

A nickel complex, an efficient cocatalyst for both electrochemical and photochemical driven hydrogen production from water

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ABSTRACT

Inspired by that nickel complexes can act as molecular catalysts for hydrogen generation from organic acid or water, we choose a nickel(II) complex, $[\text{Bz-4-MePy}]_2[\text{Ni}^{\text{II}}(\text{i-mnt})_2]$ **1** (i-mnt^{2-} = iso-maleonitriledithiolate, Bz-4-MePy^+ = 1-benzyl-4'-methylpyridinium ion) as a potential catalyst. Electro- and photochemical investigations show that this nickel complex can act as both an electrocatalyst and a photocatalyst for H_2 generation from water via an unstable nickel hydride intermediate. A homogeneous electrocatalytic system containing complex **1** can afford 577.4 mol of H_2 per mole of catalyst per hour (mol H_2 /mol catalyst/h) from neutral water at an overpotential (OP) of 837.6 mV. Together with CdS nanorod (CdS NR) as a photosensitizer, and ascorbic acid (H_2A) as a sacrificial electron donor in a pH 3.5 aqueous solution, under photoirradiation with blue light ($\lambda_{\text{max}} = 469 \text{ nm}$), complex **1** also can provide hydrogen with a turnover number (TON) of 55340 mol of H_2 per mole of catalyst during first 60 h irradiation. The highest apparent quantum yield (AQY) is $\sim 26.8\%$ at 420 nm.

1. Introduction

To decrease the growth of CO_2 emissions and its consequent effects on global climate change, many methods have been developed with the hope of using natural resources to provide renewable energy, such as hydrogen. Hopefully, hydrogen is an ideal clean energy source that can relieve these problems. Electrochemical or photochemical driven water reduction to dihydrogen is an important and simple method [1–3]. To improve the rate of these reduction reactions, it is necessary to introduce catalysts. As we know, hydrogenase enzymes, containing transition metal complexes (such as iron and nickel) can efficiently catalyze both the production and the oxidation of hydrogen [4,5]. It is impossible to get in large amounts for practical uses, as the stability is often limited outside of their native environment. My group has successfully developed a series of molecular electrocatalysts based on transition metal complexes [6–13]. However, the most viable method for large-scale growth in carbon-free energy is the light-driven splitting of water into dihydrogen and dioxygen [14–16]. Now, the key issue on the splitting of water is the design of an efficient catalyst for water reduction with high turnover rates, good stability and durability [17,18]. In a typical system, the molecular catalyst is combined with a molecular photosensitizer (PS), such as ruthenium(II) trisbipyridyl complex, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ and a sacrificial electron donor. However, these photosensitizers can suffer degradation during irradiation [19–24].

Encouraged by Honda's work that photocatalytic splitting of water can occur on TiO_2 electrode [25], photocatalysis has demonstrated wide ranging potential applications in areas such as converting solar energy. To mimic natural photosynthesis by converting solar energy into chemical energy, the research on the photocatalytic splitting of water to produce hydrogen, has been carried out extensively [26–29]. Considering that the visible light accounts for about 43% of the solar radiation energy, while the ultraviolet light only contributes to about 4%, people have been focusing the studies on the design of visible-light-responsive photosensitizers [30–33]. CdS materials are selected as photosensitizers for the conversion of solar energy into chemical energy under visible-light irradiation, because CdS has a narrow band gap (with an E_g of 2.4 eV). Moreover, the potential of its conduction band (CB) is more negative than the reduction potential of hydrogen proton (H^+/H_2), letting it more proper for the H_2 generation [34–37]. However, the photocatalytic activity of CdS itself toward water reduction is very low due to high-rate charge recombination of photogenerated electron [38].

To suppress this recombination, the introduction of a cocatalyst, which can be loaded on CdS is an ideal method for improving the photocatalytic activity [39–43]. Generally, noble metals, such as Pt, Pd and Rh are proper candidates, because they can attract and trap photoelectrons and suppress the recombination of electron-hole pairs, which together improve the efficiency of electron utilization. It is necessary to

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develop non-noble-metal catalysts, as noble metals are too expensive [41]. These considerations have led to the development of cocatalysts employing more abundant metals, and several transition metal complexes have been developed as cocatalysts to produce hydrogen [44,45]. In this paper, we report a new catalyst based on the nickel complex, [Bz-4-MePy]₂[Ni(i-mnt)₂] **1** for electrochemical and photochemical driven hydrogen production.

2. Experimental section

2.1. Materials and physical measurements

The nickel complex, [Bz-4-MePy]₂[Ni(i-mnt)₂] **1** was prepared according to the literature procedure [46]. And the CdS nanorods (CdS NRs) was provided by using the reported method [47]. The procedures for electrochemical measurements were showed in “Supplementary Materials”. A Hitachi U-3010 spectrometer was used to measure UV–vis spectra. ESI–MS experiment was performed in the negative ion mode on an AB Sciex API 3200 Spectrometer. The luminescent spectra were recorded on a F-4500 fluorescence spectrophotometer. For the photocatalytic system, each sample was prepared in a flask of buffer solution with ascorbic acid, CdS NRs, and nickel complex **1**. Then, the flask was sealed with a septum. At room temperature, blue light (469 nm) was used to irradiate each sample. After photocatalysis, a 0.50 mL aliquot of the headspace was removed and replaced with 0.50 mL of CH₄. The headspace sample was injected into the gas chromatograph (GC). An Agilent Technologies 7890A gas chromatography instrument was used for GC experiments. Measurements and analysis for the chemical compositions and valence states of the photocatalysts were carried out by ESCALAB 250 Xi X-photoelectron spectroscopy (XPS) with monochromatic Al K α (1486.6 eV) X-ray sources. Transmission Electron Microscopy (TEM) images were afforded by using a JEM-2010 electron microscope. Scanning electron microscopy (SEM) images were obtained on a Merlin emission gun SEM instrument. Measurements and analysis for the crystalline diffraction patterns of CdS NRs and the related components were carried out by using Bruker D8 Advance powder X-ray diffraction.

