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2013

Cao, S. W., Liu, X. F., Yuan, Y. P., Zhang, Z., Fang, J., Loo, S. C. J., et al. (2013). Artificial photosynthetic hydrogen evolution over g-C₃N₄ nanosheets coupled with cobaloxime. *Physical chemistry chemical physics*, 15, 18363-18366.

<https://hdl.handle.net/10356/99916>

<https://doi.org/10.1039/c3cp53350f>

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Artificial Photosynthetic Hydrogen Evolution over g-C₃N₄ Nanosheets Coupled with Cobaloxime

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

We report an economic and noble-metal-free artificial photosynthetic system, consisting of g-C₃N₄ as photosensitizer and photocatalyst, and cobaloxime as co-catalyst, for H₂ generation. This system allows for effective electron transfer from excited g-C₃N₄ to Co^{III}(dmgH)₂pyCl to generate reduced cobaloxime intermediate species for efficient H₂ evolution. Transient fluorescence studies reveal that the presence of cobaloxime and TEOA promotes the population of excited electrons to transfer from g-C₃N₄, which is responsible for the high photocatalytic activity of this g-C₃N₄-cobaloxime conjugation system.

Chemical fuels production through artificial photosynthesis is one of the most promising but also challenging approaches to exploit solar radiation for renewable and clean energy generation.¹⁻⁵ The strategy of artificial photosynthetic hydrogen evolution based on semiconductor photocatalysts has been extensively used through photocatalytic water reduction.^{6,7} While in this strategy, appropriate noble metal co-catalysts, such as Pt and Pd,⁸⁻¹⁰ are usually required to suppress recombination of photogenerated charge carriers and lower down the H₂ evolution overpotential. However, the high cost of noble metals restricts their large-scale use and pushes the needs of developing co-catalysts composed by cheap and earth-abundant elements.

As an alternative way, homogeneous photocatalytic systems, consisting of photosensitizers coupled with molecular catalysts, have also been explored for hydrogen evolution reaction (HER).¹¹⁻¹³ In these systems, organic molecules or organometallic complexes serve as photosensitizers to receive light excitation. The excited electrons would transfer to the adjacent or conjugated molecular catalysts via efficient redox cycles, resulting in proton reduction into hydrogen gas. Tremendous efforts have been made on developing earth-abundant transition-metal-based HER catalysts, such as FeFe-hydrogenase analogues,¹⁴ nickel thiolates,¹⁵ and cobaloxime-based complex.¹⁶⁻²⁵ However, the instability of organic photosensitizers under light excitation is a serious problem for long-term applications. Recently, researchers have demonstrated that the CdS or CdSe quantum dots (QDs) could act as inorganic photosensitizers to couple with cobaloxime catalysts, for efficient photocatalytic H₂ evolution.^{26,27} Cobaloximes are known as cobalt(III)-based complexes that can couple with QDs to aid electrons to reduce proton via Co^{III}-Co^I redox cycles for H₂ evolution. Though the CdS/CdSe QDs are not environmentally friendly, it did reveal that the molecular catalyst could conjugate with semiconductor nanostructures to form a heterogeneous hybrid system for H₂ generation.

Fig. 1 Schematic illustration of the photocatalytic process for H₂ evolution.

Herein, we report a simple new artificial photosynthetic system using a polymeric semiconductor photocatalyst, graphitic carbon nitride (g-C₃N₄),²⁸⁻³¹ also as the photosensitizer coupled with cobaloxime (Co^{III}(dmgH)₂pyCl) as HER catalyst to produce hydrogen in aqueous solution. As a great advantage, in this noble-metal free system, both g-C₃N₄ and cobaloxime are composed by earth-abundant elements. The g-C₃N₄ photocatalyst has a small band gap (~2.7 eV) enabling

broad solar absorption, and appropriate conduction band (CB) edges that provide sufficient reduction potential for proton reduction.²⁸ Moreover, the polymeric nanosheet structure of g-C₃N₄ provides excellent thermal and chemical stability under light excitation in ambient condition. We found that in the presence of cobaloxime, the g-C₃N₄ exhibited high photocatalytic activity for hydrogen generation in aqueous solution. Further studies reveal that an effective electron transfer process can be initiated from photoexcited g-C₃N₄ to the cobaloxime which acts as active site for efficient hydrogen evolution. The proposed principle is depicted as Fig. 1.

