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Synthesis of bio-inspired mononuclear nickel hydrogen production catalysts and photocatalytic efficiency improvement with porphyrin covalently functionalized graphene nanohybrid



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ABSTRACT

Eight nickel complexes with chelating *N*-substituted bis(diphenylphosphanyl)amine and 1,2-benzenedithiolate or 3,4-toluenedithiolate, $[RN(PPh_2)_2]Ni(1,2-SC_6H_4S)$ $[R = CH(CH_3)_2, 1; CH_2CH(CH_3)_2, 2; CH_2CH_2CH_2, 3; CH_2Ph, 4]$ and $[RN(PPh_2)_2]Ni[3,4-SC_6H_3(CH_3)S]$ $[R = CH(CH_3)_2, 5; CH_2CH(CH_3)_2, 6; CH_2CH_2CH_3, 7; CH_2Ph, 8]$, were synthesized and structurally characterized. The measurement of the electrochemical properties revealed that complex 4 can catalyze protons to hydrogen (H_2) under weak acidic conditions. Complex 4 can also be used as a molecular catalyst for light-driven H₂ evolution with a proton source, a photosensitizer, and an electron donor. Furthermore, by using tetraphenylporphyrin (TPP) amide-covalently functionalized graphene oxide (GO) nanohybrid (TPP-NH-GO) as a photosensitizer, the efficiency of photocatalytic H₂ production of complex 4 in aqueous ethanol solution had been astonishingly improved over than for the photocatalytic systems without GO. This result suggests that the excellent properties of GO with respect to electron transfer, surface area, adsorptivity, and hydrophilicity may promote the performance of the photocatalytic H₂ production system to a certain extent.

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1. Introduction

Hydrogen (H₂) is a clean and renewable energy source that can potentially replace the fossil fuels. A photoinduced H₂ production system always consists of a photocatalyst, a photosensitizer, and an electron donor [1–5]. A large number of photocatalysts have been synthesized to produce H₂ in the presence of a photosensitizer and an electron donor upon irradiation [6–14]. However, noble-metal-free photocatalysts such as nickel-containing complexes [12,15] are relatively rare in the literature. Eisenberg and co-workers [16] recently reported a series of mononuclear nickel complexes with pyridine thiolate or pyrimidine thiolate, and these nickel complexes were found to be molecular catalysts for lightdriven H₂ evolution in the presence of fluorescein as the photosensitizer and triethylamine as the electron donor. On the other hand, nickel complex precatalysts have received considerable attention because of their high activity in the vinyl polymerization of norbornene [17–20]. These nickel complexes always contain chelating bidentate ligands such as N^N [21], N^P [22], and P^P [23].

Graphene, a zero-gap semiconductor, is a thin layer of carbon atoms that are bonded together in a hexagonal lattice, which displays remarkable electron mobility at room temperature [24,25]. As the most stable form of carbon under standard conditions, graphite is a three-dimensional carbon-based material made up of layers of graphene. In oxidation of graphite using strong oxidizing agents, oxygenated functionalities are introduced to the graphite structure that not only expand the layer separation, but also make the material hydrophilic. This property enables graphite oxide to be exfoliated in water by sonication, ultimately producing singleor few-layer graphene, which is known as GO [26]. The unique π -electronic structure, together with the relatively high surface area, provides GO with predominant characteristics as an excellent adsorbent for aromatic compounds, based on π - π interaction between the aromatic ring of the complex and the GO's basal planes [27].



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Scheme 1. The suggested process of photocatalytic H₂ production for a bio-inspired photocatalytic system including a mononuclear nickel complex and a porphyrin covalently functionalized graphene nanohybrid.

In this paper, inspired by Eisenberg's studies, we strove to make the mononuclear nickel complex (catalyst) be adsorbed onto the surface of TPP (photosensitizer) amide-covalently functionalized GO nanohybrid (TPP-NH-GO) through π - π interaction between the aromatic ring and GO's basal planes, with the aim of establishing a new bio-inspired photocatalytic H₂ production system (Scheme 1). The purpose of our work is to improve the efficiency of H₂ production for the photocatalytic system in an ethanol aqueous solution by utilizing GO's outstanding hydrophilicity and electron transfer characteristics and then to attempt to find a promising approach for the direct conversion of solar energy into storable hydrogen fuel.

