 0.5 cm², 58 mesh, woven from 0.1 mm diameter wire) or a wire and the reference electrode was a commercially available aqueous Ag/AgCl (3.0 M KCl) electrode. For Fig. 5, the CVs were recorded on a PGSTAT100N potentiostat with a static mercury dropping electrode (drop size ~0.4 mm²), a platinum wire counter electrode, and an aqueous Ag/AgCl reference electrode. The potentials are reported with respect to the NHE by adding 0.197 V to the experimentally obtained values. The overpotentials were calculated by the following equation: overpotential = |applied potential| - 0.059 pH V. A dipotassium hydrogen phosphate/sodium dihydrogen phosphate buffer was used as electrolyte and deionized water was used as solvent.

All electrochemical experiments were carried out in a pear-shaped double-compartment cell (fig. S1). The counter electrode, a platinum gauze or a wire, was placed in a column-shaped compartment with a bottom of porous glass frit (G3, 1.1 cm^2), which was inserted into the main chamber of the electrolysis experiment and fixed only ~1 cm above the surface of mercury pool electrode to reduce the internal

resistance. The sample was bubbled with argon for 20 min before measurement and the electrolysis was carried out under argon atmosphere. The solutions in both compartments were constantly stirred during electrolysis experiments.

The controlled potential electrolysis experiments were conducted in a cell with the working electrode compartment containing 25 mL of 1.0 or 2.0 M phosphate buffer solution at pH 7 and with the counter electrode compartment containing 5 mL of the same buffer used in the working electrode compartment. The volume of the gas generated during electrolysis experiment was quantified by a gas burette and the H_2 evolution was determined by GC analysis using a GC 7890T instrument with a thermal conductivity detector, a 5 Å molecular sieve column (2 mm × 5 m) and with N₂ as carrying gas. Each catalytic datum was obtained from at least two paralleled experiments.

Determination of TON and TOF.

 $TON = Q \times FE / (F \times n_{ele} \times n_{cat}) \pmod{H_2 \text{ per mol catalyst}}$

Q = charge from catalyst solution during CPE (C) – charge from solution without catalyst during CPE (C) FE = Faradaic efficiency

F = Faraday's constant = 96485 (C/mol)

- $n_{\rm ele}$ = mol of electrons required to generate a mol of H₂ = 2
- n_{cat} = total mol of catalyst in solution = the concentration of catalyst (mol/L) × the volume of the solution in the working electrode compartment (L)

TOF = TON / duration of electrolysis (h) (mol H₂ per mol catalyst per hour) ^[2]

Determination of Faradaic efficiency. Gas chromatographic analysis of the electrolysis-cell headspace was made during the electrolysis of 4 μ M solution of CoP₄N₂ in 25 mL of 2.0 M phosphate buffer at pH 7 in a gas-tight electrolysis cell at an applied potential of -1.0 V vs. NHE for 1 h with a mercury pool electrode. The gas evolved from the catalytic system was quantified volumetrically by a gas burette The amount of hydrogen generated was determined by GC analysis with an external standard

method and the hydrogen dissolved in the solution was neglected. The amount of hydrogen evolved is in good agreement with that calculated from consumed charge in the CPE experiment (Fig. S7), indicating that CoP_4N_2 operates at a Faradaic efficiency close to 100%.

References

- 1 J. C. Jeffery, B. Odell, N. Stevens and R. E. Talbot, *Chem. Commun.*, 2000, 101–102.
- 2 H. I. Karunadasa, C. J. Chang and J. R. Long, *Nature*, 2010, **464**, 1329–1333.



Fig. S1 Cyclic voltammograms of (a) CoP_4N_2 (5.0 mM) in 0.1 M KCl aqueous solution at a scan rate of 200 mV s⁻¹ and (b) FeP₄N₂ (2.0 mM) in 0.2 M KCl/0.1 M phosphate buffer aqueous solution at a scan rate of 100 mV s⁻¹ with a glassy carbon electrode (0.07065 cm²) in selected regions.



