



Short communication

A heterogeneous photocatalytic system based on a nickel complex over a CdS nanorod photosensitizer for H₂ generation from water under visible light



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ABSTRACT

In this paper, we present a nickel complex, [BzPyN(CH₃)₂]₂[Ni(mnt)₂] **1** (mnt²⁻ = maleonitriledithiolate), a cocatalyst for building a photocatalytic system for H₂ generation from water. Under photoirradiation with blue light (λ_{max} = 469 nm), **1**, together with CdS nanorods (CdS NRs) as a photosensitizer, and ascorbic acid (H₂A) as a sacrificial electron donor in a pH 2.5 aqueous solution, produces hydrogen with a turnover number (TON) of 70,970 mol of H₂ per mol of catalyst during 70 h irradiation and the average value of AQY is ~18% during 10 h of irradiation.

1. Introduction

To solve the energy crisis and the environmental contamination caused by the burning of fossil fuels, many synthetic systems have been developed to get renewable and environmental-friendly alternative energy, such as hydrogen. Photochemical methods for generating hydrogen from water have been explored as cost-effective ways of producing a carbon-neutral fuel [1]. To improve the efficiency for hydrogen production, a challenging work for overcoming this issue would be to develop efficient and stable catalytic system established by abundant and cheap materials [2]. On this basis, several molecular photocatalysts based on transition metal complexes, such as nickel [3] and cobalt [4] complexes have been developed. Generally, these complexes are combined with a molecular photosensitizer (PS), such as ruthenium(II) complex, Ru(bpy)₃Cl₂ and a sacrificial electron donor. However, this molecular photosensitizer often is decomposed during irradiation [5]. Therefore, CdS materials are selected as photosensitizers for the conversion of solar energy into chemical energy under visible-light irradiation. Moreover, the potential of the conduction band (CB) is more negative than the reduction potential of hydrogen proton (H⁺/H₂), making it more proper for the H₂ generation [6]. However, it needs a co-catalyst, because the photocatalytic activity of CdS itself toward water reduction is very low due to high-rate charge recombination of photogenerated electron [7]. And the introduction of co-catalysts into CdS can significantly suppress this recombination, the design of a cocatalyst, which can be loaded on CdS is an ideal method

for improving the photocatalytic activity [8–11]. These considerations have led to the developments of cocatalysts employing more abundant metals, and several transition metal compounds have been developed as cocatalysts for hydrogen generation. Compared with nickel-based oxides and hydroxide cocatalysts [12,13], catalysts based on transition metal complexes are advantageous for mechanistic study and the resulting understanding should stimulate the development of new catalytic systems [14,15]. In this paper, we report a new photocatalytic system based on [BzPyN(CH₃)₂]₂[Ni(mnt)₂] **1**, for hydrogen production.

2. Results and discussion

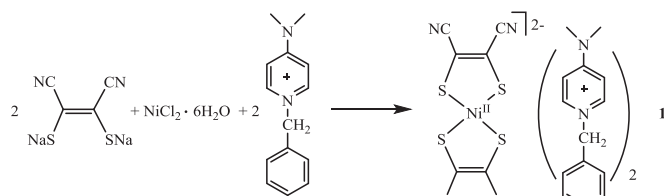
2.1. Photocatalytic system for H₂ generation

The reaction of NiCl₂·6H₂O, Na₂mnt and 1-benzyl-4-(dimethylamino)pyridinium bromide ([BzPyN(CH₃)₂]Br) afforded the nickel(II) complex, [BzPyN(CH₃)₂]₂[Ni(mnt)₂] **1** (Scheme 1) [16]. And the CdS nanorods (CdS NRs) was prepared according to the reported method [17]. To characterize the purity of complex **1**, powder X-ray diffraction of the synthesized sample was measured at room temperature. According to Fig. S1, the peak positions of experimental patterns were in good agreement with the simulated ones, which clearly indicates good purity of complex **1**. The XRD pattern of the synthesized CdS presented diffraction peaks indexed to CdS NRs (JCPDS NO. 41-1049) (Fig. S2).

Based on that this nickel complex can electrocatalyze hydrogen

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Scheme 1. The synthesis of $[\text{BzPyN}(\text{CH}_3)_2]_2[\text{Ni}(\text{mnt})_2]$ **1**.

evolution from both acetic acid and water [18], we examined the photocatalytic performance for water reduction by building a heterogeneous system containing complex **1**, ascorbic acid (H_2A) and CdS NRs. First, a series of photolysis experiments were carried out to investigate effect of pH of media on the activity of H_2 production. According to Fig. S3, the best pH for photocatalytic H_2 generation was observed at pH 2.5, with a TON of 3200 mol of H_2 (mol of cat) $^{-1}$ during 2 h of irradiation.

To obtain an optimal photocatalytic system, several measurements were carried out in parallel for comparison. To a photocatalytic system containing 0.12 M ascorbic acid, 0.02 mM complex **1** and a varying content of CdS NRs, the TON during 2 h of photolysis increased with increasing the concentrations of CdS NRs until a saturation value of 3590 mol of H_2 (mol of cat) $^{-1}$ was reached at 0.070 mg mL $^{-1}$ (Fig. S4). Other photocatalytic systems containing 0.05 mg mL $^{-1}$ CdS, 0.02 mM complex **1** and varying contents of ascorbic acid were designed to select the best ratio of ascorbic acid. According to Fig. S5, the TON used in 2 h increased with increasing concentration of ascorbic acid until a highest value of 3460 mol of H_2 (mol of cat) $^{-1}$ was reached at 0.12 M. Then, the TON decreased when the concentration of ascorbic acid was set to more.

Moreover, it was found that the photocatalytic activity was also dependent on the concentrations of the nickel complex. According to Fig. S6, under 3 h continuous irradiation, complex **1** catalyzed H_2 production with a TON of 3240 mol of H_2 (mol of cat) $^{-1}$ at 0.05 mM. When the concentration of **1** was lowered to 0.01 mM, the TON increases significantly to 7850 mol of H_2 (mol of cat) $^{-1}$ (Fig. S6), showing that the concentration of **1** has a significant effect on the photocatalytic activity for H_2 production. Based on the above analysis, we designed a three-component system, containing 0.07 mg mL $^{-1}$ CdS NRs, 0.12 M ascorbic acid, and 0.02 mM complex **1**. From Fig. 1, H_2 generation started immediately upon light irradiation of this system and their rates increased sharply and can last for about 70 h. Then the hydrogen generation build-up slightly increased until H_2 formation ceased after about 100 h. This system can photocatalyze H_2 production

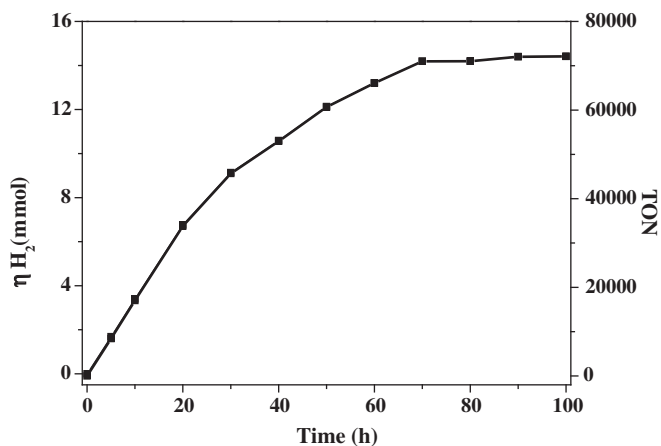


Fig. 1. Hydrogen evolution kinetics obtained upon continuous visible irradiation ($\lambda = 469$ nm) of a pH 2.5 buffer solution containing 0.07 mg mL $^{-1}$ CdS, 0.12 M ascorbic acid, and 0.02 mM complex **1**.

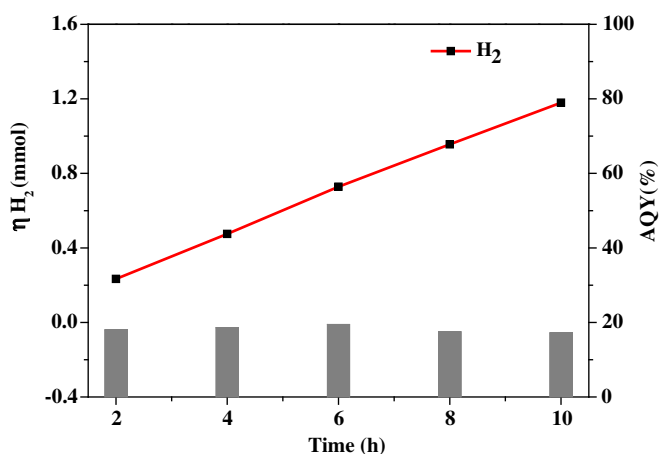


Fig. 2. Photocatalytic H_2 production of complex **1** under visible light ($\lambda = 569$ nm) and an apparent quantum yield (AQY) of complex **1** under monochromatic light ($\lambda = 420$ nm). The reaction system contained 0.070 mg mL $^{-1}$ CdS NRs, 0.020 mM complex **1**, 0.12 M ascorbic acid (pH 2.5).

over 70 h and achieve 70,970 mol of H_2 per mol of catalyst.

To know the apparent quantum yields (AQYs), the photocatalytic system was irradiated for 10 h under monochromatic light with a band-pass filter ($\lambda = 420$ nm + 5 nm). According to Eq. (1)[19], the AQYs of the photocatalytic system for H_2 generation were calculated. From Fig. 2, initially, the AQY was $\sim 18\%$ in the first 1 h. After the first 1 h, the AQYs increased. After the first 3 h, the AQYs decreased. And the average value of AQY was $\sim 18\%$ during 10 h of irradiation.

$$\text{AQY} (\%) = (2 \cdot n_{\text{H}_2} \cdot N_A \cdot h \cdot c) / (t_{\text{irr}} \cdot \lambda \cdot I \cdot A) \cdot 100 \quad (1)$$

n_{H_2} is the hydrogen generation (mol H_2), N_A is the Avogadro constant, h is the Planck constant, c is speed of light, t_{irr} is the irradiation time, I is the intensity, A is the irradiated area of the photoreactor, where, I is 5 mW cm $^{-2}$, A is 19.63 cm 2 , t_{irr} is 7200 s.

In the past several years, nickel-based compound cocatalysts have been applied for photocatalytic H_2 generation [13,14,20], with some representative examples summarized in Table 1.

2.2. Investigation for the stability and durability of the photocatalytic system

To characterize the stability of the photocatalytic system, recycling rest was performed on the hydrogen production activity of the nickel complex. Fig. 3 displayed the hydrogen production performance in a cycling photocatalytic run. After four recycles, the H_2 production rate remained almost constant, indicating the good stability of the catalyst during the photocatalytic reaction.

Next, we employed powder X-ray diffraction (XRD) to characterize the stability and durability of this photocatalytic system, and the XRD data of the related components were listed in Fig. 4. Fig. 4c showed the XRD pattern of complex **1**/CdS NRs composite (blue), in which all the different peaks are matched with the pattern of CdS NRs (Fig. 4b), indicating that the introduction of **1** does not affect the crystallinity of CdS NRs. According to Fig. 4d, the XRD signals were different from those before irradiation, indicating that CdS NRs or complex **1** or both of them are unstable after 100 h of photolysis.

Next, the X-ray photoelectron spectroscopy (XPS) was used to identify the chemical composition and oxidation state of different atoms in the composite particles before and after irradiation. As shown in Figs. S7b-c, three main peaks were located at 161.141, 162.085, and 163.309 eV, which can be attributed to S 2p in CdS NRs [21–23]. Fig. S7c demonstrated two obvious Cd 3d peaks located at 404.728 and 411.471 eV, which are consistent with the Cd character in CdS NRs [24].

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