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Neutral nickel(II) phthalocyanine as a stable catalyst for visible-light-driven hydrogen evolution from water

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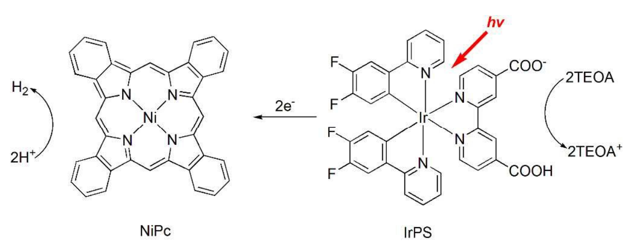
Neutral nickel(II) phthalocyanine was found to be an efficient and stable catalyst for photocatalytic H_2 evolution from water when coupled with an iridium complex as the photosensitizer and triethanolamine as the sacrificial electron donor. The result shows that the Ni-N sigma bond can enhance the stability of catalyst.

The production of hydrogen through artificial photosynthesis is an attractive and sustainable strategy for addressing both global energy and environmental problems.[1-3] The overall water splitting process can be divided in to two half reactions: water reduction for H_2 evolution and water oxidation for O_2 production. To date, only a few photocatalytic materials reported in literatures have enabled water to be decomposed into hydrogen and oxygen in a photocatalytic system.[4-6] Most of the researches with respect to H_2 production have focused on the water reduction half-reaction.[7,8] With respect to the H_2 evolution half-reaction, molecular hydrogen evolution system containing a photosensitizer (PS), a water reduction catalyst (WRC) and a sacrificial electron donor has been intensively investigated over the past decades owing to its great potential for solar-to-H_2 conversion.[9-15] So far, most of the highly efficient WRCs are based on noble metals, such as colloidal Pt,[16-19] Pd,[20-22] Ru,[23] $[Rh(dtbpy)_3]^{3+}$ (dtbpy = 4,4'-Di-tert-butyl-2,2'-bipyridine) and so on.[24-26] However, the practical application of these WRCs is limited by their high price, and it is highly desirable to develop noble-metal-free WRCs for molecular hydrogen evolution system.

During the past decade, much attention has been paid to design, synthesis, and study new noble-metal-free WRCs for solar hydrogen production, such as cobaloxime complexes,[27-31] $[Fe_3(CO)_{12}]$,[32,33] polypyridine cobalt complex,[34,35] and [Fe-Fe] hydrogenase analogues.[36-39] Very recently, the synthetic nickel-thiolate complexes, developed by Eisenberg and co-workers, have been emerged as probably the most active hydrogen evolution catalysts for efficient photocatalytic H_2 evolution.[40-42] However, these Ni(Ⅱ)-based photocatalytic H_2 generation systems were short-lived, and a further improvement of solar-to-H_2 conversion efficiency and chemical stability are still needed. Therefore, exploiting Ni(Ⅱ)-based catalysts with excellent durability and activity is a great challenge for molecular photocatalytic H_2 evolution system. In our recent study, we reported a robust noble-meter-free WRC of $[Ni(bpy)_3]^{2+}$ (bpy = 2,2'- bipyridine) for H_2 evolution using an iridium complex as the PS and triethanolamine (TEOA) as the sacrificial electron donor, and the highest turnover number (TON) with respect to $[Ni(bpy)_3]^{2+}$ achieved over 520.[43] However, most activity of $[Ni(bpy)_3]^{2+}$ WRC was lost with a few hours of irradiation, an important reason is that the breaking of Ni-N dative bonds occurs between the nickel centre and the ancillary diimine liagnds. Therefore, the development of more stable Ni-based WRCs would be of great value for obtaining long-term solar H_2 generation system. In our previous studies, we found that the replacement of a metal-N dative bond with a metal-N or metal-C sigma bond was identified to be an efficient way to improve the stability of metal complexes.[26,35] Hence, it is highly desirable to develop stable Ni(Ⅱ)-based catalysts by introduction of sigma bonds between the metal centre and ligands.



Scheme 1. Photocatalytic H_2 production system using NiPc as the catalyst and IrPs as the photosensitizer.

