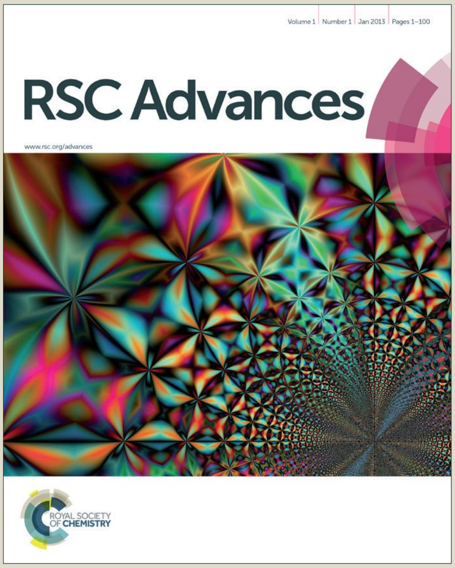
RSC Advances



ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/advances

Journal Name

ARTICLE

Co(dmgH)$_2$pyCl as a Noble-Metal-Free Co-catalyst for Highly Efficient Photocatalytic Hydrogen Evolution over Hexagonal ZnIn$_2$S$_4$

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Yanhong Gao,[a] Huaxiang Lin,[a] Shiying Zhang,[b] Zhaohui Li[a,]*

Co(dmgH)$_2$pyCl/ZnIn$_2$S$_4$ composites (dmgH = dimethylglyoxime and py = pyridine) with different amount of Co(dmgH)$_2$pyCl loaded were prepared from hexagonal ZnIn$_2$S$_4$ and Co(dmgH)$_2$pyCl via an impregnation method. The photocatalytic activity for hydrogen evolution over the as-prepared Co(dmgH)$_2$pyCl/ZnIn$_2$S$_4$ composites under visible light irradiations was investigated. It was found that the hydrogen evolution over hexagonal ZnIn$_2$S$_4$ can be significantly increased by loading Co(dmgH)$_2$pyCl as a co-catalyst. An optimum activity was achieved over 3.0 wt%-Co(dmgH)$_2$pyCl/ZnIn$_2$S$_4$ composite, with 1438.5 μmol hydrogen generated and a turnover number of 387 (based on Co(dmgH)$_2$pyCl) reached in 8 h visible light irradiations. This value is much higher than that obtained over Pt loaded ZnIn$_2$S$_4$ under similar conditions, indicating that Co(dmgH)$_2$pyCl can be a highly efficient noble-metal-free co-catalyst for photocatalytic hydrogen evolution over hexagonal ZnIn$_2$S$_4$. The mechanism for the hydrogen evolution over Co(dmgH)$_2$pyCl/ZnIn$_2$S$_4$ composite was also proposed. This work paves a way to the development of highly efficient noble-metal-free photocatalytic systems for hydrogen evolution.

Introduction

The ever increasing global demand for energy and the environmental consequences of burning fossil fuels has stimulated considerable effort to exploit renewable carbon-free energy alternatives. Semiconductor-based photocatalytic hydrogen generation is considered to be an attractive and promising strategy in solving the increasing serious energy and environmental problems.[1] Ever since the pioneering work of a photoelectron chemical cell using Pt-TiO$_2$ electrodes for hydrogen evolution reported by Fujishima and Honda in the early 1970s, a variety of inorganic semiconductors including metal oxides, sulfides and oxynitrides as well as metal-free organic semiconductors have been explored for photocatalytic hydrogen evolution.[2] Among the already reported semiconductor photocatalysts, ZnIn$_2$S$_4$, a ternary metal chalcogenide, has attracted much recent attention due to its suitable band gap (2.34-2.48eV) well responding to the visible light absorption. Previous studies have revealed that ZnIn$_2$S$_4$ exhibits two distinct polymorphs based on cubic and hexagonal lattices, and both of them are active for photocatalytic hydrogen evolution under visible light irradiations.[3] However, the photocatalytic performance for hydrogen evolution over pure ZnIn$_2$S$_4$ is low due to the short lifetime of the photo-generated electron-hole pairs.

