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A facile strategy to design and prepare a robust porous hybrid material (HO-TPA-TiO₂) is presented by combining TiO_2 with calixarene dye **HO-TPA** through a simple sol-gel method, offering efficient and persistent dual-function photocatalytic activities for hydrogen production or CO_2 reduction to CO when loaded with Pt nanoparticles or ReP as co-catalysts.

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1. Introduction

Photocatalytic techniques have long been studied to alleviate the exhaustion of energy resources and deterioration of natural environments by utilizing solar energy.^{1,2} To date, enormous attentions have been focused on photocatalytic hydrogen production from water-splitting and solar-light-driven reduction of CO₂ to fuels or other useful chemicals, which provide a direct route to the green chemical industry and a guide for design and preparation of the multi-functional artificial photosynthesis.³⁻⁷ Traditionally, some semiconductor materials (TiO₂, Ge₃N₄, GaN, $K_2Ti_2O_5$, and C_3N_4)⁸⁻¹² assisted with noble metals (Pt, Pd, and Au)¹³⁻¹⁵ as the co-catalysts have been exploited and applied in photocatalytic or photoelectric reactions under UV or limited visible light region. To take full advantage of solar energy, some strategies, such as nonmetallic element doping (N, S, and P) $^{16\text{-}18}$ semiconductors and dye-sensitized semiconductors,¹⁹⁻²¹ have been employed to utilize solar energy in the extend visible light region. Nevertheless, their low photocatalytic activity and stability greatly impede their practical implementation. Especially the common dye-sensitized systems loaded with Pt nanoparticles for photocatalytic water splitting have

A porous hybrid material based on calixarene dye and TiO₂ demonstrating high and stable photocatalytic performance

Yi-Fan Chen,^{a,b} Jian-Feng Huang,^a Min-Hui Shen,^a Jun-Min Liu,^{a, *} Li-Bo Huang,^a Yu-Hui Zhong,^a Su Qin,^a Jing Guo,^a Cheng-Yong Su^{a, *}

A highly robust hybrid material based on calixarene dye (**HO-TPA**) and titanium dioxide with micro/mesoporous structure and large surface area (denoted as HO-TPA-TiO₂) has been prepared by a facile so-gel method. When Pt nanoparticles (Pt NPs) or fac-[Re(4,4'-disphosphonic acid)-2,2'-bipyridine)(CO)₃Cl (ReP) as co-catalysts are introduced onto the hybrids respectively, the two hybrid systems can display dual-functional photocatalytic properties. Under visible-light irradiation, the optimized Pt/HO-TPA-TiO₂ system exhibits high hydrogen production activity (618.3 mmol g⁻¹ h⁻¹ based on Pt mass) and performs with excellent stability even after used for 15 times (a turnover number of 6417 after 75 h). On the other hand, the optimum ReP/HO-TPA-TiO₂ material displays persistent photocatalysis of CO₂ reduction to CO and gives a turnover number of 534 for 26 h (854.4 mmol g⁻¹ based on ReP mass), which is one of the highest among all the reported heterogeneous catalytic systems under visible light. The high activity and stability of the HO-TPA-TiO₂ based hybrid materials can be attributed to the stable coordination linkage and efficient electron transfer between **HO-TPA** and micro/mesoporous TiO₂. The current study offers an inspiration for the design and application of new multi-functional organic-inorganic hybrid systems in efficient photocatalysis.

poor stability and become inactivated easily because the dye would detach from semiconductor and degrade under light irradiation.^{22,23} In a previous paper,²⁴ we utilized cone-calix[4]arene dye **Calix-3** to sensitize Zr-containing metal-organic framework (MOF) embedded with Pt nanoparticles (Pt@UiO-66-NH₂) for photocatalytic H₂ production under visible light irradiation. **Calix-3** has four -COOH groups in one molecule and thus multiple hydrogen bonds exist between UiO-66-NH₂ and dyes, which would increase the stability of the dyes adsorbed on the MOF surface and enhance hydrogen evolution efficiency and stability. To further enhance dye adsorption stability on the semiconductor and promote surface interfacial charge transfer from dye to semiconductor simultaneously, herein we design a novel organic-inorganic hybrid materials in which organic dyes and inorganic semiconductors can be combined through strong coordination bonds.

