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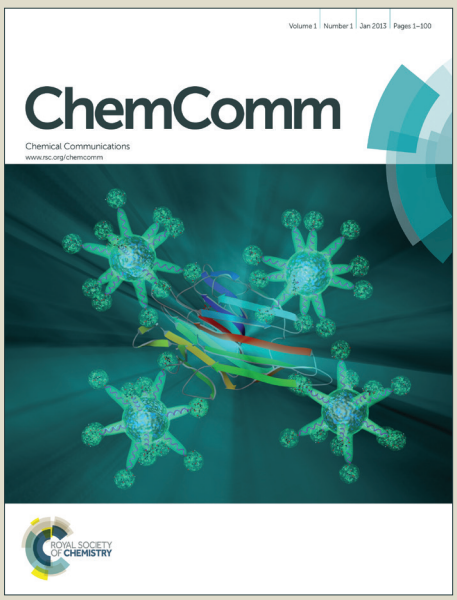

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Copper (I) Cysteine Complexes: Efficient Earth-Abundant Oxidation Co-catalysts for Visible Light-Driven Photocatalytic H_2 Production†

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Copper (I) cysteine complexes generated by mixing Cu(II) ions with cysteine in aqueous solution greatly enhance the activity of CdSe photocatalysts for H_2 production in aqueous solution under visible light excitation. The complex can enhance the H_2 evolution rate by as much as 150 times, by acting as an oxidation co-catalyst and increasing charge carrier lifetimes. Copper (I) cysteine complexes can also be applied to H_2 production performance of other semiconductor photocatalyst systems, thereby affording a new research direction in the development of co-catalysts for solar hydrogen production.

H_2 has long been targeted as the logical successor of fossil fuels for electricity generation and transportation owing to its high energy density and the natural abundance of hydrogen in the form of water, biofuels and biomass resources. Photocatalytic H_2 generation using semiconductor photocatalysts has received much attention recently due to its potential for converting solar energy to hydrogen energy via water splitting or alcohol photoreforming.[1, 2] Research in this area has focused mainly on the performance optimisation of particular inorganic semiconductors, such as TiO_2,[3, 4] C_3N_4,[5, 6] CdSe,[7] CdS[8, 9] or their heterojunction composites,[10-13] to obtain highly active photocatalysts with suitable band structures and a strong visible light response. An inherent limitation of most semiconductor photocatalaysts is fast electron-hole pair recombination after photoexcitation which reduces the number of charge carriers (conduction band electrons or valence band holes) available for photoreactions. Accordingly, co-catalysts, which facilitate charge separation and act as sites for oxygen and hydrogen evolution[14] have been developed and can enhance water splitting rates by one or more orders of magnitude. High work function metals such as Pd or Pt[15, 16] are often used as H_2 evolution co-catalysts, whereas oxides such as RuO_2[17, 18] and IrO_2[19, 20] are efficient oxygen evolution co-catalysts. However, there is intense interest in developing alternative non-noble metal co-catalysts motivated by: 1) limited supply and high cost of noble metals which hinders large-scale applications; 2) some, such as Pt, are easily poisoned by trace inhibitors (such as sulfur-containing substances or CO).

Biological enzymes provide inspiration for the development of new, low cost co-catalysts for photocatalytic reactions, including H_2 production. Several recent reports have shown that artificial mimics of hydrogenases (enzymes in nature for H_2 evolution) can efficiently catalyse the conversion of $2H^+/2e^-$ to H_2,[21-23] achieving very high reduction rates. Of equal importance to the overall reaction rate is the oxidation half reaction, which consumes photo-induced holes.[24] Artificial mimics of natural enzymes, which can enhance hole consumption, are not well studied.[25] Therefore, developing artificial biomimetic oxidation co-catalysts using earth-abundant elements is a great future challenge, motivating the current study.

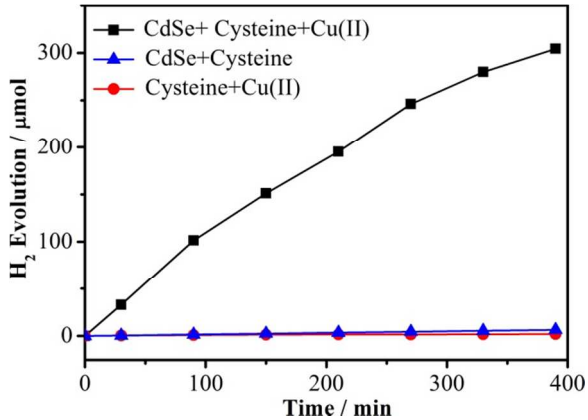


Fig. 1 Photocatalytic H_2 evolution rates under different test conditions

Copper-containing enzymes such as laccase, stellacyanin, plastocyanin are involved in a variety of biochemical oxidation processes.[26] The active site for most copper-containing enzymes involves Cu-cysteine bonds.[27] This prompted an investigation of Cu-cysteine complexes as oxidation co-catalysts for H_2 production, results for which are presented below. CdSe nanosheets with a thickness of ~5 nm (Fig. S1 and Fig. S2)[28] were used as the photocatalyst in this work, since CdSe nanosheets possess good photocatalytic H_2 evolution activity under visible light. Cu (I)

cysteine complexes were generated *in situ* by simply adding cysteine and copper nitrate to an aqueous CdSe dispersion. Control experiments reported here demonstrate that the formation of Cu(I)-cysteine complexes can enhance the H_2 productions rates by up to 150 times. Further, we show that the complex is also effective in enhancing H_2 production rates in other semiconductor systems. Cu(I)-cysteine complexes thus represent a novel and versatile earth-abundant oxidation co-catalyst system for future solar H_2 generation.

In a typical photocatalytic H_2 production experiment, 5 mg of CdSe nanosheets was dispersed in 20 mL of aqueous solution, and then 228.8 mg cysteine (0.094 M) and 4.7 μmol Cu(II) were added to the dispersion in that order. More detailed information about the procedure can be seen in ESI†. The reactor containing the dispersion was then exposed to visible light irradiation ($\lambda > 400$), and the total amount of H_2 evolved quantified by GC analysis. After 390 min irradiation, 304 μmol of H_2 evolved. In the absence of Cu(II) or CdSe, negligible H_2 evolved (2 μmol for 390 min of irradiation). We also observed that cysteine should be added to the solution prior to Cu(II), otherwise negligible H_2 evolution occurred which can be attributed to the fact that in the absence of cysteine Cu(II) is transformed to CuSe rather than the Cu-cysteine complex (K_{sp} of CdSe: 6.31×10^{-36}, K_{sp} of CuSe: 7.94×10^{-49}). The above results indicate that both CdSe semiconductor photocatalyst and Cu-cysteine complex are essential for achieving high photocatalytic H_2 production rates.

To further optimize H_2 evolution, the effect of the Cu(II) concentration on the H_2 generation rate was investigated. The H_2 evolution rates for a series of tests conducted at different Cu(II) concetrations, whilst keeping the amount of CdSe (5 mg) and cysteine (228.8 mg) constant, are shown in Fig. S3. The data show that H_2 evolution rate increased initially with Cu(II) concentration to a maximum of 4.7 μmol, and then decreased at higher concentrations. The decrease observed in the rate at high Cu(II) concentrations may be due to an excess of adsorbed Cu-cysteine complex on CdSe surface, which decreases the availability of proton reduction sites.

In order to understand the function of the Cu-cysteine complex as an oxidation catalyst, X-ray photoelectron spectroscopy (XPS) was applied to establish the valency of Cu in the complex. Fig. 2a and 2b show Cu 2p XPS and X-ray excited Cu LMM Auger spectra for the Cu-cysteine complex. The Cu 2p spectrum shows two peaks at 931.7 and 951.5 eV in a 2:1 peak area ratio, which area readily assigned to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ signals respectively, of either Cu^I or Cu^0.[29] The absence of addition shakeup satellite peaks at 938 to 946 eV indicates the absence of Cu(II). In the X-ray excited Cu LMM Auger spectrum, a strong peak is seen at 569.8 eV which can unambiguously be assigned to Cu(I), confirming the main valence state of copper in the sample as Cu(I).[30, 31] The two other peaks at 574.5 and 566.9 eV represent different Auger transitions involving Cu^I.[32] No obvious Cu^0 signal expected around 568 eV was observed.[30] The modified Auger parameter (α'), is a very useful indicator of copper oxidation state, and is calculated as follows:

$$\alpha' \text{ (eV)} = \text{BE (Cu } 2p_{3/2}\text{)} + \text{KE (Cu LMM)}$$

Where BE (Cu $2p_{3/2}$) is the Cu $2p_{3/2}$ binding energy in eV and KE (Cu LMM) is the kinetic energy of the Cu LMM Auger transition in eV. For the Cu-cysteine complex, KE (Cu LMM) = 1486.7 eV – 569.8 eV, which yields a modified Auger parameter, $\alpha' = 1848.6$ eV. This value is similar to values determined for Cu_2O (1848.7 eV) or Cu 2S (1849.9 eV) and quite different to the value expected for Cu metal (1851.3 eV). It can be concluded from the XPS spectra that Cu in the complex is monovalent, which is not unexpected since Cu(II) can be easily reduce to Cu(I) by cysteine. Elemental analysis for C, H, N and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analyses for Cu were carried out to ascertain the metal-ligand coordination number of Cu-cysteine complex is 2.2, which is in accordance with the results in literature.[33]

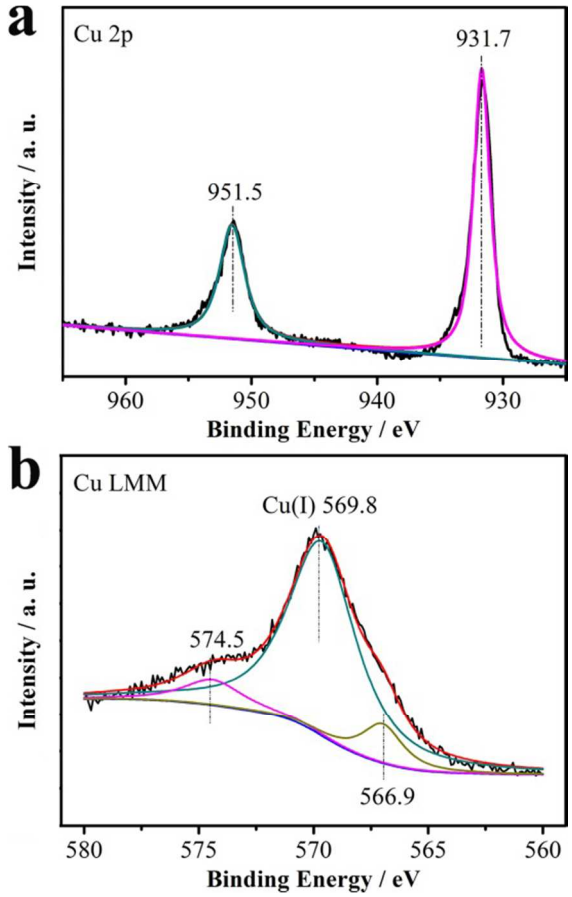


Fig. 2 (a) Peak fitted Cu 2p spectrum for the Cu-cysteine complex; (b) Peak fitted Cu LMM Auger spectrum for the Cu-cysteine complex.