For semiconductor-based photocatalytic hydrogen evolution, co-catalysts like noble metals Pt, Au, Rh, and their oxides RuO$_2$, Rh$_x$Cr$_{2-x}$O$_3$ are generally required.[4] These noble metal co-catalysts can suppress the recombination of the photo-generated charge carriers, lower the over potential for hydrogen evolution and provide redox reaction sites for hydrogen evolution to avoid the back reactions. However, due to the high price and the scarcity of the noble metal co-catalysts, extensive recent studies have been devoted to the development of noble-metal-free co-catalysts for photocatalytic hydrogen evolution. Transition metal sulfides like MoS$_2$, WS$_2$ and NiS, which are well-known electro-catalysts for hydrogen evolution, have been demonstrated to be excellent co-catalysts for photocatalytic hydrogen evolution.[5]

In addition to transition metal sulfides, cobaloximes, bis(dialkyl or diarylglyoximate) complexes composed of earth-abundant element cobalt, have also been reported for hydrogen evolution based on electro-catalytic studies as well as photochemical investigations.[6] In particular, [Co(dmgH)$_2$pyCl] (dmgH = dimethylglyoxime and py = pyridine) has already been used as an effective co-catalyst for photocatalytic hydrogen evolution over a

---

[a] State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350002, P. R. China E-mail: zhaohuili1969@yahoo.com

[b] Hunan Key Laboratory of Applied Environmental Photocatalysis, Changsha University, Changsha, Hunan, P. R. China

Electronic Supplementary Information (ESI) available: Experimental details; characterizations; figures of XPS, SEM, TEM, HRTEM, EDS, IR, XRD; table of ^{1}H NMR ESI-MS.
See DOI: 10.1039/x0xx00000x

series of semiconductors like polyoxoniobate, CdS, TiO_2, CdSe/ZnS QDs and g-C_3N_4.[7] In this manuscript, we reported the successful deposition of Co(dmgH)$_2$pyCl on hexagonal $ZnIn_2S_4$ via an impregnation method for photocatalytic hydrogen evolution under visible light irradiations. It was found that Co(dmgH)$_2$pyCl can be an effective co-catalyst for photocatalytic hydrogen evolution over $ZnIn_2S_4$ and the photocatalytic activity of Co(dmgH)$_2$pyCl/$ZnIn_2S_4$ composite can be even higher than that of Pt/$ZnIn_2S_4$ under similar reaction conditions. The mechanism for the hydrogen evolution over Co(dmgH)$_2$pyCl/$ZnIn_2S_4$ composite was also proposed.

Experimental Section

Preparation

All the reagents are analytical grade and used without further purifications. Hexagonal $ZnIn_2S_4$ powder was synthesized according to our previously reported method.[3d] Co(dmgH)$_2$pyCl was prepared according to the literature[8] and its structure was confirmed by IR (Fig. S1), ^{1}H NMR and ESI-MS (Table S1). For the preparation of Co(dmgH)$_2$pyCl/$ZnIn_2S_4$ composites, different amounts of Co(dmgH)$_2$pyCl were dissolved in a minimum amount of methanol. $ZnIn_2S_4$ (100 mg) were added to the above solution and the resultant suspension was incubated at room temperature for 12 h. The resultant product was dried at 60 ℃ under vacuum to obtain the final product. For comparison, 3.0 wt% Pt/$ZnIn_2S_4$ was also prepared following the procedure reported previously.[4b]

Characterizations

Powder X-ray diffraction (XRD) data were collected using a Bruker D8 Advance X-ray diffractometer using Cu K_α irradiations. The IR analyses were carried out on a Nicolet 670 FT-IR spectrometer. UV-visible diffraction spectra (UV–vis DRS) of the powders were obtained for the dry pressed disk samples using a UV–visible spectrophotometer (Cary 500 Scan Spectrophotometers, Varian). $BaSO_4$ was used as a reflectance standard. The diffuse reflectance spectrum has been converted into its equivalent absorption spectra using the Kubelka-Munk function, $F(R) = K/S = (1 - R)^2/2R$, where K is the absorption coefficient, R is the diffused reflectance, and S is the scattering coefficient. ^{1}H NMR spectra were obtained in DMSO-d_6 on a Bruker AVANCE III 400 NMR apparatus. Mass spectra (MS) were obtained on a LCQ Fleet (Thermo Fisher Scientific, USA) with an electro-spray ionization (ESI) interface. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantum 2000 XPS system (PHI, USA) with a monochromatic Al Kα source and a charge neutralizer. All of the binding energies were referred to the C 1s peak at 284.6 eV of the surface adventitious carbon. The morphology of the samples was characterized by a field emission scanning electron microscopy (SEM) (JSM-6700F). The transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were obtained in a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. The powder particles were supported on a carbon film coated on a 3 mm diameter fine-mesh copper grid. The sample suspension in ethanol was sonicated and a drop was dripped on the support film.