Hybrid materials containing TiO₂ inorganic component has been applied in many fields due to its high activity and chemical stability.^{25,26} Several synthetic methods for hybrid materials have been developed, such as dispersion polymerization,²⁷ hydrothermal method,²⁸ template-assisted growth²⁹ and sol-gel method.³⁰⁻³³ Particularly the sol-gel method could be adopted to obtain some well-compatible organic-inorganic nanomaterials with high surface areas.³⁴ In addition, in view of the fact that calix[4]arene derivatives possess large cavity and are easy to form supramolecular complexes with inorganic molecules,³⁵⁻³⁸ we set out to design and synthesize a calix[4]arene organic dye **HO-TPA** (Scheme 1, Fig S1) consisting of 2triphenylamine donor, oligothiophene spacer, and hydroxylsubstituted calix[4]arene acceptor, which can be combined with TiO₂ by simple sol-gel method to obtain a binary organic-inorganic hybrid system, denoted as HO-TPA-TiO₂. This kind of hybrid system loaded

^{a.} School of Chemistry and School of Materials Science and Engineering, Sun Yat-sen University, Guangzhou, 510275, China.

^{b.} Hainan Provincial Key Lab of Fine Chem, School of Chemical Engineering and Technology, Hainan University, Haikou, 570228, China.

⁺ Corresponding authors.

E-mail addresses: liujunm@mail.sysu.edu.cn (J.-M. Liu), cesscy@mail.sysu.edu.cn (C.-Y. Su).

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with co-catalyst is expected to work as a persistent photocatalyst owing to the following advantages: (1) high photo- and thermostable **HO-TPA** has four -OH groups in one molecule which can interact with $Ti(OC_4H_9)_4$ to form very strong TiO_2 -O-TPA bonds, leading to great improvement in stability of the doped dyes in hybrid system; (2) **HO-TPA** has four light-harvesting units per molecule, which is not only favourable to achieve high molar extinction coefficients but also ensures more effective electron transfer between the doped dye and surrounding TiO_2 ; (3) the hybrid material of **HO-TPA** and TiO_2 has micro/mesoporous structure, large surface area and abundant active sites for the reactions, thus enhancing light harvesting from multi-reflections and catalytic-center utilization in the pores; (4) in the hybrid materials, TiO_2 protects **HO-TPA** and works as electron transporting mediator and reservoir.

In this paper, we demonstrate the good activity and excellent stability of this kind of hybrid material with co-catalyst Pt NPs (denoted as Pt/HO-TPA-TiO₂) in photocatalytic H₂ production from water under visible-light, giving a turnover number of 6417 for 75 after used for 15 times and recycled simultaneously. Moreover, we extend the hybrid material HO-TPA-TiO₂ toward CO₂ photoreduction via immobilization of the Re complex fac-Re(2,2'-bipyridine-4,4'bisphosphonic acid)(CO)₃(Cl)] (denoted as ReP, Scheme 1), which is known to be able to photoreduce CO_2 to CO in homogeneous systems,³⁹ onto the hybrid material to prepare the ternary hybrid (denoted as ReP/HO-TPA-TiO₂) as heterogeneous photosynthesis system. While some interesting results on photocatalytic CO₂ reduction using ReP/TiO₂ and ReP/dye-sensitized TiO₂ (denoted as ReP/TiO₂/dye) hybrids have been reported,³⁹⁻⁴¹ there have been no investigations to bind ReP onto the hybrid material in photocatalytic reaction. Our results disclose that the photocatalyst ReP/HO-TPA-TiO₂ could selectively photoreduce CO₂ to CO with a high TON_{CO} of 534 with 1,3-dimethyl-2-phenyl-1,3-dihydrobenzimidazole (BIH, Scheme 1) as the sacrificial agent and triethanolamine (TEOA) as additive under visible-light irradiation for 26 h. Furthermore, the mechanisms of photocatalytic hydrogen production and CO₂ photoreduction in the hybrid system have been explored.



