

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Short communication

A photocatalytic system with a bis(thiosemicarbazonato)-nickel over CdS nanorods for hydrogen evolution from water under visible light



Wen-Xing Jiang, Zhen-Lang Xie, Shu-Zhong Zhan*

College of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords: Nickel(II) complex CdS materials Hydrogen evolution Photocatalytic system

ABSTRACT

Diacetyl-2-(4-*N*-methyl-3-thiosemicarbazone)-3-(4-*N*-amino-3-thiosemicarbazone) (H₂ATSM) reacts with NiCl₂ to form a new nickel(II) complex, Ni-ATSM, a new co-catalyst for hydrogen production. Under photoirradiation with blue light ($\lambda = 469$ nm), together with CdS nanorods (CdS NRs) as a photosensitizer, and ascorbic acid (H₂A) as a sacrificial electron donor, the nickel complex can photocatalyze hydrogen evolution with a turnover number (TON) of 11,500 mol H₂ per mol of catalyst (mol of cat⁻¹) during 80 h irradiation in a heterogeneous environment.

1. Introduction

As a secondary energy carrier, hydrogen is one ideal energy in the future, and lots of synthetic systems have been developed to get this renewable energy [1]. Among them, the direct photocatalytic water splitting into hydrogen is an effective way. To improve the efficiency for hydrogen production, a challenging work for overcoming this issue would be to develop efficient catalysts and assembly new photocatalytic systems with good stability, and high turnover rate [2,3]. To develop improved catalysts for this application, 3d metals and the related

compounds are good choice. Compared to noble metals, such catalysts would be of special advantage for costs, abundance and toxicity. Thus, significant efforts have made to apply nickel [4], cobalt [5–7] and iron [8] complexes as water reduction catalysts (WRC) in the photocatalytic hydrogen generation from water. However, this homogeneous system cannot work for a long time because of the decomposition of molecular photosensitizer, such as ruthenium(II) trisbipyridyl complex, Ru (bpy)₃Cl₂, during irradiation [9]. Considering that CdS has a narrow band gap (with an Eg of 2.4 eV), and the potential of its conduction band (CB) is more negative than the reduction potential of hydrogen

* Corresponding author.

E-mail address: shzhzhan@scut.edu.cn (S.-Z. Zhan).

https://doi.org/10.1016/j.inoche.2019.01.027 Received 16 November 2018; Received in revised form 20 January 2019; Accepted 22 January 2019 Available online 24 January 2019 1387-7003/ © 2019 Elsevier B.V. All rights reserved. proton (H^+/H_2) , letting it more proper for the H_2 generation [10], CdS is selected as photosensitizers. However, the photocatalytic activity of CdS itself for water reduction is very low because of high-rate charge recombination of photogenerated electron [11]. To inhibit this recombination, it is necessary to load a cocatalyst on CdS [12,13]. Based on that the formation of metal hydride intermediate is essential for the hydrogen evolution reaction [14], much effort has been reported preparing tetra- and pentadentate ligands and assembling coordinatively unsaturated complexes [15]. Our interests have been focusing on the design and research of new catalysts [7,14], and a new nickel-based cocatalyst, Ni-ATSM has been prepared in our lab. Combining CdS NRs and H_2A , this nickel complex serves as an efficient co-catalyst for H_2 production.

2. Results and discussion

Physical measurements and "X-ray Crystallography" for this paper were showed in "Supplementary Materials". CdS NRs was prepared by using the reported method [16] and characterized by Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) (Fig. S1). The ligand, diacetyl-2-(4-*N*-methyl-3-thiosemicarbazon ee)-3-(4-N-amino-3-thiosemicarbazone (H₂ATSM) was prepared based on the reported method [17].

2.1. General characterization for the nickel complex

The reaction of NiCl₂ and H₂ATSM afforded a new nickel complex, Ni-ATSM (Scheme 1) [18], which is in agreement with the X-ray analysis in solid state. The structure of the nickel complex was characterized by single crystal X-ray diffraction, with the results shown in Fig. 1a, Table 1 and Table S1. The nickel atom is four-coordinated by two nitrogen atoms and two sulfur atoms from the ligand (ATSM). The Ni(1)–N(1) and Ni(1)–N(2) distances are 1.856(6) and 1.843(6) Å, respectively, whilst the bond lengths of Ni(1)–S(1) and Ni(1)-S(2) are 2.154(2) and 2.142(2) Å, respectively. The result is also consistent with the ESI-MS analysis. As shown in Fig. S2, the nickel complex exhibited an ion at a mass-to-charge ratio (m/z) of 317.0148, which is assigned to [Ni-ATSM-H]⁺.