In a typical photocatalytic experiment for H₂ evolution, 10 mg of g-C₃N₄ nanosheet photocatalysts and 2 mg of Co^{III}(dmgH)₂pyCl were dispersed into 10 mL aqueous solution of triethanolamine (TEOA, 15 vol%, pH 10.4) which serves as the sacrificial agent. As shown in Fig. 2, this mixture exhibits active H₂ evolution over 8 hours under light irradiation (350~740 nm). In control experiments, when cobaloxime was absent, very little amount of H₂ evolved from the solution (0.2 μ mol after 8-hour irradiation). And without TEOA or g-C₃N₄, no hydrogen evolution was observed. This implies that the photocatalytic H₂ evolution is mainly due to the charge transfer in the hybrid system. The direction of charge transfer between g-C₃N₄ and Co^{III}(dmgH)₂pyCl can be predicted according to the energy band structure of g-C₃N₄ and the redox potential of Co^{III}(dmgH)₂pyCl. The conduction band potential of g-C₃N₄ is known as ~-1.1 V vs. NHE,³² while the second reduction potential of Co^{II} to Co^I for Co^{III}(dmgH)₂pyCl has been reported varying from -0.88 V to -0.74 V in different solvents.^{16,25} It suggests that the electron transfer from g-C₃N₄ to Co^{III}(dmgH)₂pyCl is thermodynamically favourable, which is responsible for proton reduction into H₂.

Fig. 2 Photocatalytic H₂ evolution amount from water reduction in the presence of different components.

We note that there is an induction period of around one hour at the early stage, during which the H₂ evolution rate is relatively low. After that, we observed a steady H₂ evolution rate of ~2.6 μ mol·h⁻¹, and the apparent quantum efficiency was estimated as 0.62 % at 365 nm. In some cobaloxime involved homogeneous systems, similar induction period was also observed and could be attributed to the photoinduced accumulation of reduced cobaloxime species from the reduction of Co^{III}(dmgH)₂pyCl via multiple equilibriums.^{16,23,26} In particular, intermediate Co^I species was tracked by UV-vis spectroscopy during the photoreaction as reported by Eisenberg et al.¹⁶ However, in our system, the g-C₃N₄ based suspension show strong scattering in the whole spectral range, which overwhelms all spectrum information from other species.

In order to verify the presence of intermediate species, we stopped the photocatalytic reaction after 4 hours with different pausing time (Fig. S1). Interestingly, 1-min pausing of the reaction did not obviously affect the H₂ evolution rate. While extending the pausing time to 3 min and 5 min led to obvious decrease of H₂ evolution rate. Moreover, another 1-hour induction period was observed when continuing the photo- reaction after paused for 5 minutes. We also immediately picked up the solution once pausing the reaction, quickly separated g-C₃N₄ and tested the absorption spectrum of the clear solution. As shown in Fig. S2, a broad peak centered at around 525 nm can be observed, which was not observed in the initial solution before irradiation and might correspond to the Co^I species.^{16,33} However, this absorption band disappeared within 5 minutes when irradiation was stopped. These results indicate that the intermediate Co^I species do exist, but will degrade in the absence of irradiation.^{27,34} And the degradation product could not be recovered to cobaloxime again. As a result, the effective concentration of remained cobaloxime in the suspension became much lower comparing to that at the beginning. Therefore, re-irradiation of the suspension after 5-min pause exhibited much lower H₂ evolution rate. Nevertheless, we note that under continuous light irradiation, the intermediate Co^I species can be sustained, as evidenced by the consistent H₂ evolution rate up to 8 hours.

The H₂ evolution rate is also influenced by the solution pH as shown in Fig. S3. The maximum H₂ evolution efficiency was achieved at pH 10.4 without any adjustment by acid or base. It has been reported that in a more basic condition, the

lower proton concentration is not favorable for protonation of the Co^{I} species to form the Co^{III} hydride, which is believed to be one of the crucial intermediates for hydrogen evolution in the cobaloxime-based system.^{24,35,36} While at lower pH, the hydrogen evolution rate also decreases due to the weaker electron-donor ability of TEOA and the lower formation rate of Co^{I} species. Very recently, Sun et al. reported a similar photocatalytic system composed of g- C_3N_4 and $[\text{M}(\text{TEOA})_2]\text{Cl}_2$ ($\text{M} = \text{Ni}, \text{Co}, \text{Fe}$).³⁷ The H_2 evolution principle was also proposed to rely on the conversion of $\text{M}(\text{II})$ into $\text{M}(\text{I})$ for proton reduction.

