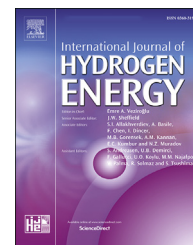




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# Photocatalytic system with water soluble nickel complex of S,S'-bis(2-pyridylmethyl)-1,2-thioethane over CdS nanorods for hydrogen evolution from water under visible light

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## ABSTRACT

In this paper, we report a new nickel complex,  $[(bpte)NiCl_2]$  ( $bpte = S,S'$ -bis(2-pyridylmethyl)-1,2-thioethane) that can serve as a catalyst both for electrochemical and photochemical driven hydrogen production from water. As an electrocatalyst,  $[(bpte)NiCl_2]$  can electrocatalyze hydrogen generation from a neutral buffer with a turnover frequency (TOF) of 555.78 mol of hydrogen per mole of catalyst per hour (mol  $H_2$ /mol catalyst/h) at an overpotential (OP) of 837.6 mV. Together with CdS nanorods (CdS NRs) as a photosensitizer, and ascorbic acid ( $H_2A$ ) as a sacrificial electron donor, the nickel complex also can photocatalyze hydrogen evolution in heterogeneous environments and can work for 107 h. Under an optimal condition, the photocatalytic system can afford 24900 mol of  $H_2$  per mole of catalyst during 83 h irradiation, with a TOF of 300 $H_2$  per catalyst per hour. The average value of apparent quantum yield (AQY) is ~24% at 420 nm.

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## Introduction

To get renewable and environmental-friendly alternative energy, such as hydrogen, several synthetic systems have been developed. Electrochemical and photochemical methods for generating hydrogen from water have been explored as cost-effective ways of producing a carbon-neutral fuel [1–3]. The most viable method for large-scale growth in carbon-free energy is the light-driven splitting of water into its constituent elements [4–6]. To rate the efficiency for hydrogen production, a challenging work for overcoming this issue would be to design efficient and stable catalytic system established by employing abundant and cheap materials [7,44].

Photocatalytic water splitting into hydrogen has inspired researchers all over the world to develop novel and economical photocatalysts for this reaction. Therefore, several nickel [8,9,45], cobalt [10–13] and iron [14] complexes have been developed as photo-catalysts for the reduction of water to  $H_2$ . Generally, a homogeneous photocatalytic system is combined by a molecular cocatalyst, a molecular photosensitizer (PS), e.g.  $Ru(bpy)_3Cl_2$  and a sacrificial electron donor. However, this system cannot work for a longer time due to the decomposition of molecular photosensitizer during irradiation [15–18]. To solve this problem, inorganic compounds, such as CdS is chose as photosensitizer for the conversion of solar energy into chemical energy under visible-light irradiation due to the

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narrow band gap (with an  $E_g$  of 2.4 eV), which is more negative than the reduction potential of hydrogen proton ( $H^+/H_2$ ), letting it more proper for the  $H_2$  generation [19–22]. Compared with cocatalysts based on nickel oxides and hydroxide cocatalysts [23,24], catalysts with transition metal complexes are advantageous for mechanistic study and the result may stimulate the design of new catalytic systems [25,26]. Considering that metal complexes act as catalysts for hydrogen production via a metal-hydride intermediate, and the ionic character of M–Cl bond makes  $Cl^-$  ion dissociate easily, leaving empty positions on the metal center, amenable to binding to  $H^+$  or  $H_2O$  and hydrogen production, a new nickel-based catalyst, [(bpte)NiCl<sub>2</sub>] has been designed in our lab. Herein, we report the synthesis, structure, characterization and electrochemical properties of the nickel complex, [(bpte)NiCl<sub>2</sub>], as well as its photocatalytic properties for water reduction.

## Experimental

Physical measurements, “X-ray Crystallography” and the calculations of turnover frequency (TOF) and apparent quantum yields (AQYs) for this paper were listed in “Supplementary Materials”.

### Synthesis of the nickel complex, [(bpte)NiCl<sub>2</sub>]

To a solution of the ligand, S,S'-bis(2-pyridylmethyl)-1,2-thioethane (bpte) (0.14 g, 0.5 mmol) in 4 mL ethanol, NiCl<sub>2</sub>·6H<sub>2</sub>O (0.10 g, 0.5 mmol) in 4 mL methanol was added and the mixture was stirred for 10 min. The solution was allowed to slowly evaporate, affording deep green crystals, which were collected and dried in vacuo, yield 0.152 g (75%). Calcd for C<sub>14</sub>H<sub>16</sub>Cl<sub>2</sub>NiN<sub>2</sub>S<sub>2</sub>: C: 41.41, H: 3.97, N: 6.90. Found: C: 41.41, H: 3.96, N: 6.89.

## Results and discussion

### Electrocatalytic performance of the nickel complex for hydrogen evolution

According to the reported method [27], the ligand, S,S'-bis(2-pyridylmethyl)-1,2-thioethane (bpte) was prepared (Figs. S1–S2). And the nickel(II) complex, [(bpte)NiCl<sub>2</sub>] was obtained by the reaction of NiCl<sub>2</sub>·6H<sub>2</sub>O and bpte (Scheme 1).