Photocatalytic hydrogen evolution

Photocatalytic hydrogen evolution experiments were carried out in a closed gas circulation and evacuation system fitted with a top Pyrex window. 50 mg of photocatalyst was dispersed in 100 mL of aqueous solution containing 0.1 M sacrificial reagents. The suspension was irradiated with a 300 W Xe lamp equipped with a 420 nm cutoff filter to provide the visible light irradiations. The temperature of the reaction system was maintained at room temperature by a flow of cooling water during the photocatalytic reaction. The amount of hydrogen evolved was determined with an on-line gas chromatography equipped with a TCD detector.

Results and discussion

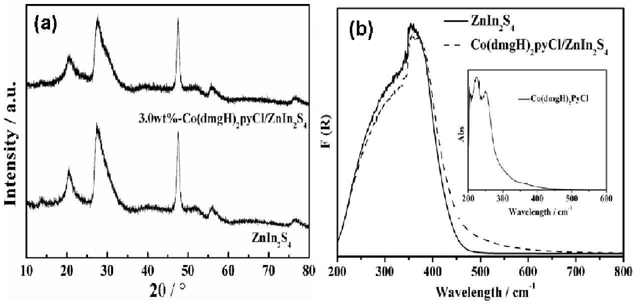


Fig. 1 (a) Powder X-ray diffraction patterns of pure $ZnIn_2S_4$ and 3.0 wt%-Co(dmgH)$_2$pyCl/$ZnIn_2S_4$ composite; (b) UV-Vis spectra of $ZnIn_2S_4$ and 3.0 wt%-Co(dmgH)$_2$pyCl/ $ZnIn_2S_4$ composite. The inset is the UV-Vis absorption spectrum of Co(dmgH)$_2$pyCl.

$ZnIn_2S_4$ was prepared according to our previously reported method, and different amounts of Co(dmgH)$_2$pyCl were loaded on $ZnIn_2S_4$ by an impregnation method to obtain Co(dmgH)$_2$pyCl/$ZnIn_2S_4$ composites. The XRD patterns of all the as-prepared Co(dmgH)$_2$pyCl/$ZnIn_2S_4$ composites show 2θ peaks at values of 14.3^o, 21.2^o, 27.7^o, 30.4^o, 39.3^o, 47.5^o, 52.1^o, 55.8^o and 76.4^o, which can be assigned to (004), (006), (102), (104), (108), (110), (116), (022) and (123) crystallographic planes of hexagonal $ZnIn_2S_4$ phase (JCPDS, No. 03-065-2023) (Fig. 1a). No diffractions peaks corresponding to Co(dmgH)$_2$pyCl are observed in the XRD patterns of the resultant products, but the existence of Co(dmgH)$_2$pyCl in the as-prepared products was confirmed by the FT-IR spectra. Take 3.0 wt%-Co(dmgH)$_2$pyCl/$ZnIn_2S_4$ for example, its IR spectrum shows peaks at 1561cm^{-1} and 3120cm^{-1}, which can be assigned to the asymmetric vibration of C=N and -OH in Co(dmgH)$_2$pyCl and indicates the successful incorporation of Co(dmgH)$_2$pyCl in the composite (Fig. S1). XPS analyses on 3.0 wt%-Co(dmgH)$_2$pyCl/$ZnIn_2S_4$ composite show characteristic binding energy of 781.7 and 796.9 eV for Co^{3+} 2p. As compared to those observed over pure $ZnIn_2S_4$, the peaks of In 3d and S 2p in Co(dmgH)$_2$pyCl/$ZnIn_2S_4$ composite shift toward lower binding energy, while a higher binding energy shift is observed for Zn 2p (Fig. S2). The SEM and TEM images show that the microspheres of $ZnIn_2S_4$, which are composed of $ZnIn_2S_4$

nanosheets, was preserved over $Co(dmgH)_2pyCl/ZnIn_2S_4$ composites. The HRTEM image shows clear lattice-fringe spacing of 0.32 nm, which can be assigned to the (102) crystal plane of hexagonal phase of $ZnIn_2S_4$. The energy dispersed spectrum (EDS) reveals the existence of Co, confirmation of the existence of $Co(dmgH)_2pyCl$ in the composite (Fig. S3). As compared with pure $ZnIn_2S_4$, a slightly red-shift of its absorption to 600 nm was observed on the UV–vis DRS spectrum of 3.0 wt%-$Co(dmgH)_2pyCl/ZnIn_2S_4$ composite, implying the existence of interaction between $ZnIn_2S_4$ and $Co(dmgH)_2pyCl$ since neither $Co(dmgH)_2pyCl$ nor $ZnIn_2S_4$ absorbs in this region (Fig. 1b).