3. Results and discussion

3.1. General characterization

The reaction of NiCl₂·6H₂O, K₂(i-mnt)·H₂O and 1-benzyl-4'-methylpyridinium bromide ([Bz-4-MePy]Br) provided the nickel(II) complex, [Bz-4-MePy]₂[Ni(i-mnt)₂] **1** (Scheme 1) [46]. This ion-pair complex was agreement with the following ESI–MS analysis. As shown in Fig. S1, complex **1** exhibited one ion at a mass-to-charge ratio (*m/z*) of 338.0, which is assigned to [Ni(i-mnt)₂-H]⁻.

Considering that nickel complexes can set up homogeneous electrocatalytic systems for hydrogen generation via an unstable hydride intermediate [48–51], we checked if this nickel complex also can act as an electrocatalyst for hydrogen generation. In CH₃CN, at a glassy carbon electrode, this nickel complex displayed a rich redox

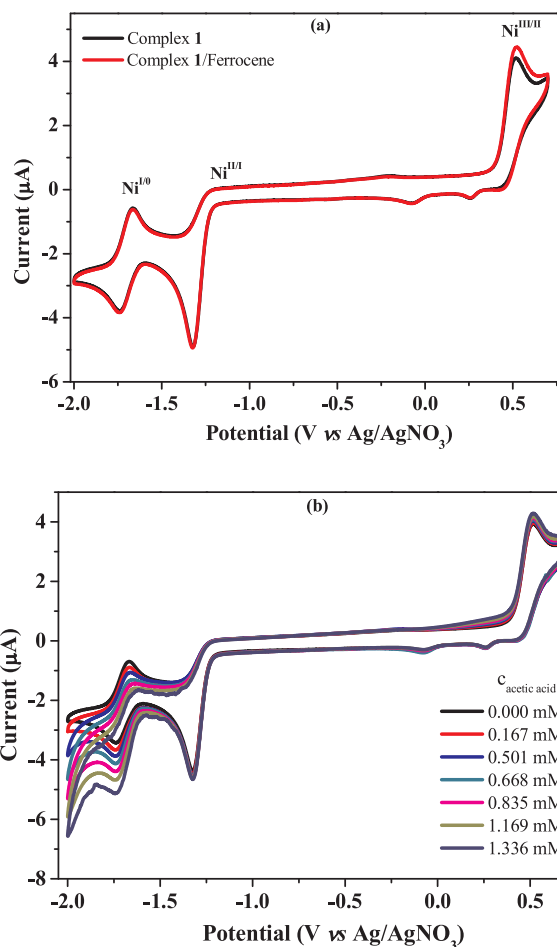
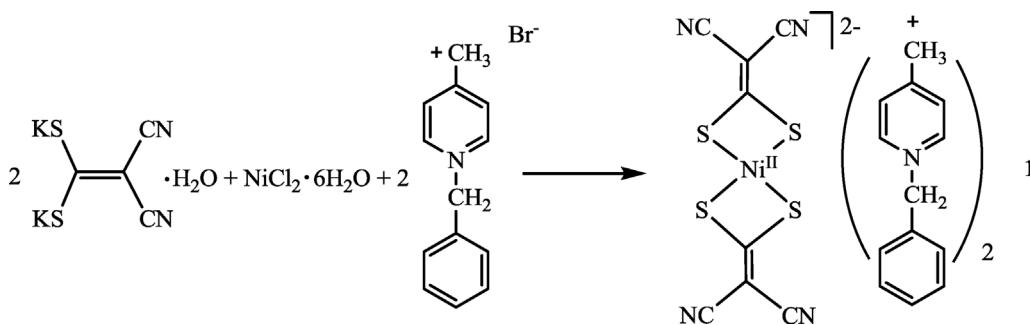


Fig. 1. (a) CVs of 1.10 mM complex **1** in CH₃CN with 0.10 M of [n-Bu₄N]ClO₄. (b) CVs of a 1.10 mM of complex **1** in CH₃CN with varying concentrations of acetic acid. Conditions: Glassy carbon working electrode (1.0 mm diameter), Pt counter electrode, Ag/AgNO₃ reference electrode, scan rate 100 mV/s.

electrochemistry, with the results plotted in Fig. 1a. Complex **1** displayed two quasi-reversible couples at 0.47 and -1.28 V, and one reversible wave at -1.70 V versus Ag/AgNO₃, which can be assigned to the Ni^{III}/Ni^{II}, Ni^{II}/Ni^I and Ni^I/Ni⁰ couples, respectively. According to Fig. S2, no significant change was found after several scans, indicating that this nickel complex is stable under these conditions.

3.2. The electrocatalytic system for hydrogen evolution from acetic acid

Next, acetic acid was selected as proton resource to test the electrocatalytic performance of the nickel complex. As shown in Fig. 1b, with the addition of varied content of acetic acid (from 0.0 to 1.336 mM), the strengths of peak currents emerging at -1.74 V versus Ag/AgNO₃ increased systematically, indicating that the reduction of Ni



Scheme 1. The synthesis of [Bz-4-MePy]₂[Ni(i-mnt)₂] **1**.

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