Considering that the nickel complex is in a coordinatively unsaturated state, leaving empty positions on the nickel center, amenable to binding to H^+ or H_2O for hydrogen generation [14], we tried to set up a photocatalytic system based on the nickel complex. We first investigated its electrochemical performance, with the result shown in Fig. 1b. The nickel complex displayed three good reversible redox



Fig. 1. (a) X-ray structure of the nickel complex, Ni-ATSM. (b) Cyclic voltammograms (CVs) of a 1.50 mM of Ni-ATSM 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. Fc internal standard (*).

Tabl	e 1	L
------	-----	---

	Selected bond lengt	hs (Å)	and angles ([°]) for the nickel	complex. Ni-ATSM
--	---------------------	--------	--------------	-------------------------------	------------------

Ni(1)-N(1)	1.856(6)	Ni(1)–N(2)	1.843(6)
Ni(1)-S(1)	2.154(2)	Ni(1)-S(2)	2.142(2)
N(2)-Ni(1)-N(1)	84.6(3)	S(2)-Ni(1)-S(1)	101.46(8)



Scheme 1. Synthesis of the ligand, H₂ATSM and the nickel complex, Ni-ATSM.

waves at -1.89, -1.31 and 0.82 V versus Ag/AgNO₃, which are assigned to the Ni^{1/0}, Ni^{II/I} and Ni^{III/II} couples, respectively. Moreover, addition of varied contents of acetic acid from 0.0 to 15.75 mM resulted in a systematic increase in the voltammetric currents emerging at -1.93 and -1.34 V, respectively and an additional positive shift in the potential from -1.93 to -1.68 V, which is consistent with a catalytic process [19]. The results indicate that the reductions of Ni(II) to Ni(I) or Ni(I) to Ni(0) and protonation are responsible for hydrogen generation. Next, electrochemical properties of this nickel complex were investigated in aqueous media. As shown in Fig. S3, with decreasing pH values from 7.0 to 3.5, the strength of the reduction wave of Ni-ATSM increased, and the onset of the catalytic wave were shifted to higher potentials, which are consistent with a catalytic process [20]. Moreover, in a pH 4.5 buffer, the nickel complex exhibited a quasi-reversible redox wave at -0.44 V versus Ag/AgCl (Fig. S3-insert), which is assigned to the Ni^{II}/Ni^I couple.

2.2. Heterogeneous photocatalytic system based on the nickel complex for H_2 generation

Based on that CdS NRs has a flat-band potential (E_{fb}) of -0.58 V [14], and Ni-ATSM exhibits a Ni^{II}/Ni^I couple at -0.44 V versus Ag/AgCl, the electron transfer from the excited CdS NRs to the nickel center is thermodynamically favorable. Such distinctive potential prompted possible usage of this complex as a co-catalyst for hydrogen generation. To characterize the catalytic activity of the nickel complex, a photocatalytic system was designed by employing Ni-ATSM as a co-catalyst, H₂A as an electron donor and CdS NRs as a photosensitizer.

To obtain an optimal photocatalytic system, a series of measurements and analysis were carried out. First, we explored the effect of pH of media on the photocatalytic activity for H₂ evolution. As shown in Fig. S4, the best pH for photocatalytic H₂ generation mediated by Ni-ATSM (0.01 mM) was found at pH 4.5, with a turnover number (TON) of 410 mol of H₂ (mol of cat)⁻¹ during 3 h of irradiation.

Next, effects of amounts of CdS NRs and H₂A on the photocatalytic activity for H₂ evolution were investigated. As shown in Fig. S5, to photocatalytic systems containing 0.10 M H₂A, 0.010 mM Ni-ATSM and a varying content of CdS NRs, the TON during 3 h of photolysis increased with increasing CdS NRs until 3260 mol of H₂ (mol of cat)⁻¹ was reached at 0.045 mL⁻¹. To photocatalytic systems containing 0.045 mg·mL⁻¹ CdS NRs, 0.01 mM Ni-ATSM and varying contents of ascorbic acid, the TON increased with increasing the concentration of ascorbic acid until a highest value of 1920 mol of H₂ (mol of cat)⁻¹ was reached at 0.12 M (Fig. S6). These observation and analysis resulted in an optimal three-component system, containing 0.045 mg·mL⁻¹ CdS



Fig. 2. Hydrogen evolution kinetics obtained upon continuous visible irradiation ($\lambda = 469 \text{ nm}$) of a pH 4.5 buffer solution containing 0.045 mg·mL⁻¹ CdS NRs, 0.12 M ascorbic acid, and 0.01 mM Ni-ATSM.

