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A Mn_{13}-cluster based coordination polymer as a co-catalyst of CdS for enhanced visible-light driven H_2 evolution†

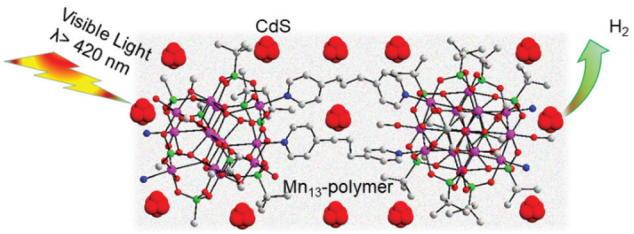
Tian Wen,[a] Lei Zhang *[a] and Wolfgang Schmitt [b]

A coordination cluster-based polymer was used for the first time as a noble-metal-free co-catalyst of CdS, giving rise to significantly enhanced photocatalytic H_2 production. This work demonstrates the feasibility of cluster materials in assembling highly-active and low-priced photocatalysts.

Photocatalytic water-splitting H_2 production is considered to be a promising solution for the global energy and environmental crisis. In the past few decades, semiconductor photocatalysts, especially metal sulfides (*e.g.* CdS), have been intensively studied due to their advantageous characteristics such as low cost, facile preparation and excellent visible light response.[1–5] Despite some tremendous achievements, the activities and applications of pure metal sulfides are still greatly obstructed due to the fast recombination of photogenerated electron–hole pairs. To overcome this obstruction, the use of co-catalyst composites has proven to be a successful method for improving the efficiency and stability of semiconductor photocatalysts.[6–9] However, the most active H_2 evolution co-catalysts are usually expensive and involve scarce noble metals (*e.g.* Pt), greatly limiting the practical applications of these photocatalytic systems. Therefore, the development of inexpensive and active co-catalysts remains a great challenge for the future to establish large-scale photocatalytic H_2 production.

Recently, several Earth-abundant co-catalyst systems for semiconductor-based H_2 evolution have been studied, involving transition metal oxides, sulfides and carbides.[10–13] In particular, the use of porous materials and assemblies of titanium-oxo clusters can also greatly increase the CdS-derived H_2 production.[14–16] On the other hand, inspired by the catalytically active Mn_4CaO_5 cubane cluster in PS II, several Mn-oxo complexes have been investigated as photocatalysts to promote the water oxidation reaction to produce O_2.[17] However, to the best of our knowledge the application of Mn-oxo clusters as co-catalysts for H_2 production has not yet been investigated.

In this work, to explore the use of a new Earth-abundant co-catalyst for hydrogen evolution from H_2O, we loaded CdS nanoparticles to a porous Mn_{13}-cluster based coordination polymer and tested the corresponding photocatalytic performances (Scheme 1).[18] The main reasons of selecting this Mn_{13}-type material are as follows: (i) this coordination polymer is highly porous and characterised by large voids (and defined hydrophilic channels) (Fig. S2†); (ii) the Mn_{13} building units present labile Jahn–Teller sites that can be used for guest exchange (possible water absorption); (iii) the red/brown-coloured crystals of the Mn_{13}-polymer may further increase the efficiency of the visible light absorption; and (iv) the Mn_{13}-polymer containing distinctive, well-distributed electronegative atoms (P and N) might facilitate enhanced electronic coupling with the CdS particles. Prior to the catalytic test reactions, the obtained Mn_{13}-polymer/CdS composites were well characterized by transmission electron microscopy (TEM) and related photochemical analysis. In comparison with pure CdS catalysts under visible-light irradiation, these composite catalysts displayed a significantly enhanced H_2 evolution activity. Furthermore the activity is dependent on the amount of the loaded Mn_{13}-polymer whereby samples that contain 7 wt% Mn_{13}-polymer give the highest H_2 production reaching values of 3600 μmol h^{-1} g^{-1}.



Scheme 1 The illustration of an idealized assembly of the Mn_{13}-polymer/CdS composites. Red, O; green, P; gray, C; blue, N; pink, Mn.

[a]*School of Chemistry, The University of Melbourne, Parkville, Victoria 3010, Australia. E-mail: lei.zhang1@unimelb.edu.au*
[b]*School of Chemistry & CRANN, University of Dublin, Trinity College, Dublin 2, Ireland*

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In the crystal structure of the selected Mn_{13}-polymer, the 1D chains with positive charges assembled from Mn_{13}-oxo clusters and 4,4′-trimethylenedipyridine ligands are packed together to form a porous architecture.[18] It has already been well established that such supramolecular channels can be used for guest pass ways (Fig. S2†). A simple and effective mechanical grinding method was then applied involving a freshly produced Mn_{13}-polymer and CdS nanoparticles to produce effective catalysts for the photocatalytic H_2-production. Firstly, the successful synthesis of the CdS nanoparticles (NPs) was corroborated by TEM and powder X-ray diffraction (PXRD) analyses (Fig. S3 and S4†). Then, the pristine samples of the Mn_{13}-polymer and CdS were mixed in an agate mortar and ground for *ca.* 30 min (see the ESI† for details). The TEM images (Fig. 1a–b), energy dispersive X-ray (EDX) spectra (Fig. S5†) and EDX elemental mapping images (Fig. 1c) of the finer fraction imply that the Mn_{13}-polymer was successfully loaded onto the surface of the CdS nanoparticles *via* electrostatic interactions to give homogeneous samples of Mn_{13}-polymer/CdS.

The photocatalytic water-splitting H_2 production experiments were performed using a white-light emitting-diode (LED) as the light source and Mn_{13}-polymer/CdS composites as catalysts at room temperature, along with triethanolamine (TEOA 16 vol%) as a sacrificial reagent. For comparative studies, samples with various Mn_{13}-polymer loadings were applied. Remarkably, the coupling of the Mn_{13}-polymer with CdS indeed leads to an enhancement in the photocatalytic activity. As displayed in Fig. 2a, pristine CdS showed a very low photocatalytic activity, producing 680 μmol h^{-1} g^{-1} of H_2. When a small quantity of the Mn_{13}-polymer (2.4 wt%) was loaded, the H_2 production was greatly increased to 1090 μmol h^{-1} g^{-1}. Then, by increasing the loading of the Mn_{13}-polymer, the photocatalytic activities of the obtained Mn_{13}-polymer/CdS samples were gradually enhanced. Using the optimal loading of the 7.0 wt% Mn_{13}-polymer, the corresponding Mn_{13}-polymer/CdS composite gave the highest photocatalytic H_2 production rate of 3600 μmol h^{-1} g^{-1}, exceeding about 5 times that of bare CdS.

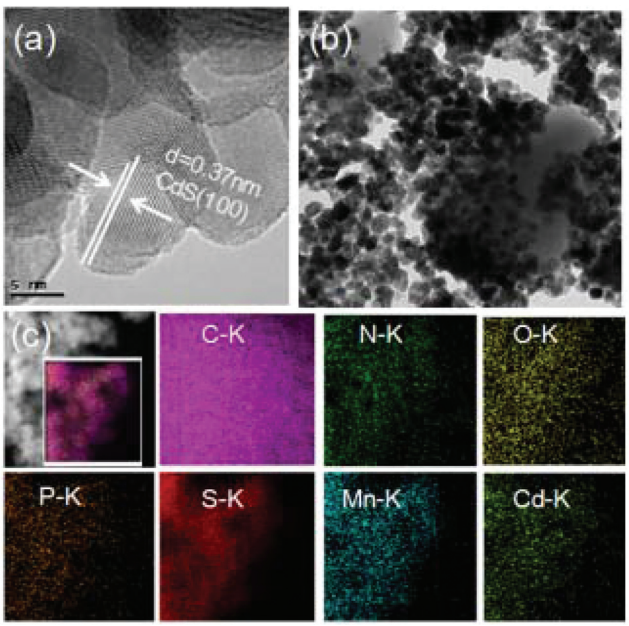

Fig. 1 (a) HRTEM image of CdS nanoparticles. (b) The typical TEM image of samples of the Mn_{13}-polymer/CdS. (c) The EDX mapping images of samples of the Mn_{13}-polymer/CdS.

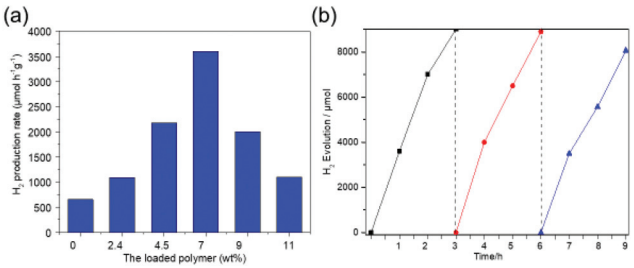

Fig. 2 (a) Mn_{13}-polymer loading amount dependent photocatalytic H_2 evolution activities of the Mn_{13}-polymer/CdS. (b) Stability test of 7 wt% Mn_{13}-polymer/CdS with prolonged visible light irradiation for 9 h.

It has been recently proven that the hetero-structured photocatalysts could successfully enhance the activity of H_2 production by binding different building blocks through electrostatic interactions.[19–24] Therefore, the superior activity of the investigated Mn_{13}-polymer/CdS composites may be ascribed to the combination between CdS and the Mn_{13}-polymer, which greatly facilitates a rapid interfacial charge transfer. Interestingly, a further increase in the loading of the Mn_{13}-polymer leads to an obvious decrease of the photocatalytic activity. It is noteworthy that the pure Mn_{13}-polymer displayed no activity towards H_2 production, whilst its PXRD pattern remained unchanged under the corresponding experimental conditions, highlighting the stability of the co-catalyst under visible light illumination (Fig. S1†). So, one can expect that excess Mn_{13}-polymer co-catalysts block the active surface sites and impede the light absorption of the CdS catalyst. Moreover, the obtained Mn_{13}-polymer/CdS composites are characterized by relatively high photocatalytic stability (Fig. 2b). These results suggest that the Mn_{13}-polymer is an excellent co-catalyst for CdS in order to significantly promote its photocatalytic H_2 production.

To further characterize the obtained Mn_{13}-polymer/CdS catalysts and gain some mechanistically insight into the above described H_2 production, additional photochemical studies were carried out. Firstly, the light harvesting capabilities of the CdS nanoparticles, the Mn_{13}-polymer, and their composites were tested by UV-Vis diffuse reflectance spectroscopy (Fig. 3a). The fresh Mn_{13}-polymer showed strong light absorption between 400 and 800 nm. Thus, the light absorption characteristics of the Mn_{13}-polymer/CdS composites became more pronounced in the region of 550–800 nm in comparison with the pure CdS materials. However, the absorption edge of the Mn_{13}-polymer/CdS showed no significant shift compared to CdS, indicating that doping effects, whereby electron-rich non-

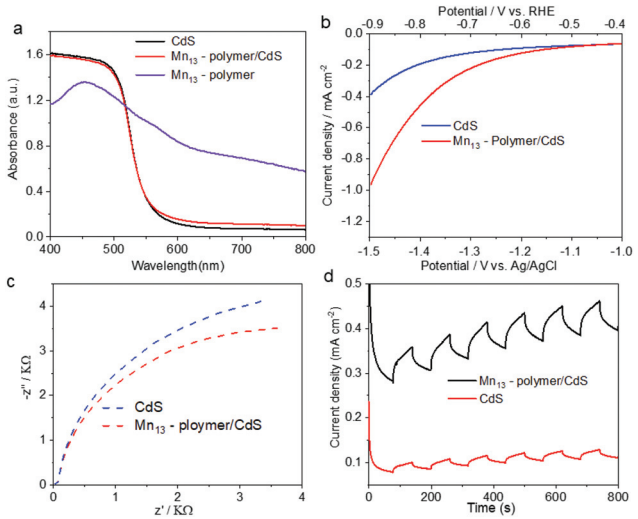

Fig. 3 (a) Ultraviolet–visible absorption spectra of CdS, Mn_{13}-polymer, and Mn_{13}-polymer/CdS. (b) Polarization curves of sample electrodes in 0.5 M Na_2SO_4 solution. (c) EIS Nyquist plots of CdS and Mn_{13}-polymer/CdS electrodes measured under the open-circle potential and visible-light irradiation in 0.5 M Na_2SO_4. (d) The transient photocurrent responses of CdS and Mn_{13}-polymer/CdS electrodes in 0.2 M Na_2S + 0.04 M Na_2SO_3 mixed aqueous solution under visible-light irradiation.

metallic elements such as N, O and P are incorporated into the crystal structure of CdS, do not occur. Similar characteristics were also observed for various Mn_{13}-polymer loadings (Fig. S6†), thus confirming the structural stability of CdS in the catalyst composites. Furthermore, electrochemical measurements and X-ray photoemission spectroscopy (XPS) studies were carried out to investigate the charge separation and transfer. As can be seen from the polarization curves shown in Fig. 3b, the Mn_{13}-polymer/CdS composite shows a remarkably smaller onset potential than CdS for an electrocatalytic HER. Moreover, as compared to pure CdS, the Mn_{13}-polymer/CdS composite also features a smaller semicircle in electrochemical impedance spectroscopy (EIS; Fig. 3c), indicating faster interfacial electron transfer. To achieve such a rapid interfacial charge transfer between the Mn_{13}-polymer and CdS, the formation of strong electronic interactions is essential. The XPS spectrum of the Mn_{13}-polymer/CdS composite shows two peaks located at 406.61/411.35 eV and 160.90/162.02 eV attributed to Cd $3d_{5/2}$/Cd $3d_{3/2}$ and S $2P_{3/2}$/S $2P_{1/2}$, respectively. Clearly, these signals of Mn_{13}-polymer/CdS samples have been lowered by *ca.* 0.21–0.23 and 0.29–0.34 eV compared to pristine CdS samples, respectively, confirming relatively strong electronic coupling between the Mn_{13}-polymer and the CdS nanoparticles (Fig. S7 and S8†). Thus, the direct electron transfer from CdS to the Mn_{13}-polymer upon respective combination can be expected. It seems reasonable to assume that the *tert*-butylphosphonate and the 4,4′-trimethylenedipyridine ligands that locate at the periphery of the Mn_{13}-polymer interact with the CdS nanoparticles whereby electronegative atoms with lone pairs, *e.g.* the P and N atoms provide pathways for electron transport. Consequently, this strong electronic coupling arises from a weak electronic push–pull effect between the CdS and Mn_{13}-polymer components. This effect involving electronegative ligand-atoms may be further facilitated by complementary charges of the polymer and the surface charges of the CdS particles, thus contributing to the effective interfacial charge separation and transfer in the Mn_{13}-polymer/CdS system. Finally, transient photocurrent (TPC) spectroscopy was applied to interpret the charge-carrier separation and transfer efficiency. As shown in Fig. 3d, the TPC value was significantly increased after the Mn_{13}-polymer loading, further confirming that the efficiency of charge separation is greatly improved in the composite material.

In conclusion, for the first time, Mn coordination clusters have been applied as highly active noble-metal-free co-catalysts facilitating enhanced visible-light driven H_2 evolution in the presence of CdS. Taking the advantage of a convenient mechanical grinding strategy, a series of Mn_{13}-polymer/CdS composite catalysts were prepared. Interestingly, the combination of the Mn_{13}-polymer and CdS nanoparticles resulted in enhanced photocatalytic H_2 production activities which were highly dependent on the loading quantities of the Mn_{13}-polymer. It was also demonstrated that the photocatalytic activity of the Mn_{13}-polymer/CdS system stems from the intimate electrostatic interaction between the Mn_{13}-polymer and CdS NPs, thus facilitating efficient charge mobility. Therefore, this work highlights the potential of Mn coordination clusters as low-cost co-catalysts for the photocatalytic H_2 production. The presented system points towards alternatives to noble metal catalysts and highlights new opportunities for the construction of hetero-structural materials towards energy related applications.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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