Scheme 1. Sensitizer (HO-TPA), reduction catalyst (ReP), and electron donor (BIH) used for the hybrid system.

2. Experiments

2.1. Preparation of photocatalysts

All solvents were purified by an MBRAUN MB SPS-800 system. Anhydrous solvents used in the Suzuki coupling reaction were degassed by bubbling with N_2 for 20 min. All other chemicals and

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reagents were used as received from commercial sources, without further purification. The P25-TiO₂ particle is a commercial product of Degussa AG without further treatment. Calix-1^{42,43} and ReP³⁹ were prepared according to the methods reported in previous literatures, respectively. The detailed synthesis of **HO-TPA** was described in supporting information. The preparation of calixarene-based dyes **HO-TPA** was performed according to Fig. S1 and detailed synthesis and characterization were included in support information.

2.1.1. Synthesis of HO-TPA-TiO₂ materials

HO-TPA-TiO₂ materials were prepared through a sol-gel process shown in Fig. S2. To prepare 5.0 wt% HO-TPA-TiO₂, THF (1 mL), acetic acid (168 μ L), distilled water (106 μ L) and butyltitanate (1 mL) were subsequently added into 20 mL glass sample bottle, and then **HO-TPA** (12.5 mg) in THF (1 mL) was added. The color of mixture changed from light yellow to dark red, and stirred to become transparent gelatum. The gelatum was heated at 50 °C for 10 h to obtain red solid. The residue was soxhleted with distilled water at 100 °C for 30 h and evaporated to dryness. The hybrid materials were calcined in Muffle furnace at 300 °C for 2 h to become brown powder. To elaborate the formation process of HO-TPA-TiO₂ materials, the intermediate products at different reaction time before calcination was collected to characterize their crystalline states by XRD patterns (Fig. S3).

Similar Gel-TiO₂ materials without doping dye and HO-TPA-TiO₂ (2.5 and 7.5 wt%) materials with different dye amounts were prepared with the above method.

2.1.2. Synthesis of Pt/HO-TPA-TiO₂ materials

Pt nanoparticles (0.6 wt%) were loaded onto HO-TPA-TiO₂ (0, 2.5, 5.0 and 7.5 wt%) materials with different dye amounts, respectively. In general, 100 mg of hybrid materials were dispersed in 60 mL H₂O and methanol (5:1, v/v) solution containing H₂PtCl₆·6H₂O (10 mM, 340 μ L) in N₂, and then stirred and illuminated for 30 min with a 300 W Xe lamp. The solid was centrifuged, washed, and dried in vacuum oven at room temperature. Pt loading (0.6 wt%) was testified by the inductively coupled plasma atomic emission spectrometry (ICP-AES).

2.1.3. Synthesis of surface dye-sensitized Pt/Gel-TiO₂/HO-TPA materials

The Pt/Gel-TiO₂ powder (prepared similarly as above without addition of HO-TPA) was dispersed in 0.3 mM CHCl₃ solution of HO-TPA at room temperature for 6 h, and then centrifuged and washed with CHCl₃ until no color was observed from the eluent. The solid was dried in vacuum oven at room temperature for overnight. The concentrations of dye solutions before and after use were determined to be 2.4 wt% by UV-vis spectra at 500 nm wavelength to calculate the adsorbing capacities of the catalysts.

2.1.4. Synthesis of ReP/HO-TPA-TiO₂ materials

5.0 wt% HO-TPA-TiO₂ materials (10 mg) were dispersed in 0.1 μ mol ReP aqueous solution (2 mL) and stirred for 4 h, and then centrifuged and washed with distilled water for 3 times. The solid was dried in vacuum oven at room temperature for overnight. The loading amounts of ReP for 10 mg samples were determined to be 0.041 μ mol by ICP-AES. For comparison, ReP/Gel-TiO₂ and ReP/Gel-

TiO₂/HO-TPA materials were prepared according to the above method for control experiments. The loading amounts of ReP were determined to be 0.054 μ mol for 10 mg ReP/Gel-TiO₂ materials and 0.050 μ mol for 10 mg ReP/Gel-TiO₂/HO-TPA materials by ICP-AES.