NRs, 0.12 M H₂A, and 0.01 mM Ni-ATSM. According to Fig. 2, H_2 production started immediately upon light irradiation of this system and their rates increased sharply and could last for about 80 h with a TON of 11,500 mol of H_2 per mol of catalyst.

To get apparent quantum yields (AQYs), a photocatalytic system was irradiated for 10 h under monochromic light with a band-pass filter ($\lambda = 420 \text{ nm} + 5 \text{ nm}$). Based on Eq. (1) [21], the AQYs of the photocatalytic system for H₂ generation were estimated. As shown in Fig. S7, in the first 1 h, the AQY was ~15.7%, then it increased until a highest value of 26.7% was reached at 4 h. The average value of AQY was ~21.2% during 10 h irradiation.

$$AQY (\%) = (2 \cdot n_{H2} \cdot N_A \cdot h \cdot c) / (t_{irr} \cdot \lambda \cdot I \cdot A) \cdot 100$$
(1)

 $n_{\rm H2}$ is the hydrogen generation (mol H₂), N_A is the Avogadro constant, h is the Planck constant, c is speed of light, $t_{\rm irr}$ 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 $cm^2,\,t_{\rm irr}$ is 7200 s.

To confirm factors responsible for H_2 generation in this photocatalytic system, any two of the three components (ascorbic acid, CdS NRs, or Ni-ATSM) were combined. According to Fig. S8, a mixture of Ni-ATSM and CdS NRs only afforded 0.20 µmol H_2 , the integration of ascorbic acid and CdS NRs gave 4.1 µmol H_2 , and 1.8 µmol H_2 was produced when ascorbic acid and Ni-ATSM was combined. Thus, the combination of the nickel complex, ascorbic acid and CdS NRs is essential for the photocatalytic system.

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

A long-time photolysis was carried out to test photo- stability and durability of the nickel complex. According to Fig. S9, 80 h irradiation led to an increase in pH values from 4.5 to 5.6, which is consistent with accumulation of OH^- by water reduction, $2H_2O + 2e \rightarrow H_2 + 2OH^-$. However, this catalytic function could be recovered in 7% when the pH was adjusted back to the original 4.5. This result indicates that CdS NRs, H₂A, the nickel complex or all of them are unstable during photocatalysis.

To give answers for these equations, several physical or physiochemical methods were employed for measurements and analysis. As shown in Fig. S10, the XRD signs were same as those before 80 h irradiation, showing that CdS NRs is stable during photolysis. From Fig. S11a, both survey spectra were quite similar, with the presence of Cd, S, O, and C elements. Before photocatalysis, two main peaks were located at 160.726 eV and 163.093 eV (Fig. S11b), which can be attributed to S 2p in CdS NRs [22], and two obvious Cd 3d peaks were located at 404.756 eV and 411.129 eV (Fig. S11c), which are consistent with the Cd character in CdS NRs [22]. According to the data shown in Fig. S11b and c, the position or strength of both S 2 s and Cd 3d peaks remained almost constant, indicating that CdS NRs was stable as a photosensitizer during photocatalysis.

As shown in Fig. S11d, before irradiation, two appreciable Ni 2p peaks were observed at 854.219 eV and 871.503 eV, indicating the presence of a Ni²⁺ ion. In contrast, the same Ni 2p peaks were found after irradiation, indicating that the nickel complex is stable over a period of 80 h photocatalysis. Next, photocurrent response versus time of Ni-ATSM/CdS NRs and CdS NRs was investigated. According to Fig. 3, the current can reproducibly increase violently under each irradiation and recover rapidly in the dark, showing that the photocurrent response of Ni-ATSM/CdS NRs was reversible and stable.

Next, electronic spectra were measured to understand the stability of the photocatalytic system. As shown in Fig. S12, before irradiation, the three-component system exhibited a main peak at 259 nm, which is assigned to that of ascorbic acid alone. And the photochemical reduction catalyzed by Ni-ATSM resulted in no new absorption, but a decrease in the strength of peak at 259 nm (Fig. S13), suggesting that the amount of ascorbic acid decreased after photolysis. However, the



Fig. 3. Current responses versus time of Ni-ATSM/CdS NRs under visible-light irradiation ($\lambda > 420$ nm) at 0.20 V using Ag/AgCl as a reference electrode.



Fig. 4. Electrochemical impedance spectroscopy Nyquist plots of CdS NRs and Ni-ATSM/CdS NRs with $0.010 \text{ M} \text{ K}_3$ Fe(CN)₆/K₄Fe(CN)₆ electrolyte in dark conditions.

adjustment of H_2A back to the original 0.12 M resumed nearly 34.6% activity of the photocatalytic system under another illumination. Then, when the solution pH was adjusted back to the original value of 4.5, the original photocatalytic function can be recovered about 89%. These results suggest that the decomposition of H_2A is the primary reason for the cease of hydrogen evolution after illumination, although several components of the photocatalytic system may deactivate during photolysis.

2.4. Investigation for photocatalytic mechanism

To understand the photocatalytic mechanism, several methods were employed. As shown in Fig. S14, the introduction of the nickel complex into CdS NRs resulted in a red shift of the absorption onset and reduction of Eg of CdS NRs, which obviously improves the range and ability of visible light absorption of CdS NRs.

We also used "the Materials Studio DMol³" to carried out orbital calculation for the nickel complex, giving the results shown in Fig. S15. As shown in Fig. S15, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of NiATSM were -4.536 and -3.384 eV, respectively. Based on that the conducting



Scheme 2. Possible mechanism for $\rm H_2$ production by the photocatalytic system with Ni-ATSM.

band of CdS (-3.8 eV) [23] is smaller than E_{LUMO} (-3.384 eV) of NiATSM, the photogenerated electrons transfer from CdS to the nickel complex is energetically favorable.

Moreover, at the excitation wavelength of 450 nm, CdS NRs exhibited two emission waves at 531 and 676 nm (Fig. S16), respectively. However, with the introduction of the nickel complex, the peak intensity of CdS NRs at 531 nm decreased, showing a lower possibility of electron–hole pair recombination because of the fast electron transfer from CdS NRs to Ni-ATSM [24,25]. Therefore, as an electron acceptor loaded on the CdS NRs surfaces, the nickel complex can trap efficiently photo-generated electrons and promoted their combination with H^+ to form H_2 .

Electrochemical impedance spectroscopy was used to investigate charge transfer properties and separation efficiency of photogenerated charge carriers, giving the results shown in Fig. 4. Compared with CdS NRs, the mixture of CdS NRs and Ni-ATSM showed much smaller arc radius, representing a faster interfacial charge transfer and higher separation efficiency of photogenerated charge carriers [26–29]. On the basis of these analysis and literature precedents [14,28–30], we put forward a possible mechanism for the photocatalytic H₂ production. As outlined in Scheme 2, a reduced nickel(I) species was afforded by the transfer of the photoexcited electron from the conduction band (CB) of CdS NRs to the nickel(II) ion of Ni-ATSM. Then the introduction of hydrogen proton (H⁺) yielded a Ni^{III}-H species. Further addition of hydrogen proton (H⁺) to the Ni^{III}-H species gave dihydrogen, and regenerated the starting nickel complex.

3. Conclusion

We described a new photocatalytic system based on the nickel(II) complex, Ni-ATSM, a new co-catalyst for hydrogen production. The studies showed that the photocatalytic activities depend on concentrations of CdS NRs, ascorbic acid, the nickel complex and the pH values of media. CdS NRs and the nickel complex were stable, but ascorbic acid was decomposed during light irradiation. Our ongoing efforts are focused on modifying the sacrificial electron donor for more stable photocatalytic system.

Acknowledgements

This work was supported by the National Science Foundation of China (No. 21271073 and 21875074).

Appendix A. Supplementary material

CCDC 1843757 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2019.01.027.

References

- [1] T.R. Cook, D.K. Dogutan, S.Y. Reece, Y. Surendranath, T.S. Teets, D.G. Nocera,
- Chem. Rev. 110 (2010) 6474–6502.
- [2] J. Barber, Chem. Soc. Rev. 38 (2009) 185–196.