2. Experimental

2.1. Materials and methods

Et₃N, 1,2-HSC₆H₄SH, 3,4-HSC₆H₃(CH₃)SH, ascorbic acid (H₂A), acetic acid (HOAc), ethanol (EtOH), alumina paste, Triton X-100, and N,N'-dimethyl-4,4'-bipyridium (methylviologen, MV^{2+}) were available commercially and were used as received. Dichloromethane (CH₂Cl₂) was distilled from CaH₂ under N₂ and ferrocene was recrystallized from hexane before use. [RN(PPh₂)₂]NiCl₂ $[R = CH(CH_3)_2, CH_2CH(CH_3)_2, CH_2CH_2CH_2CH_3, CH_2Ph]$ [28], TPP [29], TPP-NH-GO [30], and tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) [31] were prepared according to literature procedures. GO was prepared by the modified Hummers method [32]. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker 500 MHz spectrometer. Electrospray ionization mass spectrometry (ESI-MS) was performed on a Bruker Micro TOF Q-II instrument. Elemental analyses were obtained by a Germany Elementar Vario EL analyzer. Ultraviolet-visible (UV-vis) spectral measurements were performed with a Shimadzu UV-3600 spectrophotometer. The steady-state fluorescence spectra were carried out using an F-97 fluorospectrophotometer. Fourier transform infrared (FTIR) spectra were obtained by a Thermo Scientific Nicolet AVATAR 360 infrared spectrophotometer. Transmission electron microscopy (TEM) measurements were performed using a Philips Tecnai G2F20 microscope at 200 kV. Electrochemical measurements were recorded on a CHI 660D electrochemical station. H₂ production experiments were performed in a photocatalytic reactor (USA ACE GLASS, Vineland, NJ). The generated photoproduct, H₂, was detected by gas chromatography (GC) analysis (CP 3800 Varian) using nitrogen as the carrier gas with a TDX-01 column and a thermal conductivity detector. The single crystals were mounted on Rigaku MM-007 CCD diffractometer.

2.2. Synthesis of [RN(PPh₂)₂]Ni(1,2-SC₆H₄S) [R = CH(CH₃)₂, **1**; CH₂CH (CH₃)₂, **2**; CH₂CH₂CH₂CH₂CH₃, **3**; CH₂Ph, **4**]

To a solution of $[RN(PPh_2)_2]NiCl_2 (0.2 mmol) and 1,2-HSC_6H_4SH (0.2 mmol) in CH_2Cl_2 (20.0 mL) was added Et_3N (6.0 × 10⁻² mL, 0.4 mmol), and the new mixture was stirred for 1 h at room temperature. The solvent was washed with H₂O (10.0 mL) to remove Et_3NHCl and then the solvent was reduced in vacuo. The residue was subjected to TLC separation using CH₂Cl₂ as eluent. From the main red band, the target products [RN(PPh_2)_2]Ni(1,2-SC_6H_4S) were obtained as red solids in 70–90% yields.$

2.3. Synthesis of [RN(PPh₂)₂]Ni[3,4-SC₆H₃(CH₃)S] [R = CH(CH₃)₂, **5**; CH₂CH(CH₃)₂, **6**; CH₂CH₂CH₂CH₂CH₃, **7**; CH₂Ph, **8**]

To a mixture of $[RN(PPh_2)_2]NiCl_2$ (0.2 mmol) and 3,4-HSC₆H₃(CH₃)SH (0.2 mmol) in CH₂Cl₂ (20.0 mL) was added Et₃N (6.0×10^{-2} mL, 0.4 mmol), and then the new mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure after being washed with H₂O (10.0 mL) to remove Et₃NHCl. The residue was subjected to TLC separation using CH₂Cl₂ as eluent, and the target products [RN(PPh₂)₂]Ni (3,4-SC₆H₃(CH₃)S) were obtained as red solids from the main red band in 77 93% yields.

