NJC

PAPER

Check for updates

Cite this: DOI: 10.1039/d0nj01534b

Conjugated nanoporous polycarbazole bearing a cobalt complex for efficient visible-light driven hydrogen evolution[†]

Bin Guo, 📴 a Hai-Yan Li,^b Jian-Ying Chen,*^b David James Young, 💼 *^c Jian-Ping Lang 📴 and Hong-Xi Li 🕩 *^a

A conjugated nanoporous polycarbazole (CNP) cross-linked by pyridine and coordinated to Co(III) displays high catalytic performance for visible light-driven H₂ generation. The hydrogen evolution rate was up to 410 μ mol g⁻¹ h⁻¹. Spectroscopic and electrochemistry studies indicate that the redox active cobalt reduces recombination of photoexcited-charge-carriers and enhances the transmission of photoexcited-charge, thereby enriching the catalytic activity of hybrid materials *x*-Co/CNP-N (*x* = 5, 10, 15 and 20 wt%).

rsc.li/njc

Received 29th March 2020, Accepted 7th May 2020

DOI: 10.1039/d0nj01534b

Introduction

Energy generation from hydrogen combustion produces only water as a by-product, and so this lightest of all gases is a much cleaner energy vector than coal or hydrocarbons, if it can be produced sustainably.¹ Among the various methods for H₂ production,²⁻⁷ visible-light-driven hydrogen evolution reaction (HER) has been demonstrated as a green route from solar energy to this renewable fuel.8 Photocatalytic H₂ evolution typically requires a proton reducing catalyst, a photosensitizer (PS) and a sacrificial donor. Photocatalytic systems based on Pt, Pd, Ru and other noble metals in combination with a PS display excellent catalytic activity and high selectivity for HER.^{2,3,9-24} However, the expense and scarcity of noble metal catalysts limit their widespread use. Noble-metal-free co-catalysts for H2 generation have recently been developed.25,26 Cobaloxime complexes, for example, act as effective co-catalysts in photoenhanced HER systems.^{25,27,28} Molecular devices comprising a cobaloxime co-catalyst and a photosensitizer (PS) such as Ru, Ir, Pt or Re organometallic complexes,29-33 molecular organic dyes,34-36 porphyrin photosensitizers³⁷⁻⁴⁰ or boron-dipyrromethene (BODIPY) chromophores⁴¹ can be effective for photo-induced H₂ generation. Nevertheless, the development of heterogeneous HER catalytic systems that possess the inherent advantages of easy catalyst separation and recyclability are highly desirable from an industrial perspective. Cobaloxime complexes have been assembled with heterogeneous PSs such as cadmium chalcogenide quantum dots (CdX QDs, X = S, Se or Te),^{42–45} TiO₂,^{46–48} covalent organic frameworks (COF),⁴⁹ g-C₃N₄^{26,50} and metal–organic frameworks (MOFs)^{51,52} for H₂ photogeneration. However, these heterogeneous PSs suffer from narrow visible light absorption windows and/or poor stability and often require an intricate synthesis.

Conjugated nanoporous polycarbazoles (CNPs) have been widely employed as optical materials,⁵³⁻⁵⁶ for gas adsorption and for separation technologies.⁵⁷⁻⁶⁴ CNPs with strong visiblelight absorption also act as heterogeneous photocatalysts with good activity for organic transformations, such as the C-3 functionalization of indoles,65 oxidative C-H functionalization,66 aerobic oxidation,67 oxidative hydroxylation of arylboronic acids68 and degradation of lignin.⁶⁹ Very recently, Han et al. reported rhenium-metalated porous polypyridyl polycarbazoles for visiblelight CO₂ photoreduction.⁷⁰ We recently demonstrated visiblelight-promoted Suzuki-Miyaura reactions of aryl chlorides with arylboronic acids in water catalyzed by Pd nanoparticles loaded on to a CNP framework.⁷¹ CNP matrices are attractive candidates for the HER because they are inexpensive, easily prepared with high porosity, are chemically and thermally stable, and possess tunable electronic and optical properties. In this work, we selected a CNP with bridging pyridyl groups to anchor a cobaloxime complex by coordination. The resulting photocatalytic system exhibited high activity with a hydrogen evolution rate of 410 μ mol g⁻¹ h⁻¹. The Co-N coordination bond provided channels for photoexcited electron transmission reducing recombination of photoexcitedcharge-carriers and thereby enhancing transmission of photoexcited-charge. The mechanism of reaction was elucidated by steady-state photoluminescence spectroscopy, electrochemical impedance spectroscopy and cyclic voltammetry.