2.2. Characterizations

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The ¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer. Mass spectra data were obtained on an ultrafleXtreme MALDI-TOF/TOF mass spectrometer (Bruker Daltonics). The absorption spectra were observed with a Shimadzu UV-3600 spectrometer and fluorescence spectra were measured with an Edinburgh Instruments Ltd FLS980 spectrometer. Powder Xray diffraction (PXRD) was recorded on a Rigaku Smart Lab diffractometer (Bragg-Brentano geometry, Cu-K α 1 radiation, λ = 1.54056 Å). Transmission electron microscopy (TEM) images, highresolution transmission electron microscopy (HRTEM), high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) micrographs, selected area electron diffraction (SAED), energy dispersive X-ray spectroscopy (EDX), and elemental mapping were obtained by a JEM-2100F transmission electron microscope at 300 kV. Scanning electron microscopy (SEM) micrographs were recorded on Hitachi Ultra-high Resolution FE-SEM SU8010 microscope. Gas adsorption measurements were performed using ultra-high purity N₂ and CO₂ gas on Quantachrome Auto-sorbiQ2-MP analyzer. The Mott-Schottky curves were measured using a CHI760E electro-chemical analyzer (China) in a three-electrode cell. Pt plate was used as counter electrode and Ag/AgCl electrode (3 M KCI) was used as reference electrode. The electrolyte was a 0.2 M Na₂SO₄ solution. The working electrode was prepared on fluorinedoped tin oxide (FTO) glass by dipping the mixed slurry containing the sample and H₂O, and the exposed area of the electrode was 0.25 cm². Cyclic voltammograms (CVs) were recorded using a CHI760E electrochemical analyzer with platinum plate as working electrode, Ag/AgCl (3 M KCl) as reference electrode, Pt wire as counter electrode. CVs were measured using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte in THF with a scan rate of 100 mV s⁻¹. The photocatalytic hydrogen production system was Perfect Light Lab Solar-IIIAG and H₂ measurement was performed on Agilent Technologies 78. The amounts of Pt NPs and ReP loaded on samples were detected by ICP-AES (spectra range: 120-800 nm, holographic grating, 2924 line/mm, SPECTRO CIROS VISION). Attenuated total reflection-infrared intensity (ATR-IR) spectra were monitored by Frontier FT-IR spectrometer (spectra range 4000-450 cm⁻¹, an average of 64 scans). X-ray photoelectron spectroscopy (XPS) measurements were carried out using an XR6 monochromated AlK α X-ray source (hv = 1486.6 eV) with a 900 mm spot size in an ultrahigh vacuum chamber (ESCALAB 250Xi). The pass energy was 20 eV. Apparent quantum yields (AQYs) were determined using 420 nm, 450 nm and 500 nm band pass filter and an irradiation meter, and were calculated by the following equation: AQY(%) = (2 × The number of evolved CO molecules/The number of incident photons) × 100.

2.3. Photocatalytic hydrogen production

The photocatalytic hydrogen evolution by water splitting was performed in a glass reaction cell with quartz cover connected to a

closed gas circulation, which was swept by high purity Arcbefore illumination. 50 mg photocatalysts were dispersed in 200 me of 20 vol% TEOA aqueous solution (pH = 8~9). Then the suspension was exposed to a 300 W Xe lamp equipped with an optical filter ($\lambda > 420$ nm) to cut off the light in the ultraviolet region. The reaction solution was stirred continuously and cooled to room temperature by a circulation of cooling water. The amount of hydrogen evolved was determined at an interval of 1 h with online gas chromatography.