2.4. X-ray structure determination

A single crystal of **1–5** or **7** was mounted on the diffractometer. Data were collected at 113(2) K using a graphite monochromator with Mo K α radiation ($\lambda = 0.71073$ Å) in the $\omega - \phi$ scanning mode. Data collection, reduction, and absorption correction were performed by the CRYSTALCLEAR program [33]. The structure was solved by direct methods using the SHELXS-97 program [34] and refined by SHELXL-97 full-matrix least-squares techniques [35] on F^2 . Hydrogen atoms were located using the geometric method. Details of crystal data, data collection, and structure refinement are summarized in Tables S1 and S2 in the Supplementary Material.

2.5. Electrochemistry

Electrochemical measurements of **4** were performed on an electrochemical potentiostat at a scan rate of 0.1 V s^{-1} . The voltammogram was obtained on a three-electrode cell in 0.1 M *n*-Bu₄NPF₆/CH₂Cl₂ under N₂. The working electrode was a glassy carbon disk (diameter: 3 mm), the counter electrode was a Pt wire, and Ag/Ag⁺ (0.01 M AgNO₃/0.1 M *n*-Bu₄NPF₆ in CH₂Cl₂) was used as the reference electrode. The working electrode was polished with 5- and 2-µm alumina paste and sonicated in water prior to use. All potentials are quoted against the ferrocene/ferrocenium (Fc/Fc⁺) potential.

2.6. Photocatalytic H_2 evolution

A certain amount of catalyst **4** (2.5 mg, 3.7×10^{-6} mol) was dissolved in 5.0 mL ethanol to make a solution. An H₂A aqueous solution (0.1 M) was prepared, and its pH value was determined by a pH meter and was adjusted with sodium hydroxide solution or hydrochloric acid. The content ratio of the TPP moiety of TPP-NH-GO was determined from the element N through elemental analysis. We obtained the content of TPP as 4.4×10^{-7} mol/ mg of TPP-NH-GO by calculating the results of the elemental analysis. Ethanol solutions of the catalyst (0.2 mL, 1.5×10^{-7} mol), a certain amount of photosensitizer (2.2×10^{-7} mol, based on TPP), and H₂A aqueous solution (4.8 mL, 4.8×10^{-4} mol) were mixed in a quartz tube for photocatalytic H₂ production. When TPP was used as a photosensitizer, Triton X-100 (0.15 mL) was used as a surfactant to increase the dispersion of TPP in an aqueous ethanol solution and methyl viologen (MV^{2+} , 0.4 mg, 1.6 \times 10⁻⁶ mol) was used as an electron mediator. The dosages of MV²⁺ and Triton X-100 were referenced to the literature [36]. The sample was saturated with nitrogen gas to eliminate oxygen. The reactor was sealed with an airtight cap. Then the solution was kept swirling by a magneton during the photocatalytic process. The light source was an Hg lamp (450 W) with a cutoff filter (λ > 380 nm). The generated photoproduct of H₂ was characterized by GC analysis. The H₂/N₂ (1.0 mL, H₂ content is 0.477 vol.%) was injected as an internal standard for quantitative GC-TCD analysis. After irradiation, the amount of H₂ evolved was measured and calculated by comparing it with the integral area between a 1.0 mL sample in quartz tube and the internal standard.

3. Results and discussion

3.1. Synthesis and characterization

The mononuclear nickel complexes **1–8** could be prepared in good yields of 70–93%, involving the condensation reactions of the precursors $[RN(PPh_2)_2]NiCl_2$ with 1,2-benzenedithiol or 3,4-toluenedithiol and Et₃N in CH₂Cl₂ (Schemes 2 and 3). The new complexes **1–8** are air-stable red solids, which have been characterized by NMR and ESI-MS spectroscopy. And the detailed

data of NMR and ESI-MS are presented in Supplementary Material. In addition, there are three types of phenyl groups in complex 4, and we assign the signals of the phenyl groups in detail according to its chemical shifts and coupling constants. As shown in Fig. S1, the ¹H NMR spectra of **4** show a quadruplet at δ 7.84 ppm and two triplets at δ 7.55 and 7.44 ppm for the phenyl protons of PPh₂ groups, two quadruplets at δ 7.40 and 6.79 ppm with a coupling constant of 3 Hz for the phenyl protons of benzenedithiolate, two triplets at δ 7.04 and 6.89 ppm, and a doublet at δ 6.46 ppm for the phenyl protons of the benzyl group. The ³¹P{¹H} NMR spectra of complexes 1-8 display a singlet in the region of δ 60.74-65.93 ppm for the two phosphorus atoms of RN(PPh₂)₂ chelated to the nickel atom to form a four-membered ring. The ${}^{13}C{}^{1}H{}$ NMR spectrum of **4** exhibits a triplet at δ 147.95 ppm and two singlets at δ 127.69 and 121.36 ppm for the phenyl carbons of benzenedithiolate, four singlets at δ 134.61, 129.16, 128.48, and 128.03 ppm for the phenyl carbons of the benzyl group, and three triplets at δ 133.26, 130.07, and 128.98 ppm and a singlet at δ 132.13 ppm for the phenyl carbons of the PPh₂ groups in Fig. S2.

3.2. X-ray crystal structures

The molecular structures of 1–5 and 7 were further analyzed by X-ray diffraction analysis. While ORTEP views are shown in Figs. S3a-3f, selected bond lengths and angles are displayed in Tables S3 and S4 in the Supplementary Material. Since 1–5 and 7 are isostructural, we only describe 1 in detail. Complex 1 is composed of a central nickel atom coordinated with two phosphorus atoms, P1 and P2, of (CH₃)₂CHN(PPh₂)₂ and two sulfur atoms, S1 and S2, of benzenedithiolate. The nickel atom Ni1 is located in a slightly distorted square-planar coordination sphere with 0.0418 Å deviation from the plane defined by P1, P2, S1, and S2 and the sum of the bond angles around Ni1 atom being 359.96°. The four-membered metallocycle Ni1P1N1P2 and the fivemembered metallocycle Ni1S1C1C6S2 are almost coplanar, with mean deviations of 0.0128 and 0.0066 Å, respectively. The dihedral angles between the planes Ni1S1C1C6S2 and Ni1P1N1P2 or C1C2C3C4C5C6 are 175.2° and 173.9°, respectively, close to the corresponding nickel dithiolate complexes containing diphosphine ligands [37,38]. The sum of the bond angles around the N1 atom is 357.39°, which means that the N1 atom adopts sp² hybridization in the solid state due to the influence of coordination. The Ni-P bond distances [2.1435(6) and 2.1625(6) Å], the Ni-S bond distances [2.1505(6) and 2.1589(6)Å], and the P1-Ni1-P2 bond angle [73.10(2)°] are comparable to those of the analogous complexes [39-41].

3.3. Electrochemistry of complex 4

The electrochemical properties of complex **4** were studied by cyclic voltammetry. As displayed in Fig. 1, **4** shows a quasi-reversible reduction at -2.06 V, which can be assigned to



Scheme 2. Preparation of complexes 1-4.



Scheme 3. Preparation of complexes 5-8.



Fig. 1. Cyclic voltammogram of 4 (1.0 mM) in 0.1 M $\textit{n-Bu}_4 NPF_6/CH_2Cl_2$ at a scan rate of 0.1 V s^-1.

the one-electron reduction process from Ni^{II} to Ni^I [42]. We further study the electrochemical behavior of complex **4** in the presence of HOAc (0–10.0 mM). As shown in Fig. 2, the current intensity at -2.06 V increases remarkably with sequential addition of HOAc, and the current intensity has a linear correlation with the added HOAc concentration (as shown in the inset), which indicate an electrochemical catalytic process [16,43,44].