For comparison, we also used CoCl_2 to replace $\text{Co}^{\text{III}}(\text{dmgH})_2\text{pyCl}$ for photocatalytic test in the aqueous solution of TEOA with the as-prepared g- C_3N_4 . As shown in Fig. S4, the result indicated certain amount of H_2 evolution (2.8 μmol after 8-hour irradiation), but less than that of g- $\text{C}_3\text{N}_4/\text{Co}^{\text{III}}(\text{dmgH})_2\text{pyCl}/\text{TEOA}$ system. In addition, we have also evaluated the photocatalytic H_2 evolution of the g- $\text{C}_3\text{N}_4/\text{Co}^{\text{III}}(\text{dmgH})_2\text{pyCl}/\text{TEOA}$ system under visible-light ($\lambda > 420 \text{ nm}$) irradiation. Fig. S5 shows that it did exhibit a similar trend of H_2 evolution rate under visible light irradiation, though the H_2 evolution amount (2.4 μmol after 8-hour irradiation) is less than that under 350-740 nm light irradiation (20.2 μmol after 8-hour irradiation).

Fig. 3 (a) Steady-state PL spectra and (b) transient fluorescence decay for different components in H_2O , the concentrations are the same as those in photocatalytic reaction.

Table 1. Fitted lifetimes of the fluorescence decay profiles from Fig. 3b

Species	$A_1(\%)$	$\tau_1(\text{ns})$	$A_2(\%)$	$\tau_2(\text{ns})$
g- C_3N_4	\	\	100	3
g- C_3N_4 +Cobaloxime	19.6	0.72	80.4	3
g- C_3N_4 +TEOA	19.6	0.72	80.4	3
g- C_3N_4 +Cobaloxime+TEOA	30.9	0.72	69.1	3

Steady-state photoluminescence (PL) spectra were measured with excitation at 325 nm to explore the charge transfer pathways in the g-C₃N₄-cobaloxime conjugation. As shown in Fig. 3a, the g-C₃N₄ sample exhibits a strong emission peak centered at ~450 nm. However, when Co^{III}(dmgH)₂pyCl is introduced, the intensity of this emission band immediately shows significant decrease, indicating that a fast electron transfer occurred from excited g-C₃N₄ to Co^{III}(dmgH)₂pyCl and thus promotes the non-radiative decay process from the excitation status of g-C₃N₄. This rapid charge transfer might be mediated through effective collision between g-C₃N₄ and cobaloxime-related species. The direct attachment of cobaloxime on g-C₃N₄ surfaces through chemical bonding may have limited contribution to the charge transfer process due to the relatively small surface area of g-C₃N₄ as 5.4 m²·g⁻¹ according to BET measurement. Moreover, when the electron donor TEOA was added together with Co^{III}(dmgH)₂pyCl, the g-C₃N₄ PL intensity further drops. This observation suggest that in the presence of TEOA, which can consume the photogenerated holes on g-C₃N₄, the excited g-C₃N₄ electrons effectively drive Co^{III}-Co^I redox cycles for H₂ evolution instead of recombining with holes in the g-C₃N₄ valence band (VB) through radiative decay.