2.4. Photocatalyzed CO₂ reduction

Suspensions of photocatalyst particles (10 mg) in 5 mL of DMF containing BIH (134 mg) and TEOA (0 M/0.23 M/0.46 M) were placed in a quartz cell (2 cm pass length; 40 mL total volume), bubbled with CO₂ for 30 min, sealed with a septum, and then irradiated using a xenon lamp while stirring (300 W). The incident light ($\lambda > 420$ nm) was obtained by passing the light from the xenon lamp through a water layer of a 10 cm path length and a glass light filter. The amounts of CO evolved in the overhead space of the cell were determined by gas chromatography (Fuli Model GC9790 II equipped with TCD and FID detectors) using a TDX-01 packed column.

3. Results and discussion

3.1. Sample characterizations

The XRD patterns of HO-TPA-TiO2 with different dye content were recorded (Fig. 1A and Fig. 1B). The obtained peaks at 25.53°, 38.12°, 48.22°, 54.18°, and 62.94° were found for all the samples, corresponding to the (101), (103), (200), (105), and (204) planes, respectively, denoting formation of anatase TiO₂ with similar degree of crystallization. Calcination at 300 °C can remove impurities from the hybrid system and facilitate the generation and transmission of photogenerated carriers, but show little impact on the crystallinity. Nitrogen adsorption-desorption isotherms measured at 77 K gave Brunauer-Emmett-Teller (BET) surface areas and pore size distributions for HO-TPA-TiO2 systems, as shown in Fig. S4-S6 and Table S1. With the increase of dye content from 0 to 2.5, 5.0, and 7.5 wt%, the specific surface area (S_{BET}) of Gel-TiO₂ and three HO-TPA-TiO₂ materials increased gradually from 163 to 176, 185, and 188 m² $g^{-1},$ respectively, in comparison with the low S_{BET} value of P25-TiO_2 (55 m² g⁻¹). A slight decrease in S_{BET} of hybrid materials was observed after calcination at 300 °C. Nevertheless, a dramatic decrease in SBET after calcination at 500 °C was found, which was reasonable because the degradation temperature of HO-TPA dye was determined to be 400 °C, and thus high temperature treatment resulted in decomposition of dyes in hybrid materials. More interestingly, two types of pore size distributions, comprising both micropore (1.4~1.6 nm) and mesopore (3.4~4.4 nm), were observed in HO-TPA-TiO₂ materials, in contrast to that (29 nm) of mesoporous P25-TiO2. This suggests that the samples prepared through a sol-gel process features micro/mesoporous hierarchical structure which contributes to higher porosity.



Fig. 1 The XRD patterns of HO-TPA-TiO₂ with different dye content were recorded without A) and with B) 300 $^{\circ}$ C calcination.

The SEM and TEM images of HO-TPA-TiO₂ (5.0 wt%) materials were recorded (Fig. S7 and Fig. 2), showing the nanoparticle size about 10 nm (Fig. 2A and Fig. 2B). The SAED results confirmed the crystallinity of TiO₂ nanoparticles in the hybrid materials (Fig. 2C). Moreover, the elemental composition of Gel-TiO₂ and HO-TPA-TiO₂ (5.0 wt%) was measured by XPS measurements (Fig. S8-S9), revealing that **HO-TPA** was successfully doped within TiO₂ through the sol-gel process.

For the purpose of H₂ production, Pt NPs was introduced into the porous hybrid materials by reduction of H₂PtCl₆·6H₂O with methanol under full light. The typical TEM images of the Pt/HO-TPA-TiO₂ (5.0 wt%) materials with 0.6 wt% Pt loading showed the size distribution of Pt particles inside the hybrid materials was about 3-5 nm (Fig. 2D and Fig. 2E). Analysis of the HRTEM images for the Pt NPs indicated that the *d*-spacing between two adjacent lattice planes was about 0.196 nm (Fig. 2F), in agreement with the spacing of Pt (200) plane. Moreover, the HAADF-STEM elemental mapping of Pt/HO-TPA-TiO₂ (5.0 wt%) indicated the elements C, N, O, S and Pt were homogenously distributed throughout the whole hybrid materials (Fig. 2G). The EDX results of a point analysis further demonstrated the existence of Pt NPs encapsulated in hybrids (Fig. S10).