The photocatalytic activity for hydrogen evolution over $Co(dmgH)_2pyCl/ZnIn_2S_4$ composites were first investigated under visible light irradiations using triethanolamine (TEOA) as a sacrificial agent. Similar to that reported previously, pure $ZnIn_2S_4$ only showed a low activity for hydrogen evolution, with only 159.6 μmol of hydrogen evolved in 8 h irradiations.[9] Although no hydrogen was detected when pure $Co(dmgH)_2pyCl$ was irradiated, the incorporation of only a little amount of $Co(dmgH)_2pyCl$ into $ZnIn_2S_4$ led to a significant improvement of the photocatalytic activity. The hydrogen evolution rate was shown to be 130.6 μmol/h over 1.0 wt%-$Co(dmgH)_2pyCl/ZnIn_2S_4$ composite, which is about 6.5 times of that over pure $ZnIn_2S_4$ under otherwise similar condition. This indicates that $Co(dmgH)_2pyCl$ can significantly promote the photocatalytic hydrogen evolution over $ZnIn_2S_4$.

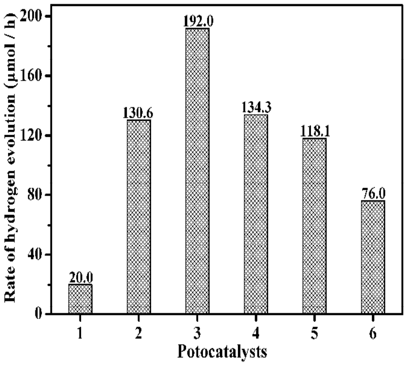


Fig. 2 Photocatalytic hydrogen evolution rate over (1) pure $ZnIn_2S_4$; $ZnIn_2S_4$ with different amounts of $Co(dmgH)_2pyCl$ (2) 1.0 wt%; (3) 3.0 wt%; (4) 5.0 wt%; (5) 10 wt%; (6)3.0 wt% $Pt/ZnIn_2S_4$ (reaction conditions: catalyst, 0.05 g; 100mL aqueous solutions containing 0.1 M TEOA).

The loading amount of $Co(dmgH)_2pyCl$ also influences the photocatalytic activity for hydrogen evolution over the $Co(dmgH)_2pyCl/ZnIn_2S_4$ composite. As shown in Fig. 2, the hydrogen evolution rate first increased with the amount of $Co(dmgH)_2pyCl$ loaded and an optimum amount of $Co(dmgH)_2pyCl$ was found to be 3.0 wt%, which exhibited the highest hydrogen evolution rate of 192.0 μmol/h. A turnover number of 387 (based on $Co(dmgH)_2pyCl$) was obtained over $Co(dmgH)_2pyCl/ZnIn_2S_4$ composite, which is much higher than that reported previously over $Co(dmgH)_2pyCl/CdS$ (TON 171).[7c] However, a further increase in the amount of $Co(dmgH)_2pyCl$ resulted in a decrease of the amount of hydrogen evolved. Such a decrease in the photocatalytic activity with a heavy loading of co-catalyst was also observed previously over other co-catalysts like Pt and NiS[5c] loaded $ZnIn_2S_4$. Although cobaloxime does not absorb in the visible light region, a heavy loading of cobaloxime on $ZnIn_2S_4$ will have a shading effect since the adsorption of cobaloxime on $ZnIn_2S_4$ block the absorption of the incident light by $ZnIn_2S_4$.

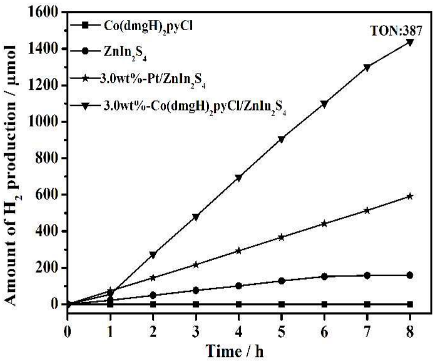
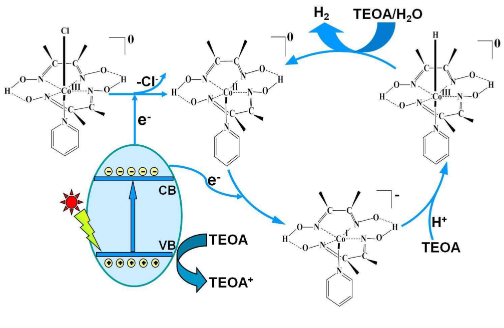


Fig. 3 Time-dependent hydrogen evolution over pure $ZnIn_2S_4$, $Co(dmgH)_2pyCl$, 3.0 wt%-$Co(dmgH)_2pyCl/ZnIn_2S_4$ composite and 3.0 wt%-$Pt/ZnIn_2S_4$ nanocomposite.

