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## COMMUNICATION

## Water-soluble Glucose-Functionalized Cobalt(III) Complex as Efficient Electrocatalysts for Hydrogen Evolution in Neutral Condition

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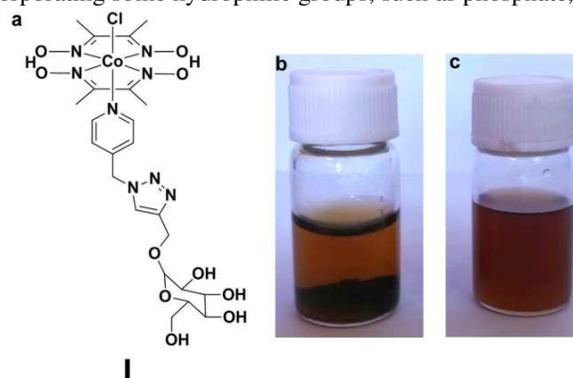
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**A water-soluble glucose-functionalized cobalt(III) complex  $[\text{Co}^{\text{III}}(\text{dmgH})_2(\text{py-glucose})\text{Cl}]$  is active and stable for electrocatalytic hydrogen production in neutral aqueous solution.**

The increasing global energy consumptions and growing environmental problems are driving the exploration of clean, alternative and sustainable energy sources.<sup>1</sup> Hydrogen derived from water splitting has attracted considerable attention due to its purity, circulation, and non-carbon sources.<sup>2</sup> Therefore, developing efficient hydrogen evolution catalysts, especially those composed of earth-abundant non-precious-metal elements is desirable. Recently, inspired by some [Fe-Fe], [Ni-Fe], and [Fe] hydrogenase enzymes<sup>3</sup> for producing  $\text{H}_2$  from water, researchers have developed some well-designed transition metal complexes featuring cobalt,<sup>4</sup> nickel,<sup>5</sup> and molybdenum<sup>6</sup> to mimic these hydrogenase enzymes, and achieve much more efficient hydrogen evolution via electrocatalysis and photocatalysis.

Cobaloxime complexes and their derivatives have been considered to be a class of well-known inexpensive and efficient  $\text{H}_2$ -evolving catalysts, and have drawn increasing attention since they were early synthesized by Chao and Espenson.<sup>7</sup> To date, lots of elegant works based on this kind of Cobaloxime complexes have been reported by several groups including Artero and Fontecave,<sup>8</sup> Reisner,<sup>9</sup> and Peters.<sup>10</sup> For example, Artero and co-workers have reported a diimine-dioxime cobalt catalyst grafted to the surface of a carbon nanotube electrode, which can generate  $\text{H}_2$  from water with high turnovers and remarkable stability.<sup>11</sup> Although great advances have been achieved, utilizing the cobalt complexes for the hydrogen evolution reaction (HER) are still facing some challenges. For instance, most of cobalt complexes, especially the cobaloxime complexes, cannot be well-dissolved in water. So the process of hydrogen production must be conducted in an

environment unfavourable system of organic solvents or a mixture of organic solvents and water,<sup>12</sup> with the assistance of organic acids. Compared with the HER in the organic solvents, the HER in neutral water are much cheaper and cleaner because most of organic solvents are expensive and environment-unfriendly. In addition, homogeneous molecular catalysts have attracted considerable attention mainly due to their much efficient electron transfer and rapid hydrogen evolution over the heterogeneous system.<sup>13</sup> Therefore, by improving the water-solubility of some insoluble metal complexes, one may achieve the transition from a heterogeneous hydrogen production system to a homogeneous system. Hence, The development of suitable and convenient methods to improve the water-solubility of some insoluble complexes is of crucial significance. Up to now, many great efforts for improving the insoluble complexes' water-solubility have been devoted by incorporating some hydrophilic groups, such as phosphate,<sup>14</sup>



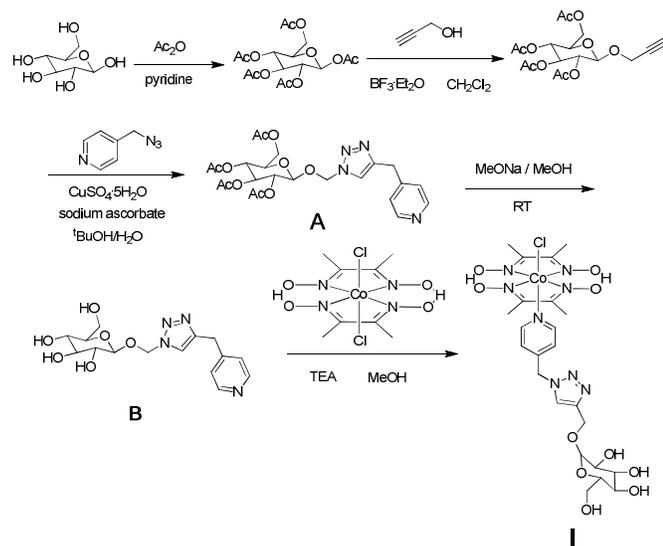
**Fig. 1** a) The structure of glucose functionalized water-soluble cobalt (III) complex. b, c) Optical images of cobalt(III) complex dispersed in pure water without functionalizing glucose (b) and with functionalizing glucose (c).