We further examined the lifetime of charge carriers in the presence of different components: g-C₃N₄, g-C₃N₄/Co^{III}(dmgH)₂pyCl, g-C₃N₄/TEOA, and g-C₃N₄/Co^{III}(dmgH)₂pyCl/TEOA, by using time-resolved transient fluorescence spectroscopy as shown in Fig. 3b. Table 1 lists the fitted lifetimes of the fluorescence decay profile. The pure g-C₃N₄ sample exhibits only one radiative lifetime of 3 ns, which is associated with the photoexcited electron-hole pairs in g-C₃N₄ that eventually undergo recombination.³⁸ In the presence of Co^{III}(dmgH)₂pyCl, a shorter PL lifetime component ($\tau_1=0.72$ ns with a weighing factor $A_1 = 19.6\%$) appears, suggesting that some excited electrons undergo rapid transfer from g-C₃N₄ to Co^{III}(dmgH)₂pyCl. A similar result was obtained in the presence of TEOA, indicating that some holes on g-C₃N₄ are consumed by such electron donor. The co-existence of TEOA and Co^{III}(dmgH)₂pyCl does not alter the PL lifetimes, but A_1 increases from 19.6% to 30.9% with a corresponding decrease in A_2 . These results indicate that the presence of TEOA decreases the electron-hole recombination in g-C₃N₄ by scavenging the holes and leads to longer-lived charge separation that allows for more effective electron transfer to the cobaloxime co-catalyst and thereby promotes the photocatalytic reactions for H₂ evolution.

On the basis of the above experiment observation and spectroscopic analyses, we considered the possible mechanism for the efficient photocatalytic H₂ generation by this g-C₃N₄-cobaloxime conjugation system as follows. As shown in Fig. 1, when g-C₃N₄ receives bandgap excitation, the electrons transit from VB to CB and transfer to Co^{III}(dmgH)₂pyCl, leading to the formation of intermediate Co^I species, which is considered as an essential process for hydrogen generation catalyzed by the cobaloxime complexes.²⁴ The Co^I species are further protonated to create Co^{III}-hydride which has been considered as the rate-limiting step.¹³ The Co^{III}-hydride may undergo cleavage to evolve molecular hydrogen accompanied by generation of Co^{II} intermediates³³ that can be reduced again to Co^I by the excited electrons from g-C₃N₄ and continue the redox cycles. Certainly, the whole processes require TEOA as a sacrifice electron donor to quench the photogenerated holes on g-C₃N₄, thus suppressing the recombination of charge carriers and allowing the forward reactions.

Despite the high photocatalytic activity in the present system, the prolonged photocatalytic test showed gradually decreased H₂ evolution rate after 8 hours. By examining the suspension by TEM after 24-hour reaction (Fig. S6), we observed some cobalt oxide (Co₂O₃) particles attached on the g-C₃N₄ surface. Therefore, the drop of H₂ evolution activity may be ascribed to the hydrolysis or decomposition of Co^{III}(dmgH)₂pyCl in the basic condition during long time irradiation.^{17,27} Further studies on enhancing the stability of the cobaloxime catalyst are undergoing. In addition, we noted that the g-C₃N₄ is relatively stable and can be re-used with fresh Co^{III}(dmgH)₂pyCl, as shown in the cycling test results (Fig. S7).

In summary, we have presented a simple artificial photosynthetic system, consisting of g-C₃N₄ nanosheet as light sensitizer and photocatalyst, and cobaloxime as co-catalyst, for H₂ generation in aqueous solution. The cobaloxime Co^{III}(dmgH)₂pyCl can readily interact with the flat g-C₃N₄ nanosheet, allowing effective electron transfer from excited g-C₃N₄ to Co^{III}(dmgH)₂pyCl to generate Co^I intermediate species for efficient H₂ evolution. Further studies by transient PL decay reveal that the presence of cobaloxime and TEOA promotes the population of excited electrons to transfer to cobaloxime, which is responsible for the high photocatalytic activity of this g-C₃N₄-cobaloxime conjugation system. This study provides a new strategy for the solar-to-hydrogen conversion by combining economic semiconductors containing only earth-abundant elements with noble-metal-free molecular catalysts.

Acknowledgements

This work was financially supported by NTU Start-Up Grant (SUG), NTU seed funding for Solar Fuels Laboratory, MOE AcRF-Tier1 RG 44/11, MOE AcRF-Tier2 (MOE2012-T2-2-041, ARC 5/13) and CRP (NRF-CRP5-2009-04) from NRF Singapore. Y. P. Yuan thanks the support from the National Natural Science Foundation of China (No. 51002001). X. F. Liu and T. C. Sum acknowledge the financial support by NRF through the Singapore-Berkeley Research Initiative for Sustainable Energy (SinBeRISE) CREATE Programme.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details; Fig. S1–S4. See DOI: 10.1039/b000000x/

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