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Herein, we report a stable and efficient noble-metal-free WRC of neutral nickel(II) phthalocyanine (NiPc) for visible-light-driven hydrogen production in a homogeneous system with [Ir(dfppy)$_2$(dcbpy)] (dfbpy = 2-(3,4-difluorophenyl)pyridine, Hdcbpy = 4-carboxy-2,2′-bipyridine-4′-carboxylate) as the PS and triethanolamine (TEOA) as the sacrificial electron donor. The iridium complex was used as the PS due to its superior photocatalytic performance and excellent stability for H_2 evolution, which has been most extensively investigated in homogeneous system.[16-23] The photocatalytic results demonstrate that the existence of Ni-N sigma bond can suppress the liberation of the ligand from nickel(II) complex. This is the first time that such a neutral nickel(II) phthalocyanine complex has been used in this capacity.

Photocatalytic H_2 production experiments were carried out in 100 mL of acetone/water mixed solvent by using the NiPc complex as the catalyst, IrPS as the PS and TEOA as the sacrificial electron donor under visible light irradiation (λ > 420 nm). Control experiments under visible light irradiation show that the presence of all three components (NiPc, IrPS and TEOA) is necessary in order to evolve H_2. If the NiPc catalyst was replaced by a simple nickel salt of nickel(II) nitrate hexahydrate, no H_2 evolution produced in reaction solution under visible light irradiation, even at higher concentration of the nickel salt (0.5 mM). The result rules out any contribution of the simple nickel cation as an active catalytic species for photoreduction of water to produce H_2. In homogeneous photocatalytic H_2 evolution system, the electrostatic properties of solvent play an important role in the rates of electron transfer between the WRC and PS components, and the solvent environment has significantly effect on the H_2 production activity of reaction system.[26,44] Therefore, the influence of solvent on the H_2 evolution performance of NiPc-IrPS-TEOA system was investigated. As shown in Figure 1(a), the photocatalytic H_2 evolution activity of NiPc-IrPS-TEOA system increases at higher acetone concentrations, and the maximum H_2 production in the present system was obtained at the optimal solvent ratio of 8:2 acetone/water, and the TON with respect to NiPc was found to be 112. However, a further increase of acetone concentration leads to a reduction of H_2 production activity. When photoinduced H_2 evolution system was conducted in acetone solution without water, the TON with respect to NiPc catalyst was reduced to 12 after 8 h of visible light irradiation. The highest TON with respect to NiPc catalyst was observed in 8:2 acetone/water mixed solution, which could be assigned to the balance between the lower dielectric constant of acetone and the need for water as a proton source for H_2 evolution. A similar phenomenon has been observed for homogeneous photocatalytic H_2 production systems in previous studies.[26,35]

It is already known that there are two quenching pathways for the excited state of PS, oxidative quenching and reductive quenching.[24,26] To gain more insight into the quenching processes and to identify the possible reaction mechanism, quenching studies were tested by using NiPc and TEOA as an oxidative and reductive quencher, respectively. As shown in Figure S1, the excited state of PS can be quenched by

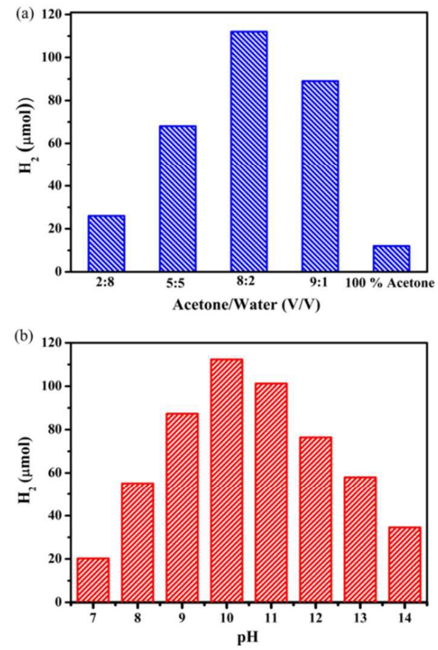

Figure 1. (a) Influence of solvents on photocatalytic H_2 production in systems containing 20 μM NiPc, 100 μM IrPS, and 0.2 M TEOA in acetone/water solutions under visible light irradiation (λ > 420 nm) at pH 10. (b) Effect of pH value on the initial rate of hydrogen in 8:2 acetone/water solution containing 20 μM NiPc, 100 μM IrPS and 0.2 M TEOA under visible light irradiation (λ > 420 nm), the pH value of solution was adjusted by adding 0.1 M HCl or 0.1M NaOH aqueous solution.

either NiPc as an electron transfer acceptor or by TEOA as an electron transfer donor. Both reductive and oxidative quenching processes follow Stern-Volmer behavior (Figure S2) with Kq values being 1.61×10^{10} M^{-1} s^{-1} and 1.80×10^{8} M^{-1} s^{-1} for NiPc and TEOA, respectively. Notably, a higher quenching constants was observed for the oxidative quenching behavior of IrPS* by NiPc catalyst, indicating that IrPS* was quenched by NiPc via an oxidative quenching pathway in NiPc-IrPS-TEOA system.