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Fig. 2 A) TEM, B) HTEM, and C) SAED of HO-TPA-TiO₂, and D) and E) TEM, F) HRTEM, and G) the elemental mappings image of Pt/HO-TPA-TiO₂ (5.0 wt%).

To meet the requirement of CO₂ reduction, ReP complex was fixed onto HO-TPA-TiO₂ (5.0 wt%) to obtain the photocatalyst ReP/HO-TPA-TiO₂. To monitor ReP adsorbed on the HO-TPA-TiO₂, XPS measurements for ReP and ReP/HO-TPA-TiO₂ after photocatalytic reaction were carried out. A composition of 23% Ti, 51% O, 0.29% Re, 0.56% P, 2.8% N and 0.43% S for ReP/HO-TPA-TiO_2 was obtained, corresponding with the composition of 2.9% Re, 5.8% P, 6.6% N and 2.1% Cl of ReP with the expected 1:2 ratio for Re:P. The excess N percentage for ReP/HO-TPA-TiO₂ was probably derived from HO-TPA, TEOA and air, and the low CI percentage suggested that the active sites resulted from CI leaving may play an important role in CO2 immobilization and photoreduction (Fig. S11- S12). To further confirm the interaction between ReP and HO-TPA-TiO₂, the ATR-IR spectra of ReP and ReP/HO-TPA-TiO₂ have been measured. For the ReP powders, the -C=O stretching bands were observed at 2027 and 1884 cm⁻¹. When the complexes were adsorbed on HO-TPA-TiO₂ surface, the -C=O stretching bands became weakened, and red shifted to 2034 and 1927 cm⁻¹, indicating the robust interaction between the -PO₃H₂ moieties of ReP complex and TiO₂ (Fig. 3).



Fig. 3 ATR-IR spectra of ReP and ReP/HO-TPA-TiO₂ (5.0 wt%).

The UV/vis solid-state diffraction spectra of **HO-TPA**, ReP, Gel-TiO₂, HO-TPA-TiO₂ and ReP/HO-TPA-TiO₂ were showed in Fig. 4A. The Gel-TiO₂ had a strong absorption peak at 325 nm with a band edge

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of 450 nm, corresponding to a 3.2 eV band gap (Fig. 4B). The HO-TPA had an intense absorption band in the region of 400-500 nm, which could be attributed to a π - π * transition with charge-transfer character. After hybridization of HO-TPA sensitizers with TiO₂, a typical absorption band of HO-TPA-TiO₂ (5.0 wt%) was significantly broadened from 320 to 750 nm, which could be attributed to the robust linkage of isoreticular organic-inorganic hybrid materials on molecular and atomic level. Different from Gel-TiO₂ with only a band gap in Tauc plots, HO-TPA-TiO₂ (5.0 wt%) showed two clear band gaps: a narrow band gap of 2.5 eV and wide band gap of 3.1 eV (Fig. 4B). We deduced that the former could be ascribed to HO-TPA and the latter was attributed to Gel-TiO₂. Interestingly, compared with the E₀₋₀ value (2.74 eV) of pure HO-TPA (Table S2), a narrow band gap (2.5 eV) of Calix-3 doped in the Calix-3-TiO₂ was observed, indicating the formation of Ti-O bonds in hybrid Calix-3-TiO₂ materials (Fig. S13). Moreover, ReP exhibited an intense absorption band in 350-550 nm regions. Therefore, incorporation of ReP contributed to the increase of light absorption intensity of the hybrid material in the visible-light region, which was consistent with the enhancement of absorption coefficients of ReP/HO-TPA-TiO₂.



Fig. 4 A) UV-vis diffraction spectra of **HO-TPA**, ReP, Gel-TiO₂, HO-TPA-TiO₂ (5.0 wt%) and ReP/HO-TPA-TiO₂ (5.0 wt%), and B) Tauc plot of Gel-TiO₂ and HO-TPA-TiO₂ (5.0 wt%).