ROYAL SOCIETY OF CHEMISTRY

View Article Online

^a College of Chemistry, Chemical Engineering and Materials Science,

Soochow University, Suzhou 215123, China. E-mail: lihx@suda.edu.cn

^b Analysis and Testing Centre, Soochow University, Suzhou 215123, China. E-mail: chenjianying@suda.edu.cn

^c College of Engineering, Information Technology and Environment,

Charles Darwin University, Darwin NT 0909, Australia. E-mail: david.young@cdu.edu.au

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/d0nj01534b

Results and discussion

Synthesis and characterization

Reaction of CoCl₂·6H₂O with dimethylglyoxime (dmgH₂) and 3,5-di(9*H*-carbazol-9-yl)pyridine (3,5-Cz)⁷¹⁻⁷³ in refluxing EtOH yielded Co(dmgH)₂(3,5-Cz)Cl in 77% isolated yield (Scheme 1). This complex's positive-ion electrospray ionization mass spectrum (ESI-MS) contained signals at m/z = 756.1518, which are ascribed to the cationic species [Co(dmgH)₂(3,5-Cz)Cl + Na]⁺ and matched well with the simulated isotopic pattern (Fig. S1, ESI†). In the ¹H NMR spectra, the singlets at $\delta = 8.67, 8.29$, and 2.56 ppm are assignable to the two *ortho* and one *para* proton of



Scheme 1 Synthesis of $Co(dmgH)_2(3,5-Cz)Cl$ and x-Co/CNP (x = 5, 10, 15 and 20 wt%).

the pyridyl moiety and the twelve protons of the four methyl groups from dmgH, respectively (Fig. S2, ESI†). Other resonances at δ = 8.14–8.16, 7.50–7.53, and 7.39–7.44 ppm are assignable to protons of the carbazolyl moiety (Fig. S2, ESI†).

Metallated polymers x-Co/CNP (x = 5, 10, 15 and 20 wt%) were synthesized by reaction of CoCl₂·6H₂O and dimethylglyoxime (dmgH₂) with the polymer of 3,5-Cz (CNP) in refluxing ethanol solution for 12 hours (Scheme 1). The powder X-ray diffraction (PXRD) patterns of all x-Co/CNP materials clearly indicated that Co loading didn't change the structure of the parent CNP, which remained amorphous in nature (Fig. S3, ESI[†]). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) revealed that the as-prepared 5-Co/CNP, 10-Co/CNP, 15-Co/CNP and 20-Co/CNP materials contained 4.56, 9.88, 13.76 and 18.32 wt% of Co, respectively (Table S1, ESI⁺). FT-IR absorption bands at approximately 3050, 1580, 1450 and 1230 cm^{-1} (Fig. 1a) correspond to the stretching vibrations of the C-H, C=N, C=C and C-N bonds, respectively. Extra peaks at 3450 and 1090 cm^{-1} correspond to the stretching vibrations of the O-H and C-O bonds of the dmgH ligand indicating coordination of the Co complex. The ¹³C CP/MAS NMR spectra showed three different signals between 100 and 150 ppm, indicating the presence of (i) an aromatic carbon atom adjacent to a nitrogen atom (140-135 ppm), (ii) an aromatic carbon with a carbon substituent (125 ppm) and (iii) an aromatic carbon atom with a hydrogen (110 ppm) (Fig. 1b). Two additional signals in the metallated x-Co/CNP at 153 and 11 ppm corresponding to the oxime carbons and methyls of the dmgH groups. The Co 2p X-ray photoelectron spectra (XPS) of x-Co/CNP (Fig. 1c) contained peaks at 781.45 and 796.48 eV assignable to Co^{III} 2p_{1/2} and Co^{III} $2p_{3/2}$, respectively. These frequencies are consistent with those of $Co(dmgH)_2(3,5-Cz)Cl$. Signals with electron-binding energy



Fig. 1 (a) FT-IR spectra, (b) ¹³C NMR spectra, (c) Co 2p, (d) N 1s XPS spectra of Co(dmgH)₂(3,5-Cz)Cl, CNP and *x*-Co/CNP (x = 5, 10, 15 and 20 wt%), (e) scanning TEM high-angle annular dark-field (STEM-HAADF) image and energy-dispersive X-ray spectroscopy (STEM-EDS) elemental mappings of 15-Co/CNP, and (f) UV-vis spectra of 3,5-Cz, Co(dmgH)₂(3,5-Cz)Cl, CNP and *x*-Co/CNP (x = 5, 10, 15 and 20 wt%).

400.55 \pm 0.05 eV were attributed to pyrrolic N (Fig. 1d and Table S1, ESI[†]). The positive shift in the N 1s binding energies of the pyridinic N of *x*-Co/CNP, compared with the corresponding values in the parent CNP, indicate N coordination to Co. Additionally, the new peak at 401.25 \pm 0.2 eV corresponding to N–O confirmed the presence of dmgH groups. TEM images indicated that CNP and Co/CNP are amorphous (Fig. S4, ESI[†]). Elemental mapping of Co/CNP showed the Co to be evenly dispersed throughout the CNP matrix (Fig. 1e and Fig. S5–S9, ESI[†]). The Co/CNP composite absorbed more visible light relative to the parent polymer, (Fig. 1f) due to charge transfer between CNP and cobalt.⁷⁴ The band-gap energy (E_g) of *x*-Co/CNP decreased relative to CNP as the loading of cobalt increased (Fig. S10 and Table S1, ESI[†]).

Catalytic performance

The photocatalytic performance of CNP and x-Co/CNP (x = 5, 10, 15 and 20 wt%) were evaluated by suspending these photocatalysts in CH₃CN containing HBF₄ (0.5 M) under the irradiation of a 300 W Xe lamp equipped with a 400 nm cutoff filter and using triethanolamine (TEOA, 10 vol%) as the sacrificial electron donor. The time-dependent hydrogen-evolution curves for CNP and x-Co/CNP (x = 5, 10, 15 and 20 wt%) over the first 5 hours all displayed a roughly linear increase with time (Fig. 2a) and 15-Co/ CNP displayed the highest hydrogen production of 2050 μ mol g⁻¹ after 5 hours. Photocatalytic activity was calculated by normalizing the amount of product formed over time relative to the photocatalyst weight (Fig. 2b). The parent CNP produced a negligible amount of H_2 (58 µmol g⁻¹ h⁻¹). An increase of Co loading from 5-Co/CNP to 10-Co/CNP and 15-Co/CNP resulted in much enhanced H₂ production rates of 179, 294 and 410 μ mol g⁻¹ h⁻¹, respectively, indicating that the Co complex is essential for photocatalysis. However, the photocatalytic activity of 20-Co/CNP dropped to 248 μ mol g⁻¹ h⁻¹ indicating a 'volcano' plot with a peak at 15-Co/CNP. Interestingly, $Co(dmgH)_2(3,5-Cz)Cl$ produced a negligible amount of H₂ under the same conditions, (Fig. 2a, b and Fig. S11, ESI[†]) possibly due to poor absorption of visible-light (Fig. 1f). Control experiments indicated that both TEOA and light were indispensable for hydrogen production (Fig. 2b). The reusability of 15-Co/CNP catalyst was demonstrated with no significant loss of catalytic activity after three cycles, during which more than 2000 μ mol g⁻¹ of hydrogen was produced (Fig. 2c). This catalytic activity of 15-Co/CNP is higher than some reported noble metal contained systems for photocatalytic HER^{75-80} and similar to that of $\text{Fe}_2(\mu$ dcbdt)(CO)₆/Ru(bpy)₃²⁺ (280 μ mol g⁻¹ h⁻¹, dcbdt = 1,4-dicarboxylbenzene-2,3-dithiolate, bpy = 2,2'-bipyridine),⁸¹ Co@NH₂-MIL-125 (Ti) (375 µmol g⁻¹ h⁻¹),⁵¹ and [Co^{II}(TPA)Cl][Cl]@MIL-125-NH₂ $(553 \ \mu mol \ g^{-1} \ h^{-1}, TPA = tris(2-pyridylmethyl)amine)^{52}$ (Table S2, ESI⁺). ICP-AES analysis indicated that 87% of Co remained after three cycles suggesting minimal leaching. Analysis of the reused 15-Co/CNP by PXRD, FT-IR, XPS and EDS elemental mapping revealed no discernible structural or compositional changes, attesting to structural stability (Fig. S12 and S13, ESI⁺). The binding energies of Co 2p and N 1s (Fig. S13, ESI⁺) in the reused 15-Co/CNP composite shifted slightly to lower binding energies



Fig. 2 (a) Time-dependent photocatalytic hydrogen production and (b) average hydrogen-production rates on CNP and *x*-Co/CNP (x = 5, 10, 15 and 20 wt%), (c) recycling performance of 15-Co/CNP.

compared with those of fresh 15-Co/CNP, presumably due to some reduction.

Mechanistic study

To gain insight into the high photocatalytic performance of Co/CNP and probe its internal electron transfer dynamics, we performed steady-state photoluminescence (PL) spectroscopy in acetonitrile (Fig. 3a). CNP showed strong PL emission between 460 and 650 nm with a maximum at 505 nm, stemming from the fast-radiative



Fig. 3 (a) Steady-state PL emission spectra (λ_{ex} = 410 nm) in CH₃CN, (b) time-resolved PL spectra, (c) photocurrent responses and (d) EIS profiles of CNP and x-Co/CNP (x = 5, 10, 15 and 20 wt%).

recombination of photogenerated electron–hole pairs. As expected, the fluorescence of CNP was partly quenched by loading of cobaloxime complex, (Fig. 3a) which further confirmed the efficient transfer of photoexcited electrons from CNP to cobaloxime complex through coordination bonds. Time-resolved PL spectra were recorded for all samples at an excitation wavelength of 410 nm (Fig. 3b) and indicated average fluorescence lifetimes (τ) of 1.30, 1.53, 2.23, 2.54 and 2.35 ns for CNP, 5-Co/CNP, 10-Co/CNP, 15-Co/CNP and 20-Co/CNP, respectively. The attenuated PL emission and prolonged fluorescence lifetime of 15-Co/CNP in comparison with other members in the family clearly indicated that the radiative recombination of photoexcitons

was effectively retarded.¹⁴ Transient photocurrent measurements and electrochemical impedance spectroscopy (EIS) were conducted to further verify activity of x-Co/CNP (x = 5, 10, 15 and 20 wt%). As expected, 15-Co/CNP exhibited the highest photocurrent response in this series, (Fig. 3c) implying that this optimized Co loading is ideal for efficient separation of photogenerated electron-hole pairs. This proposition is further supported by the electrochemical impedance spectroscopy (EIS) results (Fig. 3d) which indicated that 15-Co/CNP possessed the smallest radius, manifesting in the lowest charge-transfer resistance. Combined with the results above, it is proposed that 15 wt% Co loading is the optimized value for reducing recombination of photoexcited-charge-carriers and enhancing transmission of photoexcited-charge, leading to higher HER performance. However, 20-Co/CNP exhibited a lower photocatalytic activity of 248 μ mol g⁻¹ h⁻¹, suggesting that excess cobalt molecule catalysts could become recombination centres of photoexcited electrons and holes,⁷⁴ and so the photocatalytic activity of 20-Co/CNP is lower than that of 15-Co/CNP, consistent with PL, transient photocurrent and EIS results.

Cyclic voltammetry (CV) of Co(dmgH)₂(3,5-Cz)Cl revealed an irreversible reduction potential at $E_p = -0.37$ V and a reversible reduction potential at $E_{1/2} = -1.09$ V vs. saturated calomel electrode (SCE) (Fig. S14a, ESI†). They are assigned to the Co^{III}/Co^{II} and Co^{II}/Co^{II} couples, respectively. Irreversible reduction potentials of Co^{III}/Co^{II} and Co^{II}/Co^{II} couples in 15-Co/CNP were located at $E_p = -0.29$ V and $E_p = -1.01$ V vs. SCE, respectively (Fig. S14b, ESI†). The valence band (VB) and conduction band (CB) of CNP were calculated to be 1.02 and -1.28 V vs. SCE from the CV of CNP, respectively (Fig. S14d, ESI†). These results indicate that the excited state of CNP can reduce Co^{III} to Co^{II} by a two-step single electron transfer. The absorption spectra of Co(dmgH)₂(3,5-Cz)Cl were acquired in the presence of TEOA



Scheme 2 Proposed mechanism for photocatalyzed hydrogen evolution.

with/without irradiation (>350 nm). The formation of Co^{II} occurred within 10 min for the $Co(dmgH)_2(3,5-Cz)Cl + TEOA$ system as evidenced by the appearance of the characteristic absorption at 430 nm, and the absorbed signal gradually decreased upon further light irradiation, (Fig. S15a, ESI†) inferring the change of Co^{II} to $Co^{I,41}$ consistent with CV results. No Co^{II} formation was observed for the mixtures of $Co(dmgH)_2(3,5-Cz)Cl$ and TEOA at pH = 13.5 after photoirradiation; instead, expansion of the spectrum in the range of 600–850 nm clearly showed a broad absorption peak of Co^{I} by a single-step simultaneous two-electron transfer.⁴³

Analysing the above H_2 production experiments, spectroscopic studies and previous literature reports, ^{28,41,43,50,82–84} we propose a reaction mechanism as depicted in Scheme 2. Under visible light irradiation, the excited electrons in the VB of CNP move to the CB. The electrons in the CB of CNP reduce the coordinated Co^{III} species of Co/CNP to form Co^{II}/CNP, with the elimination of chloride ion. Under visible light irradiation, Co^{II}/CNP was further reduced to Co^I/CNP by excited electrons. Meanwhile, the holes generated inside the CNP combine with electrons from TEOA. The photogenerated Co^{II} species are then protonated to obtain a Co^{III}-H/CNP intermediate, which finally reacts with another proton to generate H₂ and Co^{III}/CNP (I) intermediates. These Co^{III}/CNP (I) intermediates are reduced to Co^{II}/CNP under visible light irradiation completing the catalytic cycle.

Conclusions

We have demonstrated efficient visible-light-promoted hydrogen evolution catalyzed by cobalt complexes loaded on to a conjugated nanoporous polycarbazole (CNP). This catalytic system showed high efficiency, good stability and reusability. Spectroscopic and electrochemical studies confirmed that cobalt loading promoted photocatalytic hydrogen evolution by reducing recombination of photoexcited-charge-carriers and enhancing transmission of photoexcited-charge. Extending the application of this photocatalytic system to other reactions, *e.g.* CO₂ reduction, is an ongoing endeavour in our laboratory.

Experimental

General information

All reagents were used as purchased without further purification. ¹H and ¹³C NMR spectra were recorded at ambient temperature on a Varian UNITY plus-400 spectrometer. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G20 electron microscope operating at 200 kV. Annular dark-field scanning TEM (ADF-STEM) was performed on a FEI Tecnai F20 electron microscope operating at 200 kV, equipped with Genesis EDS detector. Powder X-ray diffraction (PXRD) patterns were collected on a PANalytical Aeris diffractometer (Cu-K α). X-ray photoelectron spectra (XPS) were recorded on an X-ray photoelectron spectrometer (AXIS Ultra DLD) and binding energies were referenced to C 1s at

284.7 eV from hydrocarbon to compensate for effects. Co content was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Varian 710-ES instrument. Infrared (IR) spectra were recorded on a Varian Scamiter-1000 spectrometer (4000–400 cm⁻¹). Elemental analyses for C, H, and N were performed on a Carlo-Erba CHNO-S microanalyzer. The photoluminescent spectra were obtained on a HORIBA QM-40 spectrofluorometer. UV-Vis spectra were obtained with a Shimadzu UV-2600 spectrometer.