Previous researchers have suggested that the pH values can effectively influence the H_2 evolution rates of photocatalytic system.[45,46] Therefore, the effect of the pH values on the photocatalytic activities was investigated in the present study. The pH values of H_2 evolution systems were adjusted to those desired for the photocatalytic tests by addition of either 0.1 M HCl or 0.1 M KOH aqueous solution. As shown in Figure 1(b), the maximum H_2 production rate of 14.5μmol h^{-1} is observed at initial pH value of 10, and the TON with respect to NiPc catalyst was found to be 112. The decrease in H_2 evolution rate at lower pH values is most likely due to the lower TEOA concentration in solution, and the TEOA is a key component to reduce IrPS$^+$ to regenerate the PS. When the pH values below 10, the TEOA is protonated to form an ineffective sacrificial electron donor. However, a further increase in the pH values of H_2 evolution systems to 11 12, 13 and 14, which resulted in a decreasing hydrogen evolution rate. The decreasing hydrogen evolution activity of NiPc-IrPS-TEOA system could be attributed to the lower proton concentration

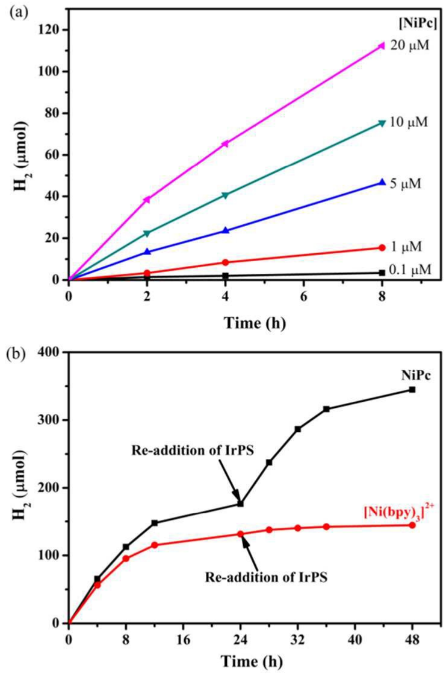

Figure 2. (a) Photocatalytic H_2 production traces with different initial concentrations of NiPc in 8:2 acetone/water solutions containing 1~20 μM NiPc, 100 μM IrPS and 0.2 M TEOA under visible light irradiation (λ > 420 nm) at pH 10. (b) Stability test for NiPc-IrPS-TEOA photocatalytic H_2 evolution system in 8:2 acetone/water solution containing 20 μM NiPc, 100 μM IrPS and 0.2 M TEOA under visible light irradiation (λ > 420 nm), pH =10.

at higher pH values. As a consequence, a suitable pH value of reaction solution is crucial for optimizing the photocatalytic activity of NiPc-IrPS-TEOA system.

After optimizing the conditions, including the composition of the solvents and pH, the effect of NiPc concentrations on H_2 production activities was also investigated. As shown in Figure 2(a), the H_2 production rate was found to depend on the concentration of catalyst. When the concentration of NiPc was increased to 20 μM from 0.1 μM, the amount of H_2 was increased to 112.2 from 3.4 μmol after 8 h of visible light irradiation. However, the TON with respect to NiPc catalyst is also lowering from 680 to 112 when the concentration of NiPc catalyst changes from 0.1 to 20 μM. The amount of H_2 produced in photocatalytic system does not increase linearly with catalyst concentration, which could be contributed to the limiting concentration of IrPS photosensitizer (Figure S3). Furthermore, the apparent quantum yield of 0.82% was obtained at 420 nm in 8:2 acetone/water solution containing of 20 μM NiPc, 100 μM IrPS and 0.2 M TEOA at pH 10.

When irradiation time was prolonged to 24 h, the H_2 evolution rate in NiPc-IrPS-TEOA system decreased obviously. As there was a large amount of TEOA existed in the photocatalytic system, the deactivation of H_2 evolution system should be caused by the consumption of NiPc and/or IrPS. To reveal the reason for this deactivation, 100 μM IrPS was added into the reaction system after 24 h irradiation. As shown in Figure 2(b), the photocatalytic system with re-addition of IrPS shows an almost totally recovered activity for H_2 production under the same reaction conditions. Therefore, the deactivation of H_2 evolution system can be assigned to the decomposition of IrPS, and the nickel catalyst has sufficient stability for photocatalytic water reduction reaction. For comparison purposes, $[Ni(bpy)_3]^{2+}$ was also used as a reference under the same conditions. As shown in Figure 2(b), 115 μmol H_2 was observed in $[Ni(bpy)_3]^{2+}$-IrPS-TEOA system after 12 h of visible light irradiation, and the plot of H_2 production *vs*. time leveled off when the irradiation time was prolonged to 24 h. Notably, the experiment with re-addition of IrPS to the H_2 evolution system could not regenerate H_2 under irradiation, indicating that the deactivation of $[Ni(bpy)_3]^{2+}$-IrPS-TEOA system should be caused by the decomposition of $[Ni(bpy)_3]^{2+}$. These photocatalytic results indicate that the neutral NiPc is a more stable and efficient catalyst in the present system. Previous studies have shown that the sigma bonds exhibited in metal complexes can efficiently improve their stability for photochemical reaction.[26,35] Therefore, the most likely reason for the high stability of NiPc catalyst could be attributed to the Ni-N sigma bonds, which prevent the phthalocyanine ligand from separating from the nickel centre. Therefore, the replacement of a Ni-N dative bond with a Ni-N sigma bond is an efficient way to improve the stability of Ni-based WRCs.

Previous researches have suggested that the active sites of nickel complexes would most likely be the metal centre and the coordination atoms.[41-43] For NiPc catalyst in the present study, the proposed mechanism for H_2 evolution was shown in Figure 3. The Ni-N coordination bond as in the NiPc catalyst breaks after the complex accepts an electron from $IrPS^*$, and then the proton can absorb on nickel centre to form a proposed Ni hydride intermediate (H-NiPc).[41] Furthermore, it is proposed that the site of initial protonation in NiPc catalyst is the N atom with dechelation and that proton transfer from this ligand is important for the formation of [H-NiPc-H] complex.[41,42] The [H-NiPc-H] intermediate was transferred to [Ni-H-H-Pc] species, which could be the key intermediate for H_2 generation. More studies are needed to reveal the mechanism of neutral nickel phthalocyanine catalyst for photocatalytic H_2 production.

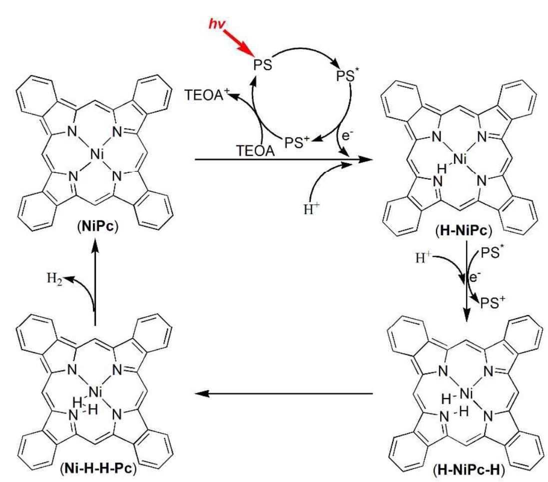

Figure 3. Proposed mechanism for the reduction of water to evolve H_2 by NiPc.

In summary, we report a neutral nickel(II) phthalocyanine complex that is an active and stable catalyst for visible-light-driven H_2 production when paired with [Ir(dfppy)$_2$(Hdcbpy)] as the photosensitizer and TEOA as the sacrificial electron donor. The total TON is up to 680 with respect to the catalyst over 8 h of visible light irradiation under optimal conditions. Due to the existence of Ni-N sigma bonds which can effectively improve the stability of NiPc, the neutral NiPc catalyst demonstrates a much higher chemical durability for solar H_2 generation than that of cationic $[Ni(bpy)_3]^{2+}$ complex. This study represents a new paradigm for constructing stable and noble-metal-free catalyst by using neutral nickel(II) phthalocyanine complex for solar hydrogen generation.

Acknowledgements

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