To elucidate the possibility for subsequent photocatalytic H_2 production and photoreduction of CO_2 , Mott-Schottky measurements of Gel-TiO₂ were monitored under different conditions (Fig. S14). It is known that the flat-band potentials (V_{fb}) of

systems with the Mott-Schottky measurement anethods. And the Mott-Schottky measurement of the state of the st positive slope was in accordance with an n-type semiconductor and the flat band potential was -0.72 V and -1.43 V (vs. Ag/AgCl) for Gel-TiO₂ in aqueous solution (Fig. S14A) and DMF solution (Fig. S 14B), respectively. Since it is generally accepted that the conduction band (CB) potential in n-type semiconductors was approximately equal to the $V_{\rm fb}$,^{46,47} the CB potential of Gel-TiO₂ was estimated to be -0.72 V vs. Ag/AgCl in aqueous solution, which was more negative than the redox potential of H^+/H_2 and thus favored the proton reduction to realize photocatalytic H₂ generation. The valence band (VB) potential can be calculated to be 2.04 V vs. Ag/AgCl based on the band gap. On the other hand, the first oxidation potential of the dyes was measured by CVs measurements to obtain HOMO value (Fig. S15 and Table S2). The zero-zero excitation energy was estimated from absorption/emission data (Fig. S16). The redox potential of excited HO-TPA* (-1.50 V vs. Ag/AgCl) was calculated from the HOMO value of HO-TPA and the zero-zero excitation energy, which was higher than the CB edge of the Gel-TiO₂, the potential of LUMO in Gel-TiO₂. Therefore, it was thermodynamically beneficial for direct electron transfer from HO-TPA^{*} to Gel-TiO₂. In addition, the $V_{\rm fb}$ of Gel-TiO₂ (-1.43 V vs. Ag/AgCl) in DMF solution was more negative than the reduction potential of ReP ($E_{1/2}^{red}$ = -0.83 V vs. Ag/AgCl) shown in Fig. S17 and Table S2, and thus the electron transfer should be favorable from the conduction-band of Gel-TiO₂ to the catalytic center ReP complex for the photoreduction CO_2 to CO_2 .

TiO₂, depend on the sample types, solvents and pHilfor aqueous

3.2. Effect of dye-doped amount on photocatalytic H₂ production

The photocatalytic activities of the HO-TPA-TiO₂ with 0.6 wt% Pt loading were evaluated in visible light region. As shown in Fig. 5, HO-TPA-TiO₂ (2.5 wt%) exhibited an H₂ production activity of 3.41 mmol g⁻¹ h⁻¹. With the mass percentage increase of **HO-TPA** to 5.0 wt%, the best photocatalytic activity of 3.71 mmol g^{-1} h^{-1} was obtained. However, further increase in the dye percentage to 7.5 wt% resulted in the activity decrease to 3.22 mmol g⁻¹ h⁻¹, suggesting the activities of the photocatalysts were not simply correlated to the dye-doped amounts. A speculation was that the excessive dye molecules might cause a loss of light harvesting and hinder effective electron transport simultaneously. To investigate the effects of different doping amounts of HO-TPA on the absorption properties and carrier separation, the UV/vis solid-state diffraction spectra and steadystate photo-luminescence (PL) spectra of HO-TPA-TiO₂ with different dye-doped amount (2.5/5.0/7.5 wt%) have been measured (Fig. S18). In Fig. S18A, the absorption intensity was relevant to the content of dye and the higher intensity at 350-510 nm appeared for HO-TPA-TiO₂ (5.0 wt%), which was coincident with the maximum H_2 evolution observed in this sample. The excessive HO-TPA dye inversely incurred the optical absorption decline and the corresponding H₂ evolution decrease. The positively related variation trend between absorption intensity and H₂ evolution rates in HO-TPA-TiO₂ indicated that the first step of light absorption to generate electron-hole pairs was crucial for this hybrid system. On the other hand, the fluorescence intensity of these hybrids in Fig. S18B followed the order of HO-TPA-TiO₂ (2.5 wt%) > HO-TPA-TiO₂ (7.5 wt%) > HO-TPA-TiO₂ (5.0 wt%), indicating that the improved excitation dissociation and more efficient charge transport between

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HO-TPA and TiO₂ interface for hybrid material HO-TPA-TiO₂ (5.0 wt%), in accordance with the photocatalytic activity. It is reasonable that lower content **HO-TPA** could be isolated in the hybrids, corresponding to lower amount of active sites for carrier separation; on the contrary, excessive **HO-TPA** could engender aggregation in the hybrids and the following decline of activity.