The time-dependent hydrogen evolution over 3.0 wt%-$Co(dmgH)_2pyCl/ZnIn_2S_4$ was shown in Fig. 3 and was compared with that of 3.0 wt% $Pt/ZnIn_2S_4$ composite. It was found that 3.0 wt%-$Co(dmgH)_2pyCl/ZnIn_2S_4$ showed much higher activity than that of 3.0 wt% $Pt/ZnIn_2S_4$ composite. A much smaller amount of hydrogen (592.1 μmol) was evolved over 3.0 wt% $Pt/ZnIn_2S_4$ composite in 8 h, as compared with 1438.5 μmol over 3.0 wt%-$Co(dmgH)_2pyCl/ZnIn_2S_4$, indicating that $Co(dmgH)_2pyCl$ is a superior co-catalyst for hydrogen evolution over $ZnIn_2S_4$ as compared to Pt. Unlike that over 3.0 wt% $Pt/ZnIn_2S_4$ composite, there was an induction period at the early stage of irradiations over 3.0 wt%-$Co(dmgH)_2pyCl/ZnIn_2S_4$, during which the hydrogen evolution rate is relatively low. However after one hour irradiation, an almost linear increase of the amount of hydrogen evolution with the irradiation time was observed over 3.0 wt%-$Co(dmgH)_2pyCl/ZnIn_2S_4$, clearly indicating that $Co(dmgH)_2pyCl/ZnIn_2S_4$ composite was stable during the photocatalytic hydrogen evolution. The stability of $Co(dmgH)_2pyCl/ZnIn_2S_4$ composite during the photocatalytic reaction was also confirmed by the similar XRD patterns of the photocatalyst before and after the reaction (Fig. S4).

The above results clearly indicates that $Co(dmgH)_2pyCl$ is a superior cocatalyst for photocatalytic hydrogen evolution over $ZnIn_2S_4$. A prerequisite for $Co(dmgH)_2pyCl$ to act as a co-catalyst for photocatalytic hydrogen evolution over $ZnIn_2S_4$ is an efficient electron transfer from $ZnIn_2S_4$ to $Co(dmgH)_2pyCl$. As previously reported, the conduction band potential of $ZnIn_2S_4$ is ca. -1.1 V vs.

NHE, while the reduction potentials of $Co^{III}(dmgH)_2pyCl$ are determined to be -0.35 V vs. NHE for $Co^{III} \rightarrow Co^{II}$ and -0.78 V vs. NHE for $Co^{II} \rightarrow Co^{I}$, respectively.[10] Therefore, the calculated Gibbs free energy change ΔG° based on these values suggested that the first and second electron transfer from the excited $ZnIn_2S_4$ to $Co(dmgH)_2pyCl$ for the conversion from Co^{III} to Co^{II} as well as the conversion from Co^{II} to Co^{I} are both thermodynamically favorable. However, the existence of an induction period during the photocatalytic hydrogen evolution over $Co(dmgH)_2pyCl/ZnIn_2S_4$ composite implies that there exists a multiple equilibriums for the reduction of Co^{III} to form Co^{II} followed by a secondary electron-transfer to reduce Co^{II} to form Co^{I} for the proton reduction to produce hydrogen.[11] A similar induction period was also observed previously over $Co(dmgH)_2pyCl$ loaded CdSe/ZnS QDs during the photocatalytic hydrogen evolution.[7e]



Scheme 1 Proposed mechanism for photocatalytic hydrogen evolution over $Co(dmgH)_2pyCl/ZnIn_2S_4$ composite under visible light irradiations.

