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Highly Efficient Electrocatalytic Hydrogen Evolution from Neutral Aqueous Solution by Water-Soluble Anionic Cobalt(II) Porphyrin

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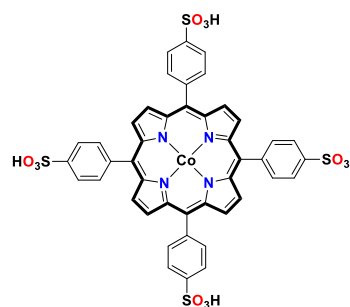
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We report the uses of water-soluble anionic cobalt(II) tetrakis(*p*-sulfonatophenyl)porphyrin (CoTPPS) as a stable, active, and efficient catalyst for electrocatalytic H₂ generation from neutral H₂O without any organic additives. The molecule features nearly quantitative Faradaic efficiency with a turnover frequency of ~1.83 s⁻¹ measured over 1 h and a turnover number of 1.9 × 10⁴ moles of H₂ per mole of catalyst with no loss in activity over 73 h at an applied potential of -1.29 V (vs SHE) in neutral phosphate buffer solution.

Climate changes due to emission of greenhouse gases upon uncontrolled burning of fossil fuels and rapidly growing global energy demands are driving development of alternative, renewable, and sustainable energy sources.¹ Molecular hydrogen, when generated from non-carbon source, is an attractive clean fuel candidate for sustainable energy storage and transport.² Although platinum and natural hydrogenases are efficient for catalytic H₂ evolution, the scarcity, high cost, instability, and oxygen sensitivity seriously limit their widespread applications.^{3,4} These considerations have spawned efforts to design catalysts based on earth abundant transition metals. Since the pioneer work by Sutin *et. al.*,⁵ macrocyclic complexes of cobalt have been extensively studied and reported as electrocatalysts for H₂ generation in aqueous and non-aqueous media.⁶⁻⁸ Cobalt porphyrins have also previously been demonstrated to act as photocatalysts or electrocatalysts for H₂ generation with high Faradaic efficiency in homogeneous solutions or when adsorbed onto an electrode surface.⁹⁻¹⁴ Most of the studies were, however, performed by utilizing acid as a proton source in organic solvents or in water. Spiro and co-workers were the first to report water-soluble cationic cobalt porphyrins for electrocatalytic H₂ generation in homogeneous and heterogeneous system.⁹ Nevertheless, their report showed very low turnover number (TON) and H₂ evolution

occurred only in acidic conditions at high overpotential. Afterwards the same cobalt complex was employed as a photocatalyst¹⁰ and heterogeneous electrocatalyst¹¹ in neutral buffer solution yielding promising TONs at low overpotentials. Kaneko and co-workers¹² also designed a heterogeneous CoTPP/Nafion/Pt and graphite electrode system for H₂ generation in acidic aqueous solution at pH 1 and obtained relatively low TONs as compared to other cobalt macrocyclic complexes. In contrast, a recent report from Bren *et. al.*¹³ described an efficient and active water-soluble bimolecular cobalt porphyrin-peptide electrocatalyst (CoMP11-Ac) that reduces H₂O to H₂ at neutral pH in aqueous phosphate buffer with quantitative Faradaic efficiency, highest turnover frequency (TOF) and TON ever reported for cobalt porphyrins.¹³

Inspired by these successes, we aimed to study anionic and highly water soluble metalloporphyrin, cobalt(II) tetrakis(*p*-sulfonatophenyl)porphyrin (CoTPPS) for electrocatalytic H₂ generation from neutral water. Several studies have been conducted on catalytic activity of CoTPPS, with special attention given to photocatalytic water oxidation,¹⁵ sulphide oxidation,^{16,17} electrocatalytic reduction of nitrite,¹⁸ four electron reduction of O₂ to water,^{19,20} and other chemical transformations.^{21,22} Surprisingly this long-standing anionic CoTPPS has never been accessed for use as an electrocatalyst for H₂ generation in neutral water. We therefore, demonstrate that water-soluble anionic CoTPPS (Scheme 1) is a readily available and efficient catalyst for H₂ generation from H₂O at neutral pH in bulk solution without any organic additives.



Scheme 1. Molecular structure of cobalt porphyrin under study.

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Moreover, we studied heterogeneous H_2 generation activity via electrochemical modification of glassy carbon working electrode (GCE) in the solution containing CoTPPS. Electrochemical and electrocatalytic studies, controlled potential electrolysis, and gas chromatographic analysis showed that CoTPPS is a long lasting, highly efficient, and active both as a homogeneous and a heterogeneous catalyst for H_2 generation from neutral water. Our study on CoTPPS-modified glassy carbon electrode with 0.07 cm^2 area revealed better catalytic activity and stability than in bulk neutral solution.

The reported catalyst was prepared by modified literature procedures.^{17,23} The sulfonation of free-base tetraphenylporphyrin (TPP) was carried out in the presence of conc. H_2SO_4 (98%) at $90\text{ }^\circ\text{C}$ followed by the cobalt metalation at $60\text{ }^\circ\text{C}$ to afford CoTPPS. The identity and purity of the cobalt complex was determined by spectroscopic methods. The complex is highly soluble in water, moderately soluble in DMSO and DMF but insoluble in all other organic solvents. The absorption spectrum of CoTPPS in DMSO and water displayed different profiles. Moreover, absorption pattern was unaltered when CoTPPS stands for long periods of time in aqueous solution or in presence of acid, indicating its stability in aqueous and acidic media. The cyclic voltammogram (CV) of CoTPPS in DMSO using 0.1 M tetra-*n*-butyl ammonium hexafluorophosphate [Bu_4NPF_6] as electrolyte features one reversible redox couple at -0.38 V vs SHE, which is assigned to be Co(II)/Co(I) redox process and one irreversible reduction peak at -1.45 V vs SHE due to Co(I)/Co(0) couple. The scan rate dependent study in DMSO shows an increase in the peak current at the potential close to Co(I)/Co(0) as the scan rate increases, indicating freely diffusing electrocatalytic species. Electrocatalytic behaviour of CoTPPS in DMSO solution was also explored by treating with weak proton source, acetic acid (AcOH). Upon successive addition of AcOH, the catalytic current enhancement at -1.45 V vs SHE was observed without affecting the Co(II)/Co(I) couple, which indicates that the protonation of Co(I) prior to reduction to Co(0) is unlikely. This is a strong evidence to suggest that Co(I)/Co(0) redox is a proton coupled electron transfer process. An irreversible oxidative peak is also observed at $+0.05\text{ V}$ vs SHE for CoTPPS in DMSO due to a Co(II)/Co(III) oxidation process. As controlled experiments, CV experiments employing AcOH alone and free ligand in AcOH were conducted and observed no hydrogen evolution activity.

Encouraged by remarkable proton reduction catalytic activity coupled with electron transfer process of the complex in DMSO at a potential close to Co(I)/Co(0) redox couple, we carried out electrochemical and electrocatalytic study in neutral water. When the CV of CoTPPS is measured in potassium phosphate buffer (KPi) at pH 7 or neutral water using $LiClO_4$ as supporting electrolyte, the Co(II)/Co(I) reduction wave appears as an electrochemically irreversible peak, followed by a sharp increase in the current. For blank solution alone, the CV showed no catalytic current rise until the potential is scanned beyond -1.3 V vs SHE with glassy carbon electrode.²⁴ However, upon addition of CoTPPS (0.1 mM), a sharp increase in catalytic current beginning at -0.823 V vs SHE in 0.1 M KPi under pH 7 or at -0.96 V vs SHE in aqueous 0.1 M $LiClO_4$ solution is observed. When the CV was scanned to more negative potential, higher catalytic current enhancement was detected as shown in

Figure S6. Catalyst concentration dependent studies in 2 M KPi at pH 7 revealed an increase in catalytic current with low onset potential and overpotential upon increasing concentration (Figure S7). Hydrogen evolution activity of the complex was further examined when the catalyst is adsorbed on GCE. To obtain modified electrode, multiple CV sweep scans (up to 200 cycles from 0 to -1.3 V vs SHE) in the catalyst solution was performed. At the end of the experiment, the electrode was rinsed with $H_2O/LiClO_4$ solution for 5 min and hydrogen evolution studies were conducted using catalyst-modified electrode.

All the CV results in aqueous solution show that the first redox event is not coupled with proton transfer process and the catalysis occurs at the potential close to second reduction process, which is significantly positive of the onset of direct H_2O reduction by bare GCE. Control experiments using free-base ligand, $Co(OAc)_2\cdot 4H_2O$ and bare GCE electrode without catalyst were performed under similar experimental conditions and no redox process or catalytic current enhancement observed within the potential window (Figure 1). Therefore, in neutral aqueous solutions of CoTPPS, the rise in current coinciding with the evolution of bubbles observed during controlled-potential electrolysis (CPE), is attributed to electrocatalytic generation of H_2 from neutral water.^{1,10,13,25} The H_2 generated was further confirmed by using gas chromatography (GC) analysis. Overall, our study shows the role of CoTPPS as a catalyst to increase the catalytic current by decreasing onset potential of catalysis.

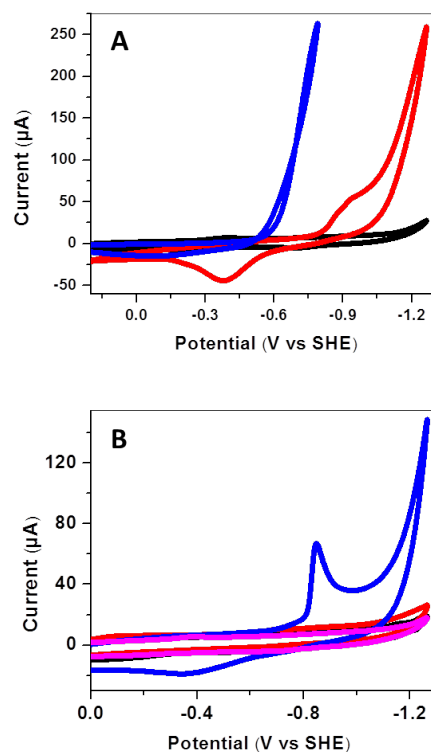


Figure 1. A) CV of 0.1 mM CoTPPS in 0.1 M KPi pH 7 using GCE (red), blank solution using GCE (black), blank solution using Pt working electrode (blue); B) CV of 0.1 mM CoTPPS in 0.1 M $LiClO_4$ aqueous solution (blue), 0.1 mM free-base (red), 0.1 mM $Co(OAc)_2\cdot 4H_2O$ (magenta) and blank control (black) with GCE at RT. (Scan rate 0.1 V/s)

In order to assess onset overpotential (defined as the potential difference between thermodynamic reduction potential of water, i.e. -0.414 V vs SHE and the potential where catalysis occurs) required for electrochemical evolution of H_2 in the presence of CoTPPS, CPE was conducted in 0.1 M KPi with pH 7. Charge build up at various applied potentials was monitored over the course of 2 min electrolyses performed using 0.05 mM cobalt complex. The total charge accumulation starts to appear at about an applied potential of -0.825 V vs SHE and increases approximately linearly with time at more negative applied potentials as depicted in Figure S9. Moreover, the CV result of this catalyst displays a catalytic current in phosphate buffer at pH 7 (Figure 1A), with the onset at -0.823 V vs SHE, corresponding to an onset overpotential about 409 mV. A 1 h CPE experiment at -1.39 V vs SHE was performed to test electrocatalytic H_2 evolution activity as well as to estimate the Faradaic efficiency and TOF with glassy carbon working electrode. Generated H_2 volume was directly measured via GC using calibration curve of standard H_2 over different time intervals (Table S2, Figure S10 and 11) and it overlaps well with the amount calculated from consumed charge as shown in Figure 2B. After 1 h electrolysis of CoTPPS in 2 M KPi at pH 7, 198 μ mol of H_2 were evolved by using 3 μ M solution of catalyst (10 mL), as measured by GC. Moreover, 38.2 Coulombs of charge were passed (after background subtraction) yielding quantitative Faradaic efficiency. A similar experiment in aqueous 0.1 M $LiClO_4$, 41 μ mol of H_2 were evolved and 8.03 Coulombs of charge were passed after 1 h CPE. Thus, TOFs of 1.83 and 0.38 mol of H_2 $s^{-1}mol^{-1}$ were determined from 1 h CPE experiments in 2 M KPi at pH 7 and in aqueous $LiClO_4$ solution, respectively.