In contrast, the H₂ generation rate of Pt/Gel-TiO₂/HO-TPA surface sensitization material with 0.6 wt% Pt loading and 2.4 wt% of HO-TPA dye amount was only 1.83 mmol g⁻¹ h⁻¹, which was much lower than all the rates of coordination hybrid Pt/HO-TPA-TiO₂ catalysts. During the photocatalytic reaction process, dye HO-TPA seriously detached from Pt/Gel-TiO₂/HO-TPA material under visible light irradiation (the corresponding experimental details and results of doping-dye shedding were described in Fig. S19.), but detaching phenomena did not occur to the Pt/HO-TPA-TiO₂ catalysts even after used for 15 times and recycled, indicating the hybrid materials have higher photocatalytic activity and stability than common surface dyesensitized system. It was expectable that the inorganic component TiO₂ in the hybrid materials could protect the organic dye HO-TPA, and the stable linkages between HO-TPA and TiO_2 were beneficial to efficient electron transfer from HO-TPA* to TiO₂. In other words, organic-inorganic components in the hybrid system have synergistic effect on the photocatalytic reaction.



Fig. 5 Effect of dye-doped amount (2.5/5.0/7.5 wt%) of HO-TPA-TiO₂ and sensitized method on photocatalytic activity for H₂ production in 100 mL H₂O/TEOA (9:1 v/v) under visible light irradiation (λ > 420 nm).

The photocatalytic action spectra of hydrogen production for Pt/HO-TPA-TiO₂ (5.0 wt%) samples have been obtained under different wavelengths of incident light irradiation (Fig. S20 and Table S3). The corresponding apparent quantum yield (AQY) of the samples followed the order of 2.2% (400 nm) > 1.9% (420 nm) > 1.3% (450 nm) > 0.6% (470 nm) > 0.1% (515 nm). The results showed that the shorter wavelength suitable for H₂ evolution corresponded well with the main absorption wavelengths of HO-TPA-TiO₂ (Fig. 4A), indicating the H₂ production reaction was indeed controlled by light absorption properties of photocatalyst. Compared with other literatures reported for heterogeneous catalytic systems under visible-light (Table S4), the AQYs of Pt/HO-TPA-TiO₂ (5.0 wt%) obtained at 420 and 450 nm were moderate.

3.3. Stability tests

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It is known that the loss in H_2 production rate is a common and challenging problem, which could be caused by the dye consumption or instability under long time visible light irradiation. To check the photo-stability of our hybrid materials, the photocatalytic performance of HO-TPA-TiO₂ photocatalysts was repeatedly evaluated to confirm the stability in this study. The details operation is same as above section **2.3**. And the catalyst was recycled by centrifugation, washing with methanol and vacuum drying after every 5 h visible light irradiation. The hybrid catalyst was recyclable for 15 times. As shown in Fig. 6, a general stable H₂ production is evidently maintained during recycling reactions under lasting visible light irradiation, verifying the excellent stability of organic-inorganic components. The TON_{H2} value was calculated as number of mole of H₂ divided by the number of mole of Pt or **HO-TPA**, giving significant results of 6417 or 8120 after 75 h photoreactions, respectively.



Fig. 6 Photocatalytic H₂ production over the recyclability of HO-TPA-TiO₂ (5.0 wt%) with 0.6 wt% Pt loading under visible light irradiation (λ > 420 nm) in 100 mL H₂O/TEOA (9:1 v/v).

3.4. Mechanism of H₂ production photocatