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Inorganic Chemistry Communications





Catalytic performance of a square planar nickel complex for electrochemical- and photochemical-driven hydrogen evolution from water

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ARTICLE INFO	A B S T R A C T			
Keywords: Nickel complex Crystal structure Electro and photocatalytic activity for HER	A square planar nickel complex bearing salicylketoxime (SAO), Ni-SAO has been synthesized and well charac- terized by ESI-MS and single-crystal X-ray diffraction, <i>etc.</i> Ni-SAO exhibits good activity in both electrocatalytic and photocatalytic hydrogen evolution reaction (HER). Under an overpotential (OP) of 837.6 mV, Ni-SAO can electrocatalyze hydrogen evolution from a neutral aqueous buffer with a turnover frequency (TOF) of 1428 mol of hydrogen per mole of catalyst per hour (mol H ₂ /mol catalyst/h). Moreover, under blue light (λ = 469 nm), a three-component system containing Ni-SAO as a catalyst, CdS nanorods (CdS NRs) as a photosensitizer, and ascorbic acid (H ₂ A) as a sacrificial electron donor also can afford hydrogen with a turnover number (TON) of 8138 mol H ₂ per mol of catalyst (mol of cat ⁻¹) during 48 h irradiation. The highest apparent quantum yield (AOY) is about 16.5% at 469 nm.			

1. Introduction

The global demand for cost-effective and user-friendly energy has sparked considerable interest in carbon-free renewable energy resources [1-3]. Hydrogen, a promising fuel, based on the photoelectric and photocatalytic H₂O splitting, will be at the vanguard of this revolution [4]. In nature, hydrogenases surviving in anaerobic organisms can be divided into [NiFe]and [FeFe] hydrogenases according to the different metal active center, which can catalyze reduction of protons efficiently [5]. Considering that hydrogenases are assembled by organic species with metal active sites, researchers focus their works on the design and study of molecular catalysts based on transition metal complexes for HER, and several complexes containing iron [6], cobalt [7], copper [8,9] and nickel [10,11] have been developed as catalysts for hydrogen generation. It is apparent that cobalt complexes with oxime can serve as catalysts for electrochemical or photochemical driven hydrogen evolution [12-14]. However, phenolic oxime nickel complexes used for electro- and photocatalytic hydrogen production have rarely been reported, although the Robertson group reported magnetic and electronic performances of several nickel complexes with phenolic oxime species [15]. Moreover, the complex with a square-planar coordination geometry is always selected as a proper candidate for HER. To this end, a new phenolic oxime, salicylketoxime (SAOH) was designed in our Lab. The reaction of the ligand, SAOH and nickel salt affords a new nickel complex, Ni-SAO that has a good activity for hydrogen evolution. Herein, we present the synthesis, characterization and catalytic activities for electrochemical and photochemical driven hydrogen evolution of Ni-SAO.

2. Experimental

2.1. Materials and experimental methods

Reagent-grade chemicals were commercially purchased and used without further purification. Tetra-butylammonium perchlorate ([$(n-Bu)_4N$]ClO₄) was used after secondary recrystallization. CdS NRs were synthesized with a simple solvothermal method [16]. According to the reported method [17], salicylketoxime (SAOH) was obtained by the reaction of hydroxylamine hydrochloride with 2-hydroxybenzaldehyde.

Electrochemical measurements were performed using a CHI-660E electrochemical workstation. Cyclic voltammograms (CVs) were recorded by using a single-compartment cell possessing a 0.00785 cm² glassy carbon electrode as a working electrode, Pt counter electrode and Ag/AgNO₃ as a reference electrode. Controlled potential electrolysis (CPE) were carried out in a two-compartment cell possessing the glassy carbon electrode as the working electrode, Pt auxiliary electrode, and Ag/AgNO₃ or Ag/AgCl reference electrode.

In a photocatalytic experiment, a tube containing 5 mL aqueous

https://doi.org/10.1016/j.inoche.2021.108780

Received 24 April 2021; Received in revised form 25 June 2021; Accepted 29 June 2021 Available online 5 July 2021 1387-7003/© 2021 Elsevier B.V. All rights reserved.

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Scheme 1. Synthesis of the ligand, SAOH and the nickel complex, Ni-SAO.