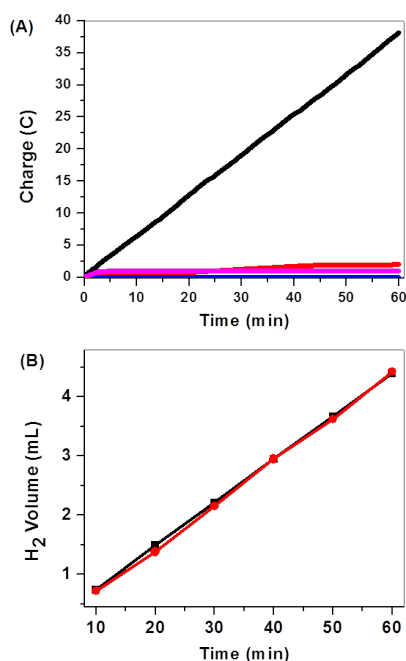


Figure 2. A) Charge vs time for 1 h CPE at -1.39 V vs SHE in 2 M KPi, pH 7 (10 mL). CoTPPS (black) is compared with buffer control (blue), free-base TPPS (magenta) and $Co(OAc)_2 \cdot 4H_2O$ (red); B) Generated H_2 volume calculated from passed charge (black) and measured from GC (red) during 1 h CPE of CoTPPS in 2 M KPi, pH 7 with an applied potential -1.39 V vs SHE.

Extended CPE experiments were conducted at -1.29 V vs SHE to assess durability of the catalyst. The catalyst affords linear charge build up over the course of 73 h in 2 M KPi solution at pH 7. During this CPE experiment, the UV-visible of the CoTPPS solution was monitored and we observed gradual decrease in absorption peak of cobalt porphyrin and the change in colour of the solution. However, as we can see from Figure 3, the charge build up still increasing owing to maintained catalyst activity during extended CPE over 73 h. Based on the bulk concentration of catalyst (0.1 mM) used in the experiment, a turnover number of 1.9×10^4 mol of H_2 per mole of catalyst was determined after 73 h, in which 3,518 C of charge passed (after background subtraction). In both bulk aqueous $LiClO_4$ homogeneous solution and CoTPPS-adsorbed heterogeneous system, the linear charge build up over time without substantial loss in activity was observed for 44 h CPE (Figure S14), yielding TON of 4.9×10^3 using 50 μ M bulk catalyst solution. These TOF values are comparable with other cobalt-based electrocatalysts previously reported for electrochemical H_2 generation in neutral phosphate buffer (Table S1). It is also important to note that adsorption of catalyst on an electrode increases TONs due to an increase in effective concentration at the electrode surface relative to the bulk concentration.¹³ The catalytic rate enhancement for H_2 generation by CoTPPS modified electrode could be due to negatively charged sulfonyl functional group, through which the molecule can anchor on to the surface.