3.4. The TEM images, schematic representations of the structures, and FTIR of GO and TPP-NH-GO

The TEM images and schematic representations of the structures of GO and TPP-NH-GO are compared in Fig. 3. From Fig. 3a, it can be seen that the typical wrinkle morphology and very thin layers of GO were as shown in the literature [45]. The result is in accord with the schematic representation of the structure of GO (Fig. 3b). As shown in Fig. 3c, the edge of GO was significantly roughened by the coverage of soft material. This phenomenon indicates that 5-4(aminophenyl)-10,15,20-triphenylporphyrin (TPP- NH_2) has been successfully attached to the GO edge by covalent bonds [30], just as in the schematic representation of TPP-NH-GO structure (Fig. 3d). The FTIR spectra of GO and TPP-NH-GO are exhibited in Fig. 4. The peak at 1720 cm⁻¹ is characteristic of the C=O stretch of the carboxylic group on the GO, according to reported data [30]. And a new broad band emerges at 1642 cm⁻¹ of TPP-NH-GO for the C=O characteristic stretching band of the amide group [46]. This result also suggests that TPP-NH-GO was synthesized successfully through the covalent bond.



Fig. 2. Cyclic voltammogram of **4** (1.0 mM) with HOAc (0–10.0 mM) in 0.1 M n-Bu₄NPF₆/CH₂Cl₂ at a scan rate of 0.1 V s⁻¹. Inset: current intensity versus HOAc concentration.

3.5. Light-driven H_2 evolution of complex 4

The photocatalytic experiments for H₂ production were performed using an Hg lamp (450 W) with a cutoff filter ($\lambda > 380$ nm) in the presence of a sacrificial electron donor (H₂A, 0.1 M), a photosensitizer (4.4×10^{-5} M, based on TPP), and a catalyst (complex **4**, 3.0×10^{-5} M) in aqueous ethanol solution (V_{EtOH} : V_{H2O} = 1:24). In order to study the influencing factors of the light-driven H₂ evolution system, the control experiments were performed, and the results are shown in Fig. 5. The results suggest that H₂A, TPP-NH-GO, **4**, and irradiation are all necessary for H₂ evolution. Only trace or unobservable amounts of H₂ are evolved in the absence of any of the components.

Moreover, in order to validate our assumption, we investigated the effect of GO on the efficiency of H_2 production by the photocatalytic system using the different photosensitizers, such as TPP-NH-GO, a mixture of TPP and MV^{2+} (which was often used as an electron acceptor to improve the efficiency of electron transfer in the photocatalytic system [47]), and only TPP under the same conditions. Triton X-100 was used as a surfactant to increase the dispersion of the organic photosensitizer (TPP) in an aqueous ethanol solution in the above experiments. As shown in Fig. 6, the efficiency of H_2 production was improved several times when TPP-NH-GO was used as a photosensitizer. These results may be attributed to the effective electron transfer from the TPP group to complex **4** adsorbed onto the GO surface by the mediation role of the GO moiety in TPP-NH-GO nanohybrids.



Fig. 3. The TEM (bar scale 20 nm) images, GO (a) and TPP-NH-GO (c), and the schematic representations of the structure, GO (b) and TPP-NH-GO (d).



Fig. 4. FTIR spectra of GO and TPP-NH-GO.

3.6. UV-vis spectrum and fluorescence spectrum

The photophysical properties of GO, TPP, TPP-NH-GO, and **4** (Fig. 7) were studied in order to verify further the efficiency



Fig. 5. The amount of photocatalytic H₂ evolution over (a) complex **4**, TPP-NH-GO, and H₂A; (b) TPP-NH-GO and H₂A; (c) complex **4** and TPP-NH-GO; (d) complex **4** and H₂A, in aqueous ethanol solution (V_{EtOH} : V_{H2O} = 1:24) with irradiation time 5 h. (e) Complex **4**, TPP-NH-GO, and H₂A in an aqueous ethanol solution (V_{EtOH} : V_{H2O} = 1:24) without light. In all of the above, complex **4** is 3.0 × 10⁻⁵ M; TPP-NH-GO of S of 4.4×10^{-5} M based on TPP; and H₂A is 0.1 M, pH 4.0.