Fig. 1. (a) X-ray crystal structure of the nickel complex, Ni-SAO. (b) 2D layered diagram of Ni-SAO along ac plane.

solution of CdS NRs, Ni-SAO and ascorbic acid was irradiated by using a LED light ($\lambda = 469$ nm) as a light source. The generated gas samples were analyzed by gas chromatograph (Agilent 7890A, with argon as a carrier gas) equipped with a thermal conductivity detector (TCD) and 5 Å molecular sieve column. Turnover numbers (TONs) for H₂ production were calculated by using Equation (1) [18,19]:

$$TON = \frac{number of product molecules}{number of cocatalyst molecules} = \frac{number of evolved H_2 molecules}{number of cocatalyst molecules}$$
(1)

2.2. Synthesis of the nickel complex, Ni-SAO

The ligand, SAOH (0.2 mmol) was added to a solution of Ni $(CH_3COO)_2$ ·4H₂O (0.10 mmol) in ethanol (20 mL) with stirring. After

14 h, the precipitate was formed. The product was collected by filtration, washed with ethanol, and dried in *vacuo* (0.15 g, 45% yield). Single crystals suitable for X-ray analysis were obtained by slow evaporation of an acetonitrile solution of Ni-SAO. Calc for $C_{14}H_{12}N_2NiO_4$: C 50.76, H 3.62, N 8.5. Found: C 50.2, H 3.40, N 8.9.

2.3. Crystallographic structure determinations

The X-ray crystallographic data collections were carried out on a Bruker Smart Apex II DUO area detector using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at room temperature. The structure was solved by SHEIXT [20] in the OLEX2 crystallographic software package [21] and refined by full-matrix least squares on F^2 using SHEIXL-2018 [22]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as idealized contributions and refined isotropically. A summary of crystallographic data for Ni-SAO was given in Table S1.



Fig. 2. (a) cyclic voltammogram (CV) of a solution of 6.0 μ M Ni-SAO in acetonitrile. (b) CVs of a solution of 6.0 μ M Ni-SAO with varying amounts of acetic acid in acetonitrile. Conditions: 0.10 M [*n*-Bu₄N]ClO₄ as supporting electrolyte, scan rate: 100 mV/s, glassy carbon working electrode (1 mm diameter), Pt counter electrode, Ag/AgNO₃ reference electrode, Fc internal standard (*).

3. Results and discussion

3.1. Characterization for the nickel complex, Ni-SAO

As shown in Scheme 1, the reaction of SAOH and Ni(CH₃COO)₂ afforded a new nickel complex, Ni-SAO, which is agreement with the following measurements and analysis. Ni-SAO exhibited one ion at a mass-to-charge ratio (m/z) of 311.0223 (Fig. S1), with mass and isotope distribution pattern corresponding to [Ni-SAO-H]⁺.

Crystal structure of Ni-SAO was determined by X-ray crystallography, giving the results shown in Tables S1-S3 and Fig. 1. As shown in Fig. 1, the nickel center is four-coordinated by two N atoms and two O atoms from phenolic oxime ligand, with a square planar geometry. From the data listed in Table S1, both bond lengths of the Ni-N1 and Ni-N1a are 1.873(3) Å. And the bond length of Ni-O2 (1.8412(19) Å) is the same as that of Ni-O2a. The bond angle of N1 – Ni – O2 angle (92.84 (10)°) is the same as that of the O2a – Ni – N1a angle. Both bond angles of O2 – Ni – N1a and O2a – Ni – N1 are 87.17(10)°. Moreover, the ligand O – H hydrogen atom is involved in hydrogen bond with oxygen atom of another ligand (Fig. 1). Distances between the O – H hydrogen and the oxygen are in the range 1.90–2.55 Å (Table S2).

Power X-ray diffraction (PXRD) was used to check the purity of Ni-SAO, giving the result shown in Fig. S2. The theoretical patterns were consistent with the experimental ones, indicating that a single phase of Ni-SAO is formed.

To further characterize Ni-SAO, infrared spectra of the nickel complex, Ni-SAO and the ligand, SAOH were measured, with the results shown in Fig. S3. Compared with the ligand, SAOH ($\nu_{O-H} = 3400 \text{ cm}^{-1}$), Ni-SAO showed the O-H stretching at 3000 cm⁻¹. This can be attributed to the formation of intramolecular hydrogen bond among oximino hydroxyl groups.

To determine oxidation state of the nickel center, X-ray photoelectron spectroscopy (XPS) spectra of Ni-SAO were measured. From Fig. S4 (a), the sample contains C, N, O, and Ni elements. As shown in Fig S4(b), the main characteristic peaks at 855.5 eV and 872.8 eV can be assigned to Ni 2p3/2 and Ni 2p1/2, respectively. The peaks centered at 860.7 eV and 877.2 eV are the satellite peaks of Ni 2p3/2 and Ni 2p1/2, respectively, a typical characteristic of Ni(II) oxidation state. These are consistent with the results reported in the literature [23].