- [3] Z. Han, R. Eisenberg, Acc. Chem. Res. 47 (2014) 2537–2544.
- [4] S. Inoue, M. Mitsuhashi, T. Ono, Y.-N. Yan, Y. Kataoka, M. Handa, T. Kawamoto, Inorg. Chem. 56 (2017) 12129–12138.
- [5] L. Tong, R. Zong, R.P. Thummel, J. Am. Chem. Soc. 136 (2014) 4881-4884.
- [6] E. Deponti, A. Luisa, M. Natali, E. Iengo, F. Scandola, Dalton Trans. 43 (2014) 16345–16353.
- [7] Q.X. Peng, D. Xue, L.F. Yang, S.Z. Zhan, Int. J. Hydrog. Energy 42 (2017) 16428–16435.
- [8] H. Lv, T.P.A. Ruberu, V.E. Fleischauer, W.W. Brennessel, M.L. Neidig, R. Eisenberg, J. Am. Chem. Soc. 138 (2016) 11654–11663.
- [9] W.T. Eckenhoff, W.W. Brennessel, R. Eisenberg, Inorg. Chem. 53 (2014) 9860–9869.
- [10] K. Wu, Y. Du, H. Tang, Z. Chen, T. Lian, J. Am. Chem. Soc. 137 (2015) 10224–10230.
- [11] R. Marschall, Adv. Funct. Mater. 24 (2014) 2421–2440.
- [12] F.Y. Wen, C. Li, Acc. Chem. Res. 46 (2013) 2355–2364.
- [13] Q. Li, B. Guo, J. Yu, J. Ran, B. Zhang, H. Yan, J.R. Gong, J. Am. Chem. Soc. 133 (2011) 10878–10884.
- [14] Q.X. Peng, D. Xue, S.Z. Zhan, C.L. Ni, Appl. Catal. B Environ. 219 (2017) 353–361.
- [15] D.Z. Zee, T. Chantarojsiri, J.R. Long, C.J. Chang, Acc. Chem. Res. 48 (2015) 2027–2036.
- [16] J.S. Jang, U.A. Joshi, J.S. Lee, J. Phys. Chem. C 111 (2007) 13280–13287.
- [17] M. Christlieb, J.R. Dilworth, Chem. Eur. J. 12 (2006) 6194–6206.
- [18] Synthesis of the nickel complex, Ni-ATSM To a solution of 0.132 g (0.50 mmol) the ligand, H₂ATSM in 20 mL N,N-Dimethylformamide (DMF), 0.120 g (0.50 mmol)

NiCl₂6H₂O in 10 mL water was added with slight stirring. The solution was allowed to slowly evaporate, affording deep green crystals. The product was isolated by filtration, washed with water (3 × 20 mL), and dried in vacuo (0.124 g, 63%). Elem anal. Found (calcd) for C₁₁H₂₁N₇S₂ONi: C, 33.78 (33.86); H, 5.42 (5.43); N, 25.17 (25.13).

- [19] P. Delahay, G.L. Stiehl, J. Am. Chem. Soc. 74 (1952) 3500-3505.
- [20] R.S. Nichloson, I. Shain, Anal. Chem. 36 (1964) 706–723.
- [21] D.J. Martin, K.P. Qiu, S.A. Shevlin, A.D. Handoko, X.W. Chen, Z.X. Guo, J.W. Tang, Angew. Chem. Int. Ed. 53 (2014) 9240–9245.
- [22] Y.T. Chen, J.B. Ding, Y. Guo, L.B. Kong, H.L. Li, Mater. Chem. Phys. 77 (2003) 734–737.
- [23] C.X. Guo, H.B. Yang, Z.M. Sheng, Z.S. Lu, Q.L. Song, C.M. Li, Angew. Chem. Int. Ed. 49 (2010) 3014–3017.
- [24] W. Zhang, J. Hong, J. Zheng, Z. Huang, J. Zhou, R. Xu, J. Am. Chem. Soc. 133 (2011) 20680–20683.
- [25] M.P. McLaughlin, T.M. McCormick, R. Eisenberg, P. Holland, Chem. Commun. 47 (2011) 7989–7991.
- [26] Y. Yu, W. Ouyang, Z. Liao, B. Du, W. Zhang, ACS Appl. Mater. Interfaces 6 (2014) 8467–8474.
- [27] L. Jia, D. Wang, Y. Huang, A. Xu, H. Yu, J. Phys. Chem. C 115 (2011) 11466–11473.
 [28] Z. Han, L. Shen, W.W. Brennessel, P.L. Holland, R. Eisenberg, J. Am. Chem. Soc. 135
- (2013) 14659–14669.
- [29] J.M. Lei, Q.X. Peng, S.P. Luo, Y. Liu, S.Z. Zhan, C.L. Ni, J. Mol. Catal. A Chem. 448 (2018) 10–17.
- [30] Q.-X. Penga, D. Xue, S.-Z. Zhan, X.-F. Jiang, Catal. Commun. 103 (2018) 15–18.