Fig. 6. Amount of photocatalytic H₂ evolution over (a) complex **4**, H₂A, TPP-NH-GO $(4.4 \times 10^{-5} \text{ M} \text{ based on TPP})$, and Triton X-100; (b) complex **4**, H₂A, TPP $(4.4 \times 10^{-5} \text{ M})$ with MV²⁺ (3.2 × 10⁻⁴ M), Triton X-100; (c) complex **4**, H₂A, TPP $(4.4 \times 10^{-5} \text{ M})$, and Triton X-100. In all of the above, complex **4** is $3.0 \times 10^{-5} \text{ M}$; H₂A is 0.1 M, pH 4.0 in aqueous ethanol solution (V_{EtOH} : V_{H2O} = 1:24); Triton X-100 is 0.15 mL; irradiation time is 5 h.



Fig. 7. UV–vis absorption of **4** (10.8 mg L⁻¹), GO (50.0 mg L⁻¹), TPP (5.4×10^{-2} - mg L⁻¹), and TPP-NH-GO (60.0 mg L⁻¹) in DMF (left; different concentrations were used for better comparison.); Fluorescence spectroscopy of TPP and TPP-NH-GO in DMF (right) with the normalization if the absorbance of the Soret band excitation wavelength (419 nm) at the same value (0.024).

improvement effect of electron transfer by the GO moiety in the TPP-NH-GO nanohybrid. The UV-vis absorption spectrum of TPP-NH-GO exhibits a strong Soret absorption band at 420 nm and Q-bands at 517, 552, 591, and 652 nm, which are slightly red shifted upon the corresponding absorption of TPP (Soret band: 417 nm; Q-bands: 514, 547, 589, and 647 nm). This illustrates that the photosensitizer porphyrin ring has an interaction at ground state with GO.

The fluorescence spectra of TPP and TPP-NH-GO showed that both of them have two emission peaks. The emission peaks of TPP-NH-GO (651 nm and 712 nm) are quenched by 80.6% upon TPP (650 nm and 713 nm), which was probably caused by the intramolecular electron transfer [48]. Moreover, since the spectroscopic overlaps between the emission of the TPP group and the absorption of **4** (298 nm) or GO (mostly below 600 nm) are limited, the energy transfer from the excited photosensitive group to **4** or GO can be nearly negligible [49]. So we speculate that the photoexcited electron is likely to transfer to the catalyst by the mediation of GO (Scheme 1), which may be the key reason for the increased efficiency of photocatalytic H_2 production.

4. Conclusions

In summary, eight nickel benzenedithiolate complexes. 1-8. were successfully synthesized with high yields and fully characterized by spectroscopy and X-ray diffraction analysis. X-ray crystal structural analysis revealed that these nickel complexes consist of a four-membered ring, a five-membered ring, and a sixmembered ring and these rings are almost coplanar, forming a slightly distorted square-planar coordination of the central nickel atom. Besides, complex **4** exhibits activity for electrocatalytic H₂ production in the presence of HOAc in CH₂Cl₂. Then we synthesized tetraphenylporphyrin amide-covalently functionalized graphene oxide nanohybrid (TPP-NH-GO) and introduced TPP-NH-GO and complex 4 into a photocatalytic system as a photosensitizer and a catalyst, respectively. Considering the advantages of GO's hydrophilicity, adsorption, and electron transfer properties, the efficiency of photocatalytic H₂ production of complex 4 had been improved obviously in an aqueous ethanol solution through a contrast test. We hope this study may open up a promising way to further promote productivity in direct conversion of solar energy into hydrogen energy using water-insoluble organic or organometallic compounds.

The Supplementary Material comprises crystal data and ORTEP views of 1-5 and 7; NMR and ESI-MS data of 1-8; the ¹H NMR spectra and ¹³C{¹H} NMR spectra of **4**.

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Appendix A. Supplementary material

CCDC 1495981–1045586 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2016.12.014.

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