ammonium salt,<sup>11</sup> hydrophilic ether chains,<sup>15</sup> and hydrophilic polymer (poly(acrylic acid)).<sup>16</sup> Very recently, the Wu group has constructed a chitosan-assisted water-soluble [Fe-Fe]

hydrogenase enzyme mimics for photocatalytic H<sub>2</sub> production in water/methanol.<sup>17</sup> Although many elegant achievements have been achieved, the development of low-cost and universal alternative method to prepare water-soluble cobalt complexes is still highly desirable.

Herein, we report a water-soluble glucose functionalized cobaloxime complex [Co<sup>III</sup>(dmgH)<sub>2</sub>(py-glucose)Cl] **I** (dmgH = dimethylglyoxime) (Fig. 1) with good electrocatalytic activity and stability for H<sub>2</sub> evolution in pure water in the absence of any organic acids. To the best of our knowledge, this is the first example to introduce glucose to the cobaloxime complex for enhancing the water-solubility.

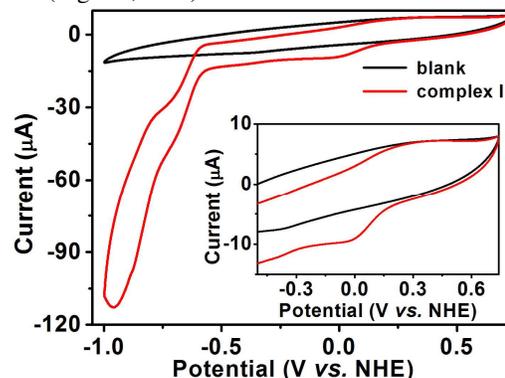
The water-soluble cobalt catalyst **I** was synthesized according to a common path as depicted in Scheme 1. Firstly, two intermediates **A** and **B** were synthesized. **A** was prepared by a click reaction of 4-(azidomethyl) pyridine and 2-(acetoxymethyl)-6-(prop-2-yn-1-yloxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate in the presence of catalytic loading of CuSO<sub>4</sub>·5H<sub>2</sub>O and sodium ascorbate in a mixture solvents of <sup>t</sup>BuOH/H<sub>2</sub>O in 85% yield.<sup>18</sup> Hydrolyzing **A** in methanol/sodium methoxide system delivered **B** in 90% yield. Then, the substitution of a chlorine atom on the [Co<sup>III</sup>(dmgH)<sub>2</sub>Cl<sub>2</sub>] (dmgH = dimethylglyoxime) with **B** in methanol and TEA (triethylamine) produced the target complex **I**. **A**, **B** and **I** were all characterized by MS, HRMS, NMR, UV/Vis and IR spectroscopy (Fig. S1, S2, ESI<sup>†</sup>).



**Scheme.1** Synthetic route of [Co<sup>III</sup>(dmgH)<sub>2</sub>(py-glucose)Cl]

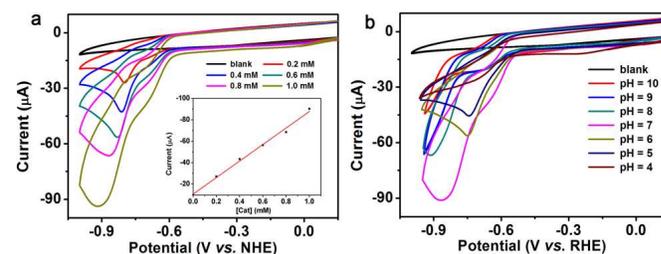
Electrochemical measurements of catalyst **I** is firstly recorded on a glassy carbon electrode in DMF with [N(Bu)<sub>4</sub>]PF<sub>6</sub> (0.1M). Cyclic voltammograms (CVs) show the two one-electron reduction waves, which are assigned to the Co<sup>III</sup>/Co<sup>II</sup> and Co<sup>II</sup>/Co<sup>I</sup> reduction process at about -0.52 V and -0.82 V versus NHE (the normal hydrogen electrode), respectively. Then, when adding TFA (trifluoroacetic acid) to this system, an onset of electrocatalytic proton reduction at approximately -0.8 V versus NHE is observed. The redox process is in agreement with the previous reports for the

electrocatalytic hydrogen production by the cobaloxime complexes (Fig. S3, ESI<sup>†</sup>).<sup>8b</sup>



**Fig. 2** CVs of a glassy carbon working electrode are recorded in an aqueous solution of 0.1 M TEOA and 0.1M Na<sub>2</sub>SO<sub>4</sub> at pH 7 with 1 mM cobalt complex **I** (red line) and without complex **I** (black line). Scan rate: 50 mV s<sup>-1</sup>. Temperature: 25<sup>o</sup>C.