Fig. S2 Cathodic scans of the solutions of 60 μ M CoP₄N₂ isolated (blue line); generated in situ from [Co(NH₄)₂][SO₄]₂ and [P(CH₂OH)₄]₂SO₄) (pink line); from CoSO₄, (NH₄)₂SO₄, and [P(CH₂OH)₄]₂SO₄) (green line) in 1.0 M phosphate buffer at pH 7 with a mercury pool electrode at a scan rate of 100 mV/s; the black and red lines indicate the cathodic scans of buffer solution in the absence of catalyst using a Hg pool and a Pt gauze as working electrode, respectively, under otherwise identical conditions. The dash line shows the value for thermodynamic hydrogen generation at pH 7.



Fig. S3 Cathodic scans of (a) a 1.0 mM solution of $[Co(NH_4)_2][SO_4]_2$ and (b) a 2.0 mM solution of $[P(CH_2OH)_4]_2SO_4$ in 1.0 M phosphate buffer at pH 7 with a mercury pool electrode at a scan rate of 100 mV s⁻¹.



Fig. S4 Cathodic scans of 1.0 M phosphate buffer solutions of (a) 200 μ M CoSO₄ (200 μ M) + (NH₄)₂SO₄ (200 μ M); (b) (NH₄)₂SO₄ (200 μ M) + [P(CH₂OH)₄]₂SO₄ (400 μ M); and (c) CoSO₄ (200 μ M) + [P(CH₂OH)₄]₂SO₄ (400 μ M) at pH 7 with mercury pool electrode at a scan rate of 100 mV/s; the black lines in (a), (b), and (c) indicate the cathodic scans of buffer solution in the absence of catalyst under otherwise identical conditions.



Fig. S5 UV-vis spectra of 1.0 M phosphate buffer solutions of $[P(CH_2OH)_4]_2SO_4$ (0.4 mM) + $[Co(NH_4)_2](SO_4)_2$ (0.2 mM) (red line), $[P(CH_2OH)_4]_2SO_4$ (0.4 mM) + $CoSO_4$ (0.2 mM) + $(NH_4)_2SO_4$ (0.2 mM) (black line), $CoSO_4$ (0.2 mM) + $(NH_4)_2SO_4$ (0.2 mM) (pink line), $[P(CH_2OH)_4]_2SO_4$ (0.4 mM) + $(NH_4)_2SO_4$ (0.2 mM) (green line), and $[P(CH_2OH)_4]_2SO_4$ (0.4 mM) + $CoSO_4$ (0.2 mM) (blue line) in 1.0 M phosphate buffer at pH 7.0.



Fig. S6 Turnover frequency versus overpotential for CoP_4N_2 in 1.0 M phosphate buffer at pH 7. The contribution from the background solution has been subtracted from the plot.



Fig. S7 The amount of hydrogen calculated from passed charge (red solid), assuming a Faradaic efficiency of 100%, and measured from gas chromatography (black square) during the electrolysis of 10 μ M CoP₄N₂ in 2.0 M phosphate buffer at pH 7 at an applied potential of -1.0 V vs NHE on a Hg pool electrode.



Fig. S8 SEM images of the amalgamated copper electrode surface (a) before used; (b) after used for electrolysis of 2.0 M phosphate buffer solution of CoP_4N_2 at -1.10 V for 20 h; (c) EDX spectra of the electrode surface before used; and (d) after used for electrolysis.



Fig. S9 Cyclic voltammograms of 1.0 M phosphate buffer at pH 7 with 0.5 mM CoP_4N_2 (red) and without catalyst (black) using glass carbon as working electrode (7 mm²).



Fig. S10 EPR spectrum of CoP_4N_4 (solid sample) at room temperature.

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Fig. S11 XPS spectra of (a) Co 2p (red, Co^{II} 2p3/2; black, Co^{II} 2p1/2), (b) N 1s, and (c) P 2p binding energy peaks.



Fig. S12 Cyclic voltammograms of a 0.2 mM solution of CoP_4N_2 (red line) in 2.0 M phosphate buffer at pH 7 and of buffer solution (black line) in the absence of catalyst under otherwise identical conditions, using an amalgamated copper electrode (0.07 cm²) at a scan rate of 100 mV s⁻¹.