3.2. Electrochemical investigation

Electrochemical properties of Ni-SAO and the related components were studied by cyclic voltammetry (CV) under N₂ atmosphere. Based on that no reduction waves were found for the ligand (SAOH) or Ni (CH₃COO)₂ (Fig. S5), Ni-SAO had three redox waves at -1.16 V, -1.43 and -1.74 V (versus Ag/AgNO₃), which can be assigned to the Ni^{III/II}, Ni^{II/I} and Ni^{I/O} couples, respectively (Fig. 2(a)). Moreover, according to Figs. S6(a) and S6(b), the linear fitting plot of i_d vs $\nu^{1/2}$ for Ni-SAO indicates that the reduction is in a diffusion-controlled regime [24].

To research catalytic activity of Ni-SAO for proton reduction, CH_3COOH (AcOH) was introduced as a proton source (pKa = 23.51) [25]. As can be seen from Fig. 2(b), upon addition of AcOH, catalytic current dramatically enhanced at the Ni^{II/1} and Ni^{I/0} redox couples, suggesting that an electro-catalytic proton reduction occurred at the Ni^{II/1} and Ni^{I/0} couples [26,27].

Next, the electrochemical properties of Ni-SAO were investigated an aqueous medium. It was observed that catalytic current increases with an increase in the concentration of Ni-SAO (Fig. S7(a)). Moreover, with the decrease of pHs, the catalytic current increased (Fig. S7(b)), which were consistent with a catalytic process [28].

3.3. Electrocatalytic hydrogen evolution by Ni-SAO

To assess the electrocatalytic activity of Ni-SAO for H_2 evolution, controlled potential electrolysis (CPE) experiments were conducted in



Fig. 3. Hydrogen evolution kinetics obtained upon continuous visible irradiation ($\lambda = 469$ nm) of a pH 4.5 solution containing 0.16 mg mL⁻¹ CdS NRs, 0.16 M ascorbic acid, and 0.01 mM Ni-SAO.

aqueous buffer. Under -1.45 V versus Ag/AgCl, only 39 mC of charge was obtained from a neutral buffer during 2 min of electrolysis (Fig. S8). Surprisingly, the introduction of Ni-SAO led to the formation of 2794 mC of charge under the same conditions (Fig. S8). Together the data listed in Fig. S9 with Equations (2) and (3) [29,30], the turnover frequency (TOF) and overpotential (OP) were estimated, respectively. As depicted in Fig. S10, when an OP was 837.6 mV, the TOF for hydrogen generation was 1428 mol of hydrogen per mole of catalyst per hour (mol H $_2$ /mol catalyst/h).

$$TOF = \Delta C / (F^* n_1^* n_2^* t)$$
⁽²⁾

$$\begin{aligned} \text{Overpotential} &= \text{Applied potential} - \text{E}(\text{pH}) = \\ \text{Applied potential} - (-0.059\text{pH}) \end{aligned} \tag{3}$$

According to Fig. S11, 11.51 mL of H_2 was generated during 1 h electrolysis using Ni-SAO as an electrocatalyst, with 31C charge accumulation (Fig. S12). To evaluate Faraday efficiency (FE) of Ni-SAO for hydrogen evolution, the CPE experiment was conducted in a 1.0 M potassium chloride solution [31]. Based on the data shown in Fig. S13, the Faraday efficiency was estimated to be 99%.

3.4. Photocatalytic behavior of Ni-SAO for hydrogen evolution

It is apparent that CdS, which has a narrow band gap (Eg = 2.4 eV), can act as a photocatalyst for hydrogen evolution under blue light conditions, however, the photocatalytic activity is very low due to the high-rate charge recombination of photogenerated electron [32-34]. To suppress this recombination and improve the photocatalytic activity, we tried to introduce Ni-SAO as a cocatalyst on CdS. The photocatalytic activity of Ni-SAO for hydrogen generation was investigated under blue light using CdS NRs (Fig. S14(a)) as a photosensitizer, ascorbic acid as an electron donor and Ni-SAO as a co-catalyst (Fig. S14(b)).

To optimize the conditions for hydrogen production, a series of experiments were conducted with varying pH, ascorbic acid concentration, or amounts of photosensitizer. To explore the dependent activity of H₂ production on the effect of pH, we performed photolysis experiments with varying pH values. As shown in Fig. S15, an optimum pH for photocatalytic H₂ generation mediated by Ni-SAO (0.01 mM) was observed at pH 4.5, with a TON of 2500 mol of H₂ (mol of cat)⁻¹ during 3 h of irradiation. Next, we examined the dependence of amounts of photosensitizer on H₂ production with varying amounts of CdS NRs from 0 to 0.2 mg·mL⁻¹, while maintaining the concentration of Ni-SAO (0.01 mM) and keeping all other reaction conditions constant. As shown in Fig. S16, with the increase of CdS NRs, the activity for hydrogen evolution increased until a highest TON of 2777 mol of H₂ (mol of cat)⁻¹ was reached at 0.16 mg·mL⁻¹. Moreover, similar experiments were

Table 1

Photocatalytic activities of some reported nickel-based catalysts for H₂ evolution.

Catalysts	Photosensitizer	Electron donor	Light source	TON mol H_2 (mol of cat) ⁻¹	Ref.
Ni-SAO	CdS nanorods	Ascorbic acid	Blue light	8138	This work
Ni-ATSM	CdS nanorods	Ascorbic acid	Blue light	11,500	[35]
[(bpte)NiCl ₂]	CdS nanorods	Ascorbic acid	Blue light	24,900	[36]
Nickel nanoparticles	CdS nanorods	Lactic acid	$\lambda = 420 \text{ nm}$	9710	[18]

H2ATSM: Diacetyl-2-(4-N-methyl-3-thiosemicarbazone)-3-(4-N-amino-3-thiosemicarbazone); bpte: S,S-bis(2-pyridylmethyl)-1,2-thioethane.



Fig. 4. Photocatalytic H₂ production of NiSAO under visible light (λ = 469 nm) and an apparent quantum yield (AQY) of Ni-SAO under monochromatic light (λ = 469 nm). Conditions: 0.16 mg CdS NRs, 0.010 mM Ni-SAO and 0.16 M ascorbic acid (pH 4.5).

performed on varying contents of ascorbic acid, with the results listed in Fig. S17. The highest value of TON of 2918 mol H_2 (mol cat.)⁻¹ was obtained by using 0.16 M ascorbic acid.

On the basis of the above observed results, an optimal threecomponent photocatalytic system (pH 4.5) containing 0.01 mM Ni-SAO, 0.16 mg·mL⁻¹ CdS NRs and 0.16 M ascorbic acid was provided. The time courses of observed products under this optimal photocatalytic system are shown in Fig. 3. The H₂ evolution process was ceased after 50 h irradiation, with a TON of 8138 mol H₂ (mol cat)⁻¹.

Making a comparison for the photocatalytic activity among different catalytic systems in term of TON values is not easy, because of possible differences in the experimental conditions conducted and calculated methods, *etc.* The activities for hydrogen evolution of some reported photocatalytic systems [18,35,36] were listed in Table 1.

The apparent quantum yields (AQYs) were measured under monochromic light with a band-pass filter ($\lambda = 469$ nm). Based on the data listed in Fig. 4 and Equation (4) [19], the AQYs of the photocatalytic system for H₂ generation were calculated, with the results listed in Fig. 4. The average of AQY was about 10.24% during 10 h of irradiation.

AQY (%) = $(2 \cdot n_{H2} \cdot N_A \cdot h \cdot c)/(t_{irr} \cdot \lambda \cdot I \cdot A) \cdot 100$ (4)

3.5. Stability of the photocatalytic system

Powder X-ray diffraction (XRD) technology was used to examine the stability of the photocatalytic system during irradiation. As shown in Fig. S18, after 50 h irradiation, the peaks were agreement with the ones before irradiation, indicating that both CdS NRs and Ni-SAO are stable during 50 h of photolysis.

Furthermore, XPS spectra of the related components were measured, giving the results shown in Fig. S19. As shown in Fig. S19(a), both survey spectra are quite similar, with the presence of Cd, S, Ni, O, and C elements. Two main peaks at 405.02 eV and 411.69 eV are attributed to Cd 3d of CdS NRs (Fig. S19(b)). And Two obvious peaks at 161.32 eV and 162.53 eV can be assigned to S 2p of CdS NRs (Fig. S19(c)) [37]. The



Fig. 5. HOMO-LUMO energy level diagram of Ni-SAO.



Fig. 6. The transient photocurrent responses of CdS NRs with or without Ni-SAO.

high resolution XPS spectrum of Ni 2p in the mixture of CdS NRs and Ni-SAO is shown in Fig. S19(d). Before irradiation, two appreciable Ni 2p peaks are observed at 855.43 eV and 872.76 eV, indicating the presence of a Ni²⁺ ion. In contrast, no apparent Ni 2p peaks can be seen in the sample after irradiation, further confirming no metallic nickel formation during 50 h photocatalysis.

3.6. Investigation for photocatalytic reaction mechanism

To explore more insights into the photocatalytic reaction mechanism, several measurements and analysis were performed. According to the data listed in Fig. S20(a), the band gaps of CdS NRs and CdS NRs/Ni-SAO were estimated to be 2.38 and 2.26 eV, respectively (Fig. S20(b)), suggesting that light absorption range of CdS NRs is extended. Next, the photoluminescence (PL) spectra were employed to investigate the photocatalytic mechanism for hydrogen generation [38]. As shown in Fig. S21, CdS NRs had a strong PL emission peak at 675 nm, which can be attributed to the band-band PL phenomenon of the photoinduced charge carriers. Compared with CdS NRs, the addition of Ni-SAO led to a



Scheme 2. Possible mechanism for H_2 production by the photocatalytic system with Ni-SAO.

decrease on the emission peak intensity of CdS NRs. This result suggests that the recombination of photogenerated electron is suppressed, and the efficient separation of charge carriers is accelerated, letting more free electrons transfer from CdS NRs to Ni-SAO [39]. This result is also consistent with the following orbital calculation.

The orbital calculation for Ni-SAO was conducted using "Gaussian B3LYP/6-31G", giving the results shown in Fig. 5. The highest occupied molecular orbital (HOMO) of Ni-SAO was -5.43 eV and lowest unoccupied molecular orbital (LUMO) was -1.88 eV [40]. Based on that the energy of the gap of Ni-SAO (3.55 eV) is higher than that of CdS (2.4 eV) [32-34], the photogenerated electrons transfer from CdS NRs to Ni-SAO is favorable. Moreover, the transient photocurrent responses of CdS NRs/Ni-SAO exhibited much higher transient photocurrent than that of CdS NRs (Fig. 6), indicating the higher electron-hole pairs separation in CdS NRs/Ni-SAO. The electrochemical impedance spectroscopy (EIS) was also used to check the electron transfer efficiencies of CdS NRs and the mixture of CdS NRs and Ni-SAO, with the results shown in Fig. S22. The mixture of CdS NRs/Ni-SAO exhibited a much smaller arc radius than the CdS NRs, suggesting that CdS NRs/Ni-SAO has a lower electron transfer resistance and higher electrical conductivity. Additionally, based on the mixture of CdS NRs/Ni-SAO has lager surface area than Ni-SAO (Fig. S23), more active sites for the catalytic hydrogen evolution reactions are provided [41].

Together the above observation, analysis, with the reported procedures [42-44], a possible photocatalytic mechanism for H₂ production is presented in Scheme 2. Under visible light, the electrons are excited from the valance band to the conduction band (CB) of CdS in the process of photocatalytic hydrogen production [45], and the electron transfer from CdS to Ni-SAO is workable from the thermodynamic point [46]. This is like that the electron in the CB of a semiconductor is transferred to a metal [47-49]. Then, the electrons generated from CdS are transferred to Ni-SAO and directly react with the adsorbed water/H⁺ to yield H₂. Meanwhile, ascorbic acid (sacrificial reagent) can provide electrons for the valance band of CdS, and photogenerated holes are trapped.

4. Conclusions

In summary, we demonstrate the synthesis of a square plane nickel complex, Ni-SAO, which has been fully characterized. Ni-SAO exhibits good photocatalytic and electrocatalytic activity for H_2 production. Based on that Ni-SAO can effectively extend the visible light absorption region of CdS NRs and reduce the recombination rate of photoinduced electrons in CdS NRs, as a co-catalyst, Ni-SAO can photo-catalyze hydrogen evolution. Moreover, DFT calculation of Ni-SAO also indicates that the electrons in the CB of CdS can be transferred to the nickel center of Ni-SAO. This finding may afford a new method for the design of catalyst for hydrogen evolution.

CRediT authorship contribution statement

Chun-Li Wang: Data curation, Formal analysis, Investigation, Writing – original draft. **Hao Yang:** Formal analysis, Investigation. **Juan Du:** Formal analysis, Investigation. **Shu-Zhong Zhan:** Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was financially supported by the National Science Foundation of China (No. 21271073 and 21875074), and the Student Research Program (SRP) of South China University of Technology.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2021.108780.

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