To probe the electrochemical activity of the as-prepared catalyst, cyclic voltammetric experiment is performed with catalyst **I** (1 mM) in an aqueous solution of Na<sub>2</sub>SO<sub>4</sub> and TEOA (triethanolamine) (0.1 M each) at pH 7 and room temperature. As shown in Fig. 2, a reversible cathodic wave at about -0.05 V versus NHE is assigned to the Co<sup>III</sup>/Co<sup>II</sup> reduction process (the inset). And then another one-electron reduction wave, which is assigned to Co<sup>II</sup>/Co<sup>I</sup> process, is observed at about -0.66 V versus NHE with a scan rate of 50 mV s<sup>-1</sup>. The onset of electrocatalytic proton reduction to hydrogen is observed at approximately -0.74 V versus NHE with an overpotential of ~341 mV. These voltammetric responses are consistent with the published reports.<sup>9a,c</sup>



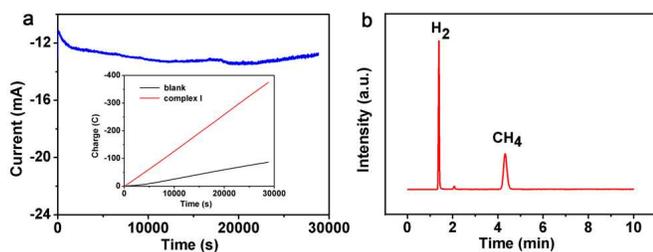
**Fig. 3** (a) CVs of different concentrations of catalyst **I** recorded in an aqueous solution of 0.1 M TEOA and Na<sub>2</sub>SO<sub>4</sub> at pH 7. The inset is the dependence of peak current on the concentrations of catalyst **I**. (b) CVs of 1.0 mM catalyst **I** at different pH values (4.0-10.0). Scan rate: 50 mV s<sup>-1</sup>.

Next, the effect of the concentrations of catalyst **I** and the pH values are investigated on the electrochemical performance of hydrogen evolution, respectively. As depicted in Fig. 3a, the CVs recorded with varying concentrations of catalyst **I** (0.2 mM to 1.0 mM) in a pH 7 aqueous media reveal that the catalytic peak current experience a gradual increase along with the addition of catalyst loading. And the catalytic current is found to be linearly dependent on the concentration of catalyst **I** (the inset of Fig. 3a). This demonstrates that the concentrations of catalyst **I** make a dominant contribution to the catalytic current when the concentration is relatively low. Upon

adjusting the pH value of the electrolyte from 10 to 7, the catalytic peak current first increase and then reach the maximum at pH 7. The continuous lowering the pH value of the solution to 4, the peak current decrease (Fig. 3b). This phenomenon may be due to the instability of the molecular catalyst in acid environment.<sup>19</sup> This result also indicates that the optimum pH condition of our catalyst in this electrocatalytic hydrogen production system is neutral.

Then, to explore the function of TEOA in our electrocatalytic hydrogen evolution system, KPi (0.1 M) buffer solution and the pure Na<sub>2</sub>SO<sub>4</sub> (0.1 M) aqueous solution are also utilized to replace the neutral TEOA/Na<sub>2</sub>SO<sub>4</sub> aqueous solution, respectively. Cyclic voltammetry curves (Fig. S4, ESI<sup>†</sup>) display that the catalyst delivers good hydrogen production performance when in the presence of neutral TEOA/Na<sub>2</sub>SO<sub>4</sub> aqueous solution (blue line) and KPi (0.1 M) buffer system (red line). But, the catalyst shows very poor hydrogen production performance without the assistance of TEOA (black line). It is reported that the triethanolamine is easily protonated by acid and form proton buffer solution.<sup>20</sup> Thus, in our system, the TEOA may mainly functions as proton buffering, as phosphate buffer which offers a suitable catalytic media for HER.

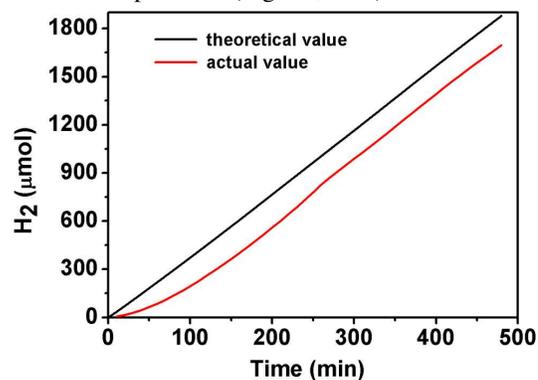
Additionally, we also analyze the diffusion-limitation process of our catalyst in solution. The CVs are conducted in a pH 7 aqueous solution with several different scan rates ranging from 25 mVs<sup>-1</sup> to 300 mVs<sup>-1</sup> (Fig. S5, ESI<sup>†</sup>). It is found that catalytic peak current varies linearly with the square of the scan rate (Fig S6, ESI<sup>†</sup>), indicating that the diffusion-limited redox process is dominated in the electrocatalytic hydrogen evolution reaction.



**Fig. 4** Controlled-potential electrolysis experiment (a) and coulometry for bulk electrolysis (the inset) is performed with 0.5 mM catalyst **I** at a carbon paper electrode (4.0 cm<sup>2</sup>) in an aqueous solution of TEOA/Na<sub>2</sub>SO<sub>4</sub> (0.1 M each) at -0.90 V vs NHE and neutral condition. (b) The H<sub>2</sub> is detected by gas chromatography with methane as the internal standard.

To estimate the stability of the catalyst **I** for H<sub>2</sub> production, an 8 h controlled-potential electrolysis (CPE) experiment at -0.90 V versus NHE is performed with 0.5 mM **I** in a TEOA and Na<sub>2</sub>SO<sub>4</sub> (0.1 M each) aqueous solution at pH 7 by using a carbon paper electrode (4.0 cm<sup>2</sup>) as working electrode under the nitrogen condition. A lot of gas bubbles are rapidly observed on the surface of working electrode. As shown in Fig. 4a, the catalyst reveals a preferable stability and affords a robust and essentially charge build-up, with no substantial loss in activity over the course of 8 h. In contrast, smaller charge is passed when a blank carbon paper electrode is used as the working electrode under the same conditions (the inset in Fig. 4a). Then,

the evolved H<sub>2</sub> during the 8 h electrolysis (CPE) experiment is analyzed by an on-line gas chromatography (GC Agilent 7890A) with methane as the internal standard (Fig. 4b). Note that the tiny peak at about 2 minutes originated from the impurity in carrier gas. Fig. 5 depicts the dependence of the amount of H<sub>2</sub> on time, ~1693 μmol H<sub>2</sub> is collected over an electrolysis period of 8 h with a Faradaic efficiency of 90%. The turnover numbers (TON) of hydrogen evolution during the 8 h CPE experiment is 33 mol H<sub>2</sub> per mol cat. after subtracting the contribution of blank experiment. What's more, to further verify whether our catalyst still maintains the preferable electrocatalytic activity after an 8 h CPE experiment, a comparative test is carried out before and after CPE experiment. As shown in Fig. S7 (ESI<sup>†</sup>), the catalyst **I** still retains catalytic activity even after an 8 h CPE experiment, suggesting the good stability of the as-synthesized water-soluble glucose functionalized cobaloxime complex **I**. The UV/Vis spectroscopic measurements further confirm that most of the catalysts are stable during the electrochemical experiment (Fig. S8, ESI<sup>†</sup>).



**Fig. 5** H<sub>2</sub> evolution during electrolysis experiment at -0.9 V vs NHE using a carbon paper (4.0 cm<sup>2</sup>) as the working electrode with 0.5 mM catalyst **I** in 80 ml aqueous solution of TEOA/Na<sub>2</sub>SO<sub>4</sub> (0.1 M each) at pH 7. Black line was calculated according to the accumulative charge on the assumption of a 100% Faradaic yield. Red line is the amount of H<sub>2</sub> measured during electrolysis by the gas chromatography.

In summary, we have developed, for the first time, a robust, inexpensive, and efficient glucose functionalized method to synthesize water-soluble cobaloxime complex. It is found that the as-synthesized glucose functionalized cobalt complex **I** is a highly active and stable HER electrocatalyst for the electrocatalytic water splitting under a neutral pH condition. The glucose-functionalized strategy enable the metal complex molecular catalyst to hold good water-solubility and preferable biocompatibility, which may be find wide applications in producing water-soluble metal complexes for photocatalytic and electrocatalytic hydrogen evolution in pure water with a wide pH range.<sup>21</sup>

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## Notes and references

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Electronic Supplementary Information (ESI) available: [details of experimental procedures, additional characterization, and electrochemistry methods]. See DOI: 10.1039/c000000x/

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## Graphic Abstract

# Water-soluble Glucose-Functionalized Cobalt(III) Complex as Efficient Electrocatalysts for Hydrogen Evolution in Neutral Condition

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