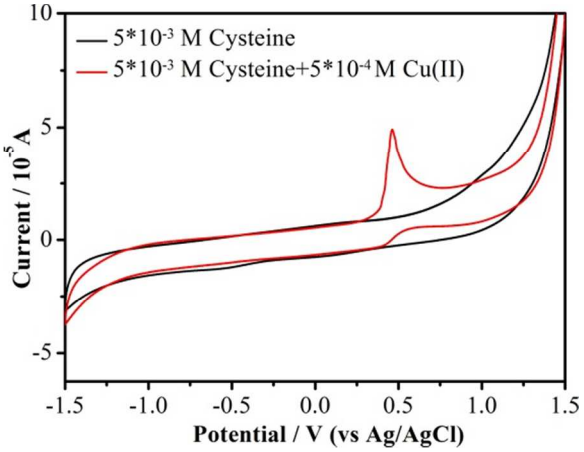


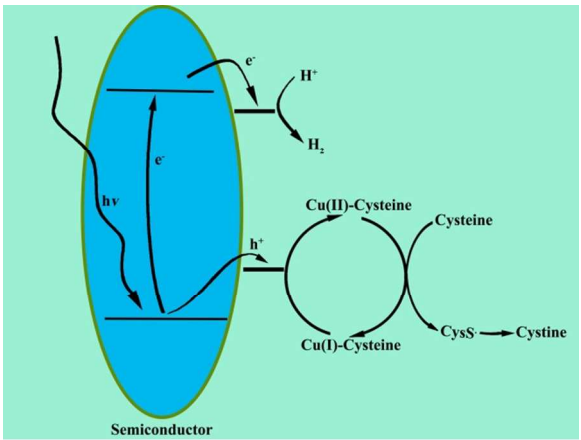
Fig. 3 Cyclic voltammograms collected in a 0.1 M solution of KNO_3. Scan Rate: 100 mV/s with a glassy carbon working electrode. Scan range: -1.5~1.5 V.

To gain insight into the mechanism by which the Cu-cyteine complex enhanced H_2 evolution, cyclic voltammetry (CV) was carried out in a N_2 saturated cysteine solution containing an electrolyte (0.1 M KNO_3). Fig. 3 shows that the redox current for H^+/H_2 did not change on adding Cu(II) to the cysteine solution, which is quite different behaviour to that observed for Ni-complexes

or Co-complexes which function as proton reduction co-catalysts reducing the over potential of H^+/H_2.[34-36] These results suggest that Cu-cysteine complex doesn't enhance the rate of H_2 evolution on CdSe by acting as a reduction co-catalyst. The appearance of an oxidation peak at 0.47 V (*vs* Ag/AgCl) after adding 10^{-4} M Cu(II) to the cysteine solution, which can be assigned to the oxidation of Cu(I)-thiolate to Cu(II)-thiolate complex.[26, 37] Since the reduction current of Cu(II)-cysteine/Cu(I)-cysteine couple is very weak, we speculate that the formed Cu(II) was easily reduced back to Cu(I) by cysteine, generating cystine as an oxidation product.[26, 38] The formation of cystine under visible light irradiation is well demonstrated by high resolution electrospray ionization mass (HR-ESI-MS) spectrometry and ^{1}H NMR (Fig. S4 and Fig. S5, respectively). In Fig. S4, a molecular peak at m/z = 120.0111 corresponds to [cysteine – H]$^-$ species and molecular peak at m/z = 239.0152 corresponds to [cystine – H]$^-$ species, the latter confirming the formation of cystine. Fig. S5a and Fig. S5b are the ^{1}H NMR results of initial cysteine and the products after visible light irradiation. Both of them display two compounds - cysteine and cystine, while cystine shows a much stronger signal after visible light irradiation.

Previous reports revealed that copper ions catalyse the oxidation of thiol via the generation of sulfanyl radicals.[38-40] In this work, sulfanyl radicals were also detected by electron paramagnetic resonance (EPR) spectroscopy with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the trapping agent. A weak signal of spin-adduct features for DMPO (labelled with *) trapped with sulfanyl radical (CysS·, a^N= 15.2 G, a^H= 17.5 G) was observed in the absence of visible light irradiation (Fig. S6a), and the signal became more intense after irradiation for a few seconds (Fig. S6b). The concentration of sulfanyl radicals increases with visible light irradiation time.

Based on results above, we proposed a schematic diagram of photocatalytic H_2 generation in the CdSe-Cu-cysteine system, which is shown in Scheme 1. CdSe nanosheets absorb visible light, and generate electron-hole pairs. Electrons excited into the conduction band of CdSe reduce H^+ to H_2. Valence band holes oxidise the Cu(I)-cysteine complex to a Cu(II)-cysteine complex, which subsequently transforms back to Cu(I)-cysteine complex with the formation cystine as a byproduct, completing a complete catalytic cycle, and achieving a high reaction rate. Cysteine serves as a sacrificial agent in this system.



Scheme 1 Possible mechanism by which copper-cysteine complex co-catalyst facilitates the hole consumption and enhances photocatalytic H_2 evolution rate.

To demonstrate the universality of the Cu-cysteine complex in enhancing photocatalytic H_2 production, further studies were conducted using another visible light driven photocatalyst, $Sn_2Nb_2O_7$ synthesized according to our previous work was adopted to replace of CdSe nanosheets (Fig. S7 and Fig. S8).[41] As shown in Fig. 4, $Sn_2Nb_2O_7$ without any co-catalyst or with the Cu-cysteine complex did not generate H_2, which can be attributed to the high overpotential for H_2 production on the bare $Sn_2Nb_2O_7$ surface. When 0.5 wt. % Pt was deposited on $Sn_2Nb_2O_7$ as a H_2 evolution co-catalyst, 1.2 μmol H_2 evolved in 240 min irradiation. Pt is known to be an efficient H^+ reduction co-catalyst by accepting electrons photo-excited in the semiconductor support and by creating active sites for H_2 evolution. The amount of H_2 evolved increased to 17.9 μmol in 240 min when both Pt and the Cu-cysteine complex were used as co-catalysts. This corresponds to a rate increase of approximately 15 times compared with the system containing only Pt as a co-catalyst. Clearly, the Cu-cysteine complex increased the number of charge carriers available for photoreactions by consuming valence band holes. The above results indicate that the Cu-cysteine complex has not only universality in other semiconductor-based photocatalytic H_2 producing systems but also imparts a synergistic effect when used in conjunction with a proton reduction co-catalyst.

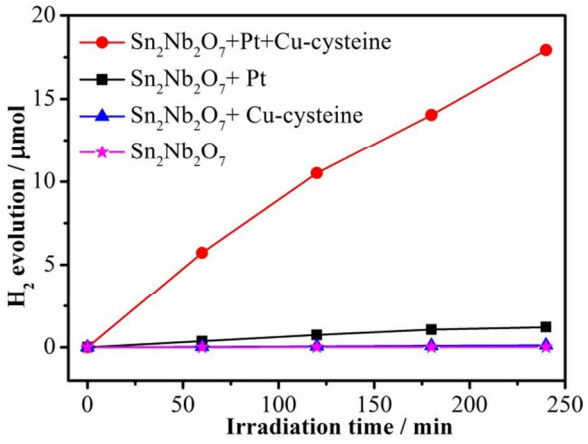


Fig. 4 Photocatalytic H_2 evolution rates with 10 mg $Sn_2Nb_2O_7$ and 228.8 mg cysteine.

In conclusion, low cost Cu(I)-cysteine complexes greatly enhance the activity of CdSe for H_2 production in aqueous systems under visible light irradiation, serving as hole consumption co-catalyst and suppressing electron-hole pair recombination in CdSe following photo-excitation. Reaction of the resulting Cu(II)-cysteine with cysteine regenerates the active Cu(I)-cysteine complex, generating cystine as a byproduct. Importantly, Cu(I)-cysteine complexes can be used cooperatively with proton reduction co-catalysts, such as Pt, to greatly enhance the H_2 production rate of other photocatalyst systems. The Cu(I)-cysteine complex may be useful in the development of improved photocatalytic systems for solar H_2 production.

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Notes and references

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†Electronic supplementary information (ESI) available: Experimental details, characterization, and Fig. S1 to S8. See DOI: 10.1039/b000000x/

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