Synthesis of Co(dmgH)₂(3,5-Cz)Cl. Co(dmgH)₂(3,5-Cz)Cl was synthesized as previously reported.⁷³ 3,5-Cz (0.44 g, 1.05 mmol) was added to a hot solution of CoCl₂·6H₂O (0.13 g, 0.53 mmol) and dimethylglyoxime (0.14 g, 1.2 mmol) in 20 ml ethanol. The mixture was stirred in refluxing ethanol for 2 hours, cooled to room temperature and stirred for a further 60 min. The brown precipitate was collected by filtration, washed successively with water, ethanol, and diethyl ether and recrystallized from dichloromethane and diethyl ether. Yield 0.30 g (77%). HRMS (ESI) m/z: $[M + Na]^+$, calcd for $C_{37}H_{35}ClCoN_7O_4Na^+$: 756.1507; found: 756.1518. Anal. calcd for C37H35ClCoN7O4: C, 60.37; H, 4.79; N, 13.32. Found: C, 60.36; H, 4.68; N, 13.26. ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3) \delta 8.67 \text{ (s, 2H)}, 8.29 \text{ (s, 1H)}, 8.15 \text{ (d, } J = 7.6 \text{ Hz},$ 4H), 7.51 (t, J = 7.6 Hz, 4H), 7.41 (dd, J = 15.5, 7.8 Hz, 8H), 2.56 (s, 12H). ¹³C NMR (101 MHz, $CDCl_3$) δ 153.2, 145.8, 139.3, 137.3, 131.9, 127.1, 124.9, 122.4, 121.2, 109.2, 13.5. IR (KBr disk, cm⁻¹): 3475 (w), 3056 (w), 1582 (s), 1492 (m), 1477 (m), 1445 (s), 1336 (m), 1307 (m), 1240 (s), 1220 (s), 1160 (w), 1094 (m), 1018 (w), 999 (w), 980 (w), 923 (w), 753 (s), 720 (m), 700 (m), 653 (w), 511 (w).

Synthesis of *x*-Co/CNP (x = 5, 10, 15 and 20 wt%). *x*-Co/CNP (x = 5, 10, 15 and 20 wt%) were prepared in a similar method to that described above for Co(dmgH)₂(3,5-Cz)Cl. CNP (100 mg) was added a hot solution of CoCl₂·6H₂O (amount calculated for cobalt loadings of 5, 10, 15 and 20 wt%) and dimethylglyoxime (2.3 eq. for CoCl₂·6H₂O) in 30 ml ethanol. The mixture was stirred in refluxing ethanol for 12 hours in air before cooling to room temperature. The resulting brown precipitate was collected by filtration, washed successively with water, ethanol, and diethyl ether and dried at room temperature *in vacuo*.

Photocatalytic H₂ evolution reactions. Photocatalyst powder, *x*-Co/CNP (x = 5, 10, 15 and 20 wt%, 15 mg), was dispersed in 27 ml of 0.5 M HBF₄ CH₃CN solution and TEOA (3 ml, 10 vol%) in a top-irradiation Pyrex vessel. This dispersion was ultrasonicated for 30 min and the resulting suspension purged with nitrogen for 30 min to remove air. The reaction vessel was linked to a full glass automatic on-line trace gas analysis system (Labsolar-6A, Beijing PerfectLight Technology Co., Ltd, China) and the amount of H₂ was determined using online gas chromatography (GC7900, Tianmei, China) with a TCD detector using argon as carrier gas. The photocatalytic experiments involved direct irradiation of the solution by a 300 W Xe-lamp with a cut-off filter ($\lambda > 400$ nm). The reaction temperature was maintained at 15 °C using a water-cooling system.

Photoelectrochemical measurements. Photoelectrochemical measurements were conducted using a CHI660E electrochemical system with a conventional three-electrode cell consisting of a Pt

plate as the counter electrode, an Ag/AgCl electrode as the reference electrode and 0.01 M nBu_4NPF_6 as electrolyte by directly irradiating the working electrode from the back side using a 300 W Xe lamp with a 400 nm cut-off filter. The working electrode was prepared on indium-tin oxide (ITO) glass previously cleaned by sonication in ethanol for 30 min and dried at 60 °C. The boundary of the ITO glass was protected with Scotch tape. Catalyst (5 mg) was dispersed in isopropanol (1 ml) containing 30 µl 0.5 wt% Nafion solution by sonication for 0.5 h to obtain a slurry, and the slurry was spread onto the pretreated ITO glass, and then dried at room temperature. EIS analysis was performed at -0.5 V *vs.* Ag/AgCl condition at the frequency range 0.01 to 100 000 Hz using 0.5 M HBF₄ as electrolyte.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the National Natural Science Foundation of China (21771131 and 21971182), the "Priority Academic Program Development" of Jiangsu Higher Education Institutions and the Project of Scientific and Technologic Infrastructure of Suzhou (SZS201708 and SZS201905) for financial support.

Notes and references

- 1 S. Chu and A. Majumdar, Nature, 2012, 488, 294-303.
- 2 G. G. Zhang, Z. A. Lan and X. C. Wang, *Angew. Chem., Int. Ed.*, 2016, **55**, 15712–15727.
- 3 Y. Wang, A. Vogel, M. Sachs, R. S. Sprick, L. Wilbraham,
 S. J. A. Moniz, R. Godin, M. A. Zwijnenburg, J. R. Durrant,
 A. I. Cooper and J. Tang, *Nat. Energy*, 2019, 4, 746–760.
- 4 B. Zhu, R. Zou and Q. Xu, Adv. Energy Mater., 2018, 8, 1801193.
- 5 H. Zhong, C. Campos-Roldán, Y. Zhao, S. Zhang, Y. Feng and N. Alonso-Vante, *Catalysts*, 2018, **8**, 559.
- 6 Y. Shi, A.-F. Yang, C.-S. Cao and B. Zhao, *Coord. Chem. Rev.*, 2019, **390**, 50–75.
- 7 Y. Hua, X. Li, C. Chen and H. Pang, *Chem. Eng. J.*, 2019, **370**, 37–59.
- 8 J. A. Turner, Science, 2004, 305, 972-974.
- 9 Z. Hu, X. Zhang, Q. Yin, X. Liu, X.-F. Jiang, Z. Chen, X. Yang,
 F. Huang and Y. Cao, *Nano Energy*, 2019, 60, 775–783.
- 10 N. Wang, G. Cheng, L. Guo, B. Tan and S. Jin, Adv. Funct. Mater., 2019, 1904781.
- 11 H. Yu, R. Shi, Y. Zhao, T. Bian, Y. Zhao, C. Zhou, G. I. N. Waterhouse, L. Z. Wu, C. H. Tung and T. Zhang, *Adv. Mater.*, 2017, **29**, 1605148.
- 12 L. Shang, B. Tong, H. Yu, G. I. N. Waterhouse, C. Zhou, Y. Zhao, M. Tahir, L.-Z. Wu, C.-H. Tung and T. Zhang, *Adv. Energy Mater.*, 2016, 6, 1501241.
- 13 X. Ma, L. Wang, Q. Zhang and H. L. Jiang, Angew. Chem., Int. Ed., 2019, 58, 12175–12179.

- 14 W. Huang, Q. He, Y. Hu and Y. Li, Angew. Chem., Int. Ed., 2019, 58, 8676-8680.
- 15 Q. Zuo, T. Liu, C. Chen, Y. Ji, X. Gong, Y. Mai and Y. Zhou, Angew. Chem., Int. Ed., 2019, **58**, 10198–10203.
- 16 E. Jin, Z. Lan, Q. Jiang, K. Geng, G. Li, X. Wang and D. Jiang, *Chem*, 2019, 5, 1632–1647.
- 17 G. Lan, Y. Y. Zhu, S. S. Veroneau, Z. Xu, D. Micheroni and W. Lin, J. Am. Chem. Soc., 2018, 140, 5326–5329.
- 18 P. Pachfule, A. Acharjya, J. Roeser, T. Langenhahn, M. Schwarze, R. Schomacker, A. Thomas and J. Schmidt, *J. Am. Chem. Soc.*, 2018, **140**, 1423–1427.
- 19 Y. Song, Z. Li, Y. Zhu, X. Feng, J. S. Chen, M. Kaufmann, C. Wang and W. Lin, *J. Am. Chem. Soc.*, 2019, **141**, 12219–12223.
- 20 H. Yang, J. Wang, J. Ma, H. Yang, J. Zhang, K. Lv, L. Wen and T. Peng, *J. Mater. Chem. A*, 2019, 7, 10439–10445.
- 21 X. Wang, L. Chen, S. Y. Chong, M. A. Little, Y. Wu, W. H. Zhu, R. Clowes, Y. Yan, M. A. Zwijnenburg, R. S. Sprick and A. I. Cooper, *Nat. Chem.*, 2018, **10**, 1180–1189.
- V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, F. Podjaski,
 C. Ochsenfeld and B. V. Lotsch, *Nat. Commun.*, 2015,
 6, 8508.
- 23 K. Mori, R. Osaka, K. Naka, D. Tatsumi and H. Yamashita, *ChemCatChem*, 2019, **11**, 1963–1969.
- 24 L. Guo, Y. Niu, H. Xu, Q. Li, S. Razzaque, Q. Huang, S. Jin and B. Tan, *J. Mater. Chem. A*, 2018, **6**, 19775–19781.
- 25 M. Wang, K. Han, S. Zhang and L. Sun, Coord. Chem. Rev., 2015, 287, 1–14.
- 26 J. Dong, M. Wang, X. Li, L. Chen, Y. He and L. Sun, *ChemSusChem*, 2012, 5, 2133-2138.
- 27 Y. Huang and B. Zhang, Angew. Chem., Int. Ed., 2017, 56, 14804-14806.
- 28 J. Willkomm and E. Reisner, Bull. Jpn. Soc. Coord. Chem., 2018, 71, 18–29.
- 29 O. Schott, A. K. Pal, D. Chartrand and G. S. Hanan, *Chem-SusChem*, 2017, **10**, 4436–4441.
- 30 C. Lentz, O. Schott, T. Auvray, G. Hanan and B. Elias, *Inorg. Chem.*, 2017, 56, 10875–10881.
- 31 P. Du, J. Schneider, G. Luo, W. W. Brennessel and R. Eisenberg, *Inorg. Chem.*, 2009, 48, 4952–4962.
- 32 B. Probst, A. Rodenberg, M. Guttentag, P. Hamm and R. Alberto, *Inorg. Chem.*, 2010, **49**, 6453–6460.
- 33 P. Du, K. Knowles and R. Eisenberg, J. Am. Chem. Soc., 2008, 130, 12576–12577.
- 34 F. Lakadamyali, M. Kato, N. M. Muresan and E. Reisner, Angew. Chem., Int. Ed., 2012, 51, 9381–9384.
- 35 T. Lazarides, T. McCormick, P. Du, G. Luo, B. Lindley and R. Eisenberg, *J. Am. Chem. Soc.*, 2009, **131**, 9192–9194.
- 36 D. W. Wakerley and E. Reisner, Phys. Chem. Chem. Phys., 2014, 16, 5739–5746.
- 37 P. Zhang, M. Wang, C. Li, X. Li, J. Dong and L. Sun, *Chem. Commun.*, 2010, 46, 8806–8808.
- 38 T. Lazarides, M. Delor, I. V. Sazanovich, T. M. McCormick, I. Georgakaki, G. Charalambidis, J. A. Weinstein and A. G. Coutsolelos, *Chem. Commun.*, 2014, **50**, 521–523.
- 39 M. Natali, M. Orlandi, C. Chiorboli, E. Iengo, V. Bertolasi and F. Scandola, *Photochem. Photobiol. Sci.*, 2013, 12, 1749–1753.

- 40 J. C. Manton, C. Long, J. G. Vos and M. T. Pryce, *Dalton Trans.*, 2014, **43**, 3576–3583.
- 41 G. G. Luo, H. Lu, X. L. Zhang, J. C. Dai, J. H. Wu and J. J. Wu, *Phys. Chem. Chem. Phys.*, 2015, **17**, 9716–9729.
- 42 X. B. Li, C. H. Tung and L. Z. Wu, Angew. Chem., Int. Ed., 2019, 58, 10804–10811.
- 43 Y. Xu, Y. Ye, T. Liu, X. Wang, B. Zhang, M. Wang, H. Han and C. Li, *J. Am. Chem. Soc.*, 2016, **138**, 10726–10729.
- 44 F. Wen, J. Yang, X. Zong, B. Ma, D. Wang and C. Li, *J. Catal.*, 2011, **281**, 318–324.
- 45 J. C. Hu, S. Sun, M. D. Li, W. Xia, J. Wu, H. Liu and F. Wang, *Chem. Commun.*, 2019, 55, 14490–14493.
- 46 F. Lakadamyali and E. Reisner, *Chem. Commun.*, 2011, 47, 1695–1697.
- 47 F. Lakadamyali, A. Reynal, M. Kato, J. R. Durrant and E. Reisner, *Chem. Eur. J.*, 2012, **18**, 15464–15475.
- 48 A. Reynal, F. Lakadamyali, M. A. Gross, E. Reisner and J. R. Durrant, *Energy Environ. Sci.*, 2013, **6**, 3291–3300.
- 49 T. Banerjee, F. Haase, G. Savasci, K. Gottschling, C. Ochsenfeld and B. V. Lotsch, J. Am. Chem. Soc., 2017, 139, 16228–16234.
- 50 X.-W. Song, H.-M. Wen, C.-B. Ma, H.-H. Cui, H. Chen and C.-N. Chen, *RSC Adv.*, 2014, 4, 18853–18861.
- 51 M. A. Nasalevich, R. Becker, E. V. Ramos-Fernandez, S. Castellanos, S. L. Veber, M. V. Fedin, F. Kapteijn, J. N. H. Reek, J. I. van der Vlugt and J. Gascon, *Energy Environ. Sci.*, 2015, 8, 364–375.
- 52 Z. Li, J.-D. Xiao and H.-L. Jiang, ACS Catal., 2016, 6, 5359-5365.
- 53 S. Y. Byeon, J. H. Kim and J. Y. Lee, ACS Appl. Mater. Interfaces, 2017, 9, 13339–13346.
- 54 C. Tang, R. Bi, Y. Tao, F. Wang, X. Cao, S. Wang, T. Jiang, C. Zhong, H. Zhang and W. Huang, *Chem. Commun.*, 2015, 51, 1650–1653.
- 55 X. Yang, G. Zhou and W. Y. Wong, *Chem. Soc. Rev.*, 2015, **44**, 8484–8575.
- 56 B. Wex and B. R. Kaafarani, J. Mater. Chem. C, 2017, 5, 8622-8653.
- 57 Q. Q. Dang, H. J. Wan and X. M. Zhang, ACS Appl. Mater. Interfaces, 2017, 9, 21438–21446.
- 58 X. Zhu, C. Tian, T. Jin, K. L. Browning, R. L. Sacci, G. M. Veith and S. Dai, ACS Macro Lett., 2017, 6, 1056–1059.
- 59 T. Jin, Y. Xiong, X. Zhu, Z. Tian, D. J. Tao, J. Hu, D. E. Jiang, H. Wang, H. Liu and S. Dai, *Chem. Commun.*, 2016, 52, 4454–4457.
- 60 Q. Chen, M. Luo, P. Hammershoj, D. Zhou, Y. Han, B. W. Laursen, C. G. Yan and B. H. Han, *J. Am. Chem. Soc.*, 2012, 134, 6084–6087.
- 61 Y. Zhang, S. A, Y. Zou, X. Luo, Z. Li, H. Xia, X. Liu and Y. Mu, J. Mater. Chem. A, 2014, 2, 13422–13430.
- 62 Q. Chen and B. H. Han, *Macromol. Rapid Commun.*, 2018, 39, 1800040.

- 63 F. Jiang, T. Jin, X. Zhu, Z. Tian, C.-L. Do-Thanh, J. Hu, D.-E. Jiang, H. Wang, H. Liu and S. Dai, *Macromolecules*, 2016, **49**, 5325–5330.
- 64 Y. Liao, Z. Cheng, M. Trunk and A. Thomas, *Polym. Chem.*, 2017, 8, 7240–7247.
- 65 W. Zhang, J. Tang, W. Yu, Q. Huang, Y. Fu, G. Kuang, C. Pan and G. Yu, *ACS Catal.*, 2018, **8**, 8084–8091.
- 66 Y. Zhi, S. Ma, H. Xia, Y. Zhang, Z. Shi, Y. Mu and X. Liu, *Appl. Catal., B*, 2019, **244**, 36–44.
- 67 J. Luo, J. Lu and J. Zhang, J. Mater. Chem. A, 2018, 6, 15154–15161.
- 68 J. Luo, X. Zhang and J. Zhang, ACS Catal., 2015, 5, 2250-2254.
- 69 J. Luo, X. Zhang, J. Lu and J. Zhang, ACS Catal., 2017, 7, 5062–5070.
- 70 H.-P. Liang, A. Acharjya, D. A. Anito, S. Vogl, T.-X. Wang, A. Thomas and B.-H. Han, ACS Catal., 2019, 9, 3959–3968.
- 71 B. Guo, H. X. Li, C. H. Zha, D. J. Young, H. Y. Li and J. P. Lang, *ChemSusChem*, 2019, **12**, 1421–1427.
- 72 S. Ding, C. Tian, X. Zhu, C. W. Abney, Z. Tian, B. Chen, M. Li, D.-E. Jiang, N. Zhang and S. Dai, *ChemSusChem*, 2017, 10, 2348–2351.
- 73 G. N. Schrauzer, Inorg. Synth., 1968, 11, 61-70.
- 74 J. S. Zhang and W. D. Zhang, *ChemCatChem*, 2019, **11**, 2657–2666.
- 75 Y. Horiuchi, T. Toyao, M. Saito, K. Mochizuki, M. Iwata, H. Higashimura, M. Anpo and M. Matsuoka, *J. Phys. Chem. C*, 2012, **116**, 20848–20853.
- 76 T. Toyao, M. Saito, S. Dohshi, K. Mochizuki, M. Iwata, H. Higashimura, Y. Horiuchi and M. Matsuoka, *Chem. Commun.*, 2014, 50, 6779–6781.
- 77 J. He, J. Wang, Y. Chen, J. Zhang, D. Duan, Y. Wang and Z. Yan, *Chem. Commun.*, 2014, 50, 7063–7066.
- 78 L. Shen, M. Luo, L. Huang, P. Feng and L. Wu, *Inorg. Chem.*, 2015, 54, 1191–1193.
- 79 Z. L. Wu, C. H. Wang, B. Zhao, J. Dong, F. Lu, W. H. Wang, W. C. Wang, G. J. Wu, J. Z. Cui and P. Cheng, *Angew. Chem.*, *Int. Ed.*, 2016, 55, 4938–4942.
- 80 T. Toyao, M. Saito, Y. Horiuchi, K. Mochizuki, M. Iwata, H. Higashimura and M. Matsuoka, *Catal. Sci. Technol.*, 2013, 3, 2092–2097.
- 81 S. Pullen, H. Fei, A. Orthaber, S. M. Cohen and S. Ott, J. Am. Chem. Soc., 2013, 135, 16997–17003.
- 82 J. T. Muckerman and E. Fujita, Chem. Commun., 2011, 47, 12456–12458.
- 83 A. Bhattacharjee, E. S. Andreiadis, M. Chavarot-Kerlidou, M. Fontecave, M. J. Field and V. Artero, *Chem. – Eur. J.*, 2013, 19, 15166–15174.
- 84 B. H. Solis and S. Hammes-Schiffer, *Inorg. Chem.*, 2011, 50, 11252–11262.