Though several cobalt porphyrins have been reported for H_2 production from organic acids and water with high Faradaic efficiencies as discussed above, the TOF values have been rarely reported. Electrocatalytic hydrogen generation using cationic water soluble cobaltporphyrins showed a TOF ~ 0.011 s^{-1} in 0.1 M TFA solution using mercury as working electrode.^{9a} A TON of 725 (1 h) and a TOF of 10.9 min^{-1} was also reported for photocatalytic H_2 generation by water soluble CoTMPyP.¹⁰ Furthermore, a TON of 23 (1 h) in aqueous (pH 1) solution was reported by using heterogeneous CoTPP/Nafion/Pt electrode system.¹² Quite recently CoMP11-Ac, was reported for H_2 evolution from neutral water under aerobic conditions with TON of 2.5×10^4 and TOF of 6.7 s^{-1} .¹⁵ However, the catalytic activity of CoMP11-Ac falls off appreciably after 15 minute of CPE experiment due to catalyst degradation. In contrast, CoTPPS is long-lasting (over 73 h, yielding 1.9×10^4 TON), active (with a TOF of 1.83 s^{-1}), and efficient ($\sim 100\%$) for electrochemical H_2 evolution from neutral water at overpotential comparable with other reported molecular electrocatalysts in phosphate buffer solution with pH 7. In addition, this molecule can function as a heterogeneous electrocatalyst, after electrochemical modification of working electrode in catalyst solution. Another valuable characteristic of a robust and useful H_2 evolution catalyst is its atmospheric air tolerance. In this regard, we notice that the CV and CPE results of CoTPPS obtained under aerobic conditions and in a tight cell are identical (Figure S15), indicating that atmospheric air has no interference on catalytic activity. Altogether, these combined results establish that CoTPPS is a robust, efficient, and active electrocatalyst for H_2 generation from neutral water.

Mechanistically, there are four steps for H_2 evolution, according to our electrochemistry results and literature reports: two reduction steps of the cobalt complex and two water reduction steps by the reduced complex, as depicted in Figure 4.²⁶

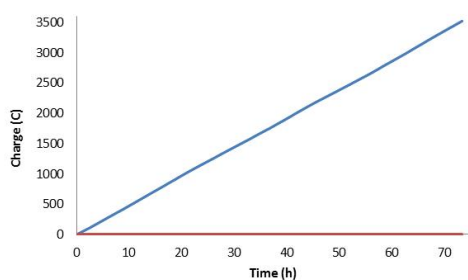


Figure 3. Extended CPE of 0.1 mM CoTPPS (blue) and blank control (Red) in 2 M KPi, pH 7 at -1.29 V vs SHE.

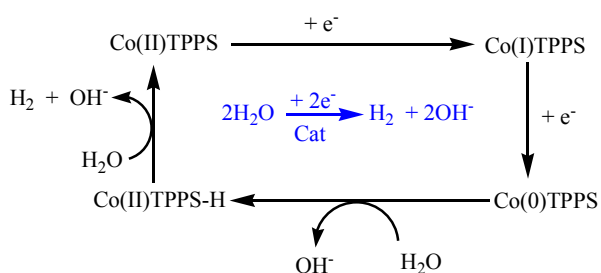


Figure 4. Electrochemical mechanism of water reduction by CoTPPS.

Our cyclic voltammograms confirm that the effective catalytic species for H₂ evolution is the second reduced complex, Co(0)TPPS. It is believed that Co(0) is protonated to afford Co(II)H, an unstable and reactive hydride intermediate for hydrogen evolution process. Since electron transfer processes are faster than reaction of reduced complex with water, overall catalytic H₂ generation could favour bimolecular mechanism in which Co(II)H involves as reactive intermediate. The OH⁻ formation is consistent with our observation of an increase in pH value, which was detected by monitoring pH change of CoTPPS/LiClO₄ aqueous solution during electrolysis. Thus H₂ is evolved with the formation of OH⁻ when the intermediate react with another water molecule with recovery of original catalyst. In conclusion, an anionic and water-soluble cobalt (II) porphyrin, is reported as a stable, highly efficient and active electrocatalyst for hydrogen generation from neutral water. This molecule can be used in both homogeneous and heterogeneous systems. Higher catalytic activity and TONs were observed when it is electrochemically adsorbed on glassy carbon electrode. Moreover, easy and step-effective synthesis, high water solubility, presence of anchoring groups that can effectively bind with the surface and oxygen tolerance make CoTPPS a future candidate for practical applications and optimizations in the field of electrocatalytic H₂ generation from neutral water.

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