Based on the above observations and discussion, the mechanism for the promoting photocatalytic hydrogen evolution over $Co(dmgH)_2pyCl/ZnIn_2S_4$ composite under visible light irradiation was proposed. When $ZnIn_2S_4$ was irradiated, the photo-generated electrons in the conduction band of $ZnIn_2S_4$ transfer to $Co^{III}(dmgH)_2pyCl$, leading to the formation of $[Co^{II}(dmgH)_2pyCl]^-$ species, which maybe dissociate a Cl^- ion to form five-coordinate Co^{II} intermediate $[Co^{II}(dmgH)_2py]$. The later species is probably reduced to the corresponding Co^{I} anionic $[Co^{I}(dmgH)_2py]^-$.[12] The Co^{I} species are further protonated by reacting with TEOA to form the Co^{III} hydride, which can be promoted by the presence of base in the reaction environment. The as-formed Co^{III} hydride can further react with TEOA or water, which may undergo bond cleavage to evolve molecular hydrogen accompanied by the generation of Co^{II} intermediate that can be reduced back to Co^{I} by the excited electrons from $ZnIn_2S_4$.[13] Sacrificial reagents like TEOA were required as electron donors to quench the photo-generated holes on $ZnIn_2S_4$ to complete the whole redox cycle. In addition to playing as a sacrificial agent, TEOA acts also as a hydrogen source during this reaction since controlled experiment using a mixture of TEOA and D_2O to carry out this reaction under otherwise similar condition produced both D_2 and H_2 although the amount of H_2 was small as compared with that of D_2.

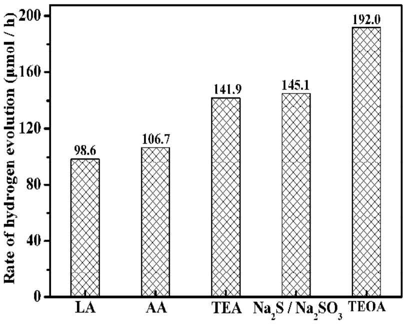


Fig. 4 Photocatalytic hydrogen evolution rate over 3.0 wt%-$Co(dmgH)_2pyCl/ZnIn_2S_4$ composite in the presence of different electron donors (reaction conditions: catalyst, 0.05 g; 100mL aqueous solutions containing 0.1 M electron donors).

Since sacrificial agents are involved in the photocatlaytic hydrogen evolution process, the influence of different sacrificial agents on the photocatalytic hydrogen evolution over $Co(dmgH)_2pyCl/ZnIn_2S_4$ composites were also investigated and the results were shown in Fig. 4. Although hydrogen was evolved In the presence of ascorbic acid (AA), lactic acid (LA), triethylamine (TEA) and TEOA as sacrificial agent, the activity over these sacrificial agents was different. The highest activity was achieved over TEOA, while the lowest one was observed over AA. This result can not be simply explained in terms of the different electron donating capability of the sacrificial agents since all the five sacrificial agents used are known to be good electron donators.[14] As reported previously, suitable alkaline environment is beneficial for the formation of Co^{III}-hydride, which is the most crucial intermediate for hydrogen evolution in the cobaloxime-based system. Therefore the photocatalytic activity for hydrogen evolution in the presence of Na_2S/Na_2SO_3, TEA and TEOA is much higher as compared with that in AA and LA as sacrificial agents. To confirm the effect of alkaline environment on hydrogen evolution rate, controlled experiments using AA and LA as sacrificial agents in alkaline condition (pH = 8) were also carried out. It was found that the rate of hydrogen evolution increased from the original 98.6μmol/h to 103.5μmol/h for AA, while from 106.7μmol/h to 114.8μmol/h for LA. In addition to the alkaline environment, the formation of the Co^{III}-hydride intermediate also involves the supply and transfer of the hydrogen.[15] TEOA is a better hydrogen supplier as compared with TEA and water as in the aqueous solution of Na_2S/Na_2SO_3. Therefore, $Co(dmgH)_2pyCl/ZnIn_2S_4$ composite show the highest photocatalytic activity for hydrogen evolution in the presence of TEOA as a sacrificial agent.

Conclusion

In summary, $Co(dmgH)_2pyCl/ZnIn_2S_4$ composites prepared via an impregnating method show efficient photocatalytic hydrogen evolution under visible light irradiations. The highest photocatalytic activity for hydrogen evolution was observed over 3.0 wt%-$Co(dmgH)_2pyCl/ZnIn_2S_4$ composite, with 1438.5 μmol of hydrogen evolved in 8 h irradiations, which is much higher than that over Pt/$ZnIn_2S_4$ under similar reaction conditions. This work demonstrates a highly efficient photocatalytic system for hydrogen evolution under visible light and provides some guidance for the development of cheap noble-metal-free co-catalysts for photocatalytic hydrogen generation.

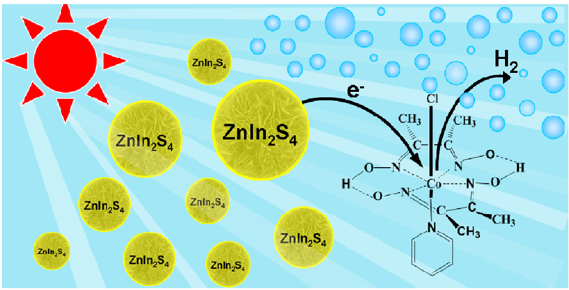
Acknowledgements

This work was supported by 973 Program (2014CB239303), NSFC (21273035), Specialized Research Fund for the Doctoral Program of Higher Education (20123514110002) and Independent Research Project of State Key Laboratory of Photocatalysis on Energy and Environment (NO. 2014A03). Z. Li thanks the Award Program for Minjiang Scholar Professorship for financial support.

References

1 (a) X. Chen, S. Shen, L. Guo and S. S. Mao, *Chem. Rev*., 2010, **110**, 6503; (b) X. Li, J. Yu, J. Low, Y. Fang, J. Xiao and X. Chen, *J. Mater. Chem. A*, 2015, **3**, 2485.
2 (a) A. Fujishima, K. Honda, *Nature*., 1972, **238**, 37; (b) S. Martha, P. C. Sahoo and K. M. Parida, *RSC Adv*., 2015, **5**, 61535; (c) I. Fujimoto, N. Wang, R. Saito, Y. Miseki, T. Gunji and K. Sayama, *Int. J. Hydrogen Energy*., 2014, **39**, 2454; (d) W. Luo, Z. Yang, Z. Li, J. Zhang, J. Liu, Z. Zhao, Z. Wang, S. Yan, T. Yu and Z. Zou, *Energy Environ. Sci*., 2011, **4**, 4046; (e) J. Yang, H. Fu, D. Yang, W. Gao, R. Cong and T. Yang, *Inorg Chem*., 2015, **54**, 2467; (f) X. Zong, H. Yan, G. Wu, G. Ma, F. Wen, L. Wang and C. Li, *J. Am. Chem. Soc*., 2008 **130** 7176; (g) C. Pan, T. Takata, M. Nakabayashi, T. Matsumoto, N. Shibata, Y. Ikuhara and K. Domen, *Angew. Chem. Int. Ed*., 2015, **54**, 2955; (h) X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater*., 2009, **8**, 76.
3 (a) Z. Lei, W. You, M. Liu, G. Zhou, T. Takata, M. Hara, K. Domen and C. Li, *Chem. Commun*., 2003, 2142; (b) Y. Chen, R. Huang, D. Chen, Y. Wang, W. Liu, X. Li and Z. Li, *ACS Appl. Mater. Interfaces*., 2012, **4**, 2273; (c) Y. Chen, S. Hu, W. Liu, X. Chen, L. Wu, X. Wang, P. Liu and Z. Li, *Dalton Trans*., 2011, **40**, 2607; (d) L. Ye, J. Fu, Z. Xu, R. Yuan and Z. Li, *ACS Appl. Mater. Interfaces*., 2014, **6**, 3483.
4 (a) C. Lu, Y. Chen, Y. Li, C. Ma, H. Zhang, Y. Guo and J. Wang, *RSC Adv*.,2015, **5**, 54769; (b) Y. Li, K. Zhang, S. Peng, G. Lu and S. Li, *J. Mol. Catal. A: Chem*., 2012, **363-364**, 354;(c) Z. Fang, Y. Wang, J. Song, Y. Sun, J. Zhou, R. Xu and H. Duan, *Nanoscale*., 2013, **5**, 9830; (d) G. Zhang, Z. Zhao, H. Tan, H. Zhao, D. Qu, M. Zheng, W. Yu and Z. Sun, *RSC Adv*., 2015, **5**, 21237; (e) Y.-S. Chen and P. V. Kamat, *J. Am. Chem. Soc*., 2014, **136**, 6075; (f) Y. Zhang, D.A.J. M. Ligthart, X.-Y. Quek, L. Gao and E. J.M. Hensen, *Int. J. Hydrogen Energy*., 2014, **39**, 11537; (g) C. Gómez-Solís, M. A. Ruiz-Gómez, L. M. Torres-Martínez, I. Juárez-Ramírez and D. Sánchez-Martínez, *Fuel*., 2014, **130**, 221; (h) T. Takata and K. Domen, *J. Phys. Chem. C*, 2009, **113**, 19386.
5 (a) L. Wei, Y. Chen, Y. Lin, H. Wu, R. Yuan and Z. Li, *Appl. Catal., B,* 2014, **144**, 521; (b) X. Zong, J. Han, G. Ma, H. Yan, G. Wu and C. Li, *J. Phys. Chem. C*, 2011, **115**, 12202; (c) L. Wei, Y. Chen, J. Zhao and Z. Li, *Beilstein J. Nanotechnol*., 2013, **4**, 949; (d) L. Zhang, B. Tian, F. Chen and J. Zhang, *Int. J. Hydrogen Energy*., 2012, **37**,17060; (e) Y. Zhong, J. Yuan, J. Wen, X. Li,. Y. Xu, W. Liu, S. Zhang and Y. Fang, *Dalton Trans*.,2015, **44**, 18260.
6 (a) M. Razavet, V. Artero and M. Fontecave, *Inorg Chem*., 2005, **44**, 4786; (b) G. W. Wangila and R. B. Jordan, *Inorg. Chem. Acta*., 2005, **358**, 2804.
7 (a) P. Huang, C. Qin, Z.-M. Su, Y. Xing, X.-L. Wang, K.-Z. Shao, Y.-Q. Lan and E.-B. Wang, *J. Am. Chem. Soc*., 2012, **134**, 14004; (b) Z.-L. Wang, H.-Q. Tan, W.-L. Chen, Y.-G. Li and E.-B. Wang, *Dalton Trans*., 2012, **41**, 9882; (c) F. Wen, J. Yang, X. Zong, B. Ma, D. Wang and C. Li, *J. Catal*., 2011, **281**, 318; (d) F. Lakadamyali and E. Reisner, *Chem. Commun*., 2011, **47**, 1695; (e) J. Huang, K. L. Mulfort, P. Du and L. X. Chen, *J. Am. Chem. Soc*., 2012, **134**, 16472; (f) S.-W. Cao, X.-F. Liu, Y.-P. Yuan, Z.-Y. Zhang, J. Fang, S. C. J. Loo, J. Barber, T. C. Sum and C. Xue, *Phys. Chem. Chem. Phys*., 2013, **15**, 18363.
8 G. N. Schrauzer, *Inorg. Synth*., 1968, **11**, 61.
9 Y. Chen, H. Ge, L. Wei, Z. Li, R. Yuan, P. Liu and X. Fu, *Catal. Sci. Technol*., 2013, **3**, 1712.
10 P. Du, J. Schneider, G. Luo, W. W. Brennessel and R. Eisenberg, *Inorg. Chem*., 2009, **48**, 4952.
11 J. L. Dempsey, B. S. Brunschwig, J. R. Winkler and H. B. Gray, *Acc. Chem. Res*., 2009, **42**, 1995.
12 G. Smolentsev, B. Cecconi, A. Guda, M. Chavarot-Kerlidou, J. A. van Bokhoven, M. Nachtegaal and V. Artero, *Chem. Eur. J*., 2015, **21**, 15158.
13 (a) V. Artero, M. Chavarot-Kerlidou and M. Fontecave, *Angew. Chem. Int. Ed*., 2011, **50**, 7238; (b) D. Basu, S. Mazumder, X. Shi, R. J. Staples, H. B. Schlegel and C. N. Verani, *Angew. Chem. Int. Ed*., 2015, **54**, 1; (c) X. Hu, B. S. Brunschwig, J. C. Peters, *J. Am. Chem. Soc*., 2007, **129**, 8988.
14 (a) X. Liu, D. Sun, R. Yuan, X. Fu and Z. Li, *J. Catal*., 2013, **304**, 1; (b) X. Zhang, B. Peng, S. Zhang and T. Peng, ACS Sustainable *Chem.Eng*., 2015, **3**, 1501; (c) H. Rao, Z.-Y. Wang, H.-Q. Zheng, X.-B. Wang, C.-M. Pan, Y.-T. Fan and H.-W. Hou, *Catal. Sci. Technol*.,2015, **5**, 2332; (d) Y. Fu, D. Sun, Y. Chen, R. Huang, Z. Ding, X. Fu and Z. Li, *Angew. Chem. Int. Ed*., 2012, **51**, 3364.
15 (a) T. Lazarides, T. McCormick, P. Du, G. Luo, B. Lindley and R. Eisenberg, *J. Am. Chem. Soc*., 2009, **131**, 9192; (b) P. Zhang, M. Wang, X. Li, H. Cui, J. Dong and L. Sun, *Sci. China Chem*., 2012, **55**, 1274.

Table of contents



Co(dmgH)$_2$pyCl is an efficient co-catalyst for photocatalytic hydrogen evolution and the activity over Co(dmgH)$_2$pyCl/ZnIn$_2$S$_4$ is superior to that over Pt/ZnIn$_2$S$_4$.