The X-ray crystal structure of the nickel complex was obtained, Table S1 gave crystallographic data for [(bpte)NiCl<sub>2</sub>] and the selected bond lengths were listed in Table S2. As shown in Fig. 1, the nickel atom is six-coordinated by two nitrogen atoms and two sulfur atoms from the ligand (bpte), and two chlorine atoms; The  $Cl^-$  ligands are in mutually cis positions. The Ni–N distance is 2.1069 Å, and the Ni–S bond lengths are 2.4280 and 2.4279 Å, respectively. The Ni–Cl distance is 2.3795 Å. To characterize the performance in solution, ESI-MS measurement was carried out in methanol. As shown in Fig. S3, ESI-MS exhibited one ion at a mass-to-charge ratio ( $m/z$ ) of 368.9791, with the mass and isotope distribution pattern consistent with that of [(bpte)Ni(Cl)]<sup>+</sup>. The dissociation of the  $Cl^-$  ion leaves empty positions on the nickel center, amenable to binding to  $H^+$  or  $H_2O$

and hydrogen production. Such result prompted possible usage of this complex as a catalyst for hydrogen evolution.

Inspired by that nickel complexes can serve as both electrocatalyst and photocatalyst for hydrogen generation via an unstable hydride intermediate [26,28], we also tried to set up a photocatalytic system based on the nickel complex. To explore the relationship between the electrocatalytic and photocatalytic behaviors of the nickel complex, we first investigated its electrochemical properties. Cyclic voltammograms (CVs) were conducted in CH<sub>3</sub>CN to characterize electrochemical properties of [(bpte)NiCl<sub>2</sub>] in organic media, giving the results listed in Fig. 2a. The nickel complex displayed one good reversible redox wave at –0.86 V versus Ag/AgNO<sub>3</sub>, which is assigned to the Ni<sup>III/I</sup> couple.

Next, employing acetic acid as proton resource to test the catalytic activity of this nickel complex. From Fig. 2b, with the addition of varied content of acetic acid from 0.0 to 0.023 M, voltammetric currents emerging at –0.86 V exhibited a systematic increase. The result indicates that this nickel complex exhibits electrocatalytic activity for hydrogen evolution via the reduction of Ni(II) to Ni(I) and protonation.

On the basis of these observations, analyses and literature precedent [29,42], a possible catalytic cycle for proton reduction to be hydrogen was put forward. As shown in Scheme 2, a nickel(I) species, [(bpte)Ni]<sup>+</sup> was formed by an one-electron reduction of [(bpte)Ni]<sup>2+</sup>. Then the introduction of proton ( $H^+$ ) resulted in a Ni<sup>III</sup>–H species, [H–Ni<sup>III</sup>(bpte)]<sup>2+</sup>. Another one-electron reduction of the Ni<sup>III</sup>–H species led to the formation of a Ni<sup>II</sup>–H species, [H–Ni<sup>II</sup>(bpte)]<sup>+</sup>. Further introduction of proton to [H–Ni<sup>II</sup>(bpte)]<sup>+</sup> afforded a H<sub>2</sub> molecule and the starting complex, and finished a catalytic cycle.

Next, we used bulk electrolysis to characterize the electrocatalytic activity of [(bpte)NiCl<sub>2</sub>]. As shown in Fig. S4a, with the introduction of [(bpte)NiCl<sub>2</sub>], the electrocatalytic system afforded 85 mC of charge during 2 min of electrolysis under –1.45 V versus Ag/AgNO<sub>3</sub>, with accompanying production of a gas, which was confirmed as H<sub>2</sub> by gas chromatography. From Fig. S4b, a CPE experiment under same conditions without [(bpte)NiCl<sub>2</sub>] only gave a charge of 3 mC, indicating that this nickel complex does indeed acts as an electrocatalyst for hydrogen evolution. Using Evans's method, Eq. (1) [30] and Eq. (2) [31] to estimate the overpotential (OP) and turnover frequency (TOF), giving the results listed in Fig. S5.

$$\begin{aligned} \text{Overpotential} &= \text{Applied potential} - E_{\text{HA}}^{\ominus} \\ &= \text{Applied potential} - \left( E_{\text{H}^+}^{\ominus} + \right. \\ &\quad \left. - (2.303RT/F)pK_{\text{aHA}} \right) \end{aligned} \quad (1)$$

$$\text{TOF} = \Delta C / (F * n_1 * n_2 * t) \quad (2)$$

Next, we characterized electrocatalytic behavior of this nickel complex in aqueous media. As shown in Fig. S6, with decreasing pH values from 7.0 to 3.5, the strength of the reduction of [(bpte)NiCl<sub>2</sub>] wave increased, and the onset of the catalytic wave were shifted to higher potentials, which are assigned to a catalytic process [32]. Moreover, in neutral buffer, the nickel complex exhibited a quasi-reversible redox wave at –0.37 V versus Ag/AgCl (Fig. S6-insert), which is assigned to the Ni<sup>II</sup>/Ni<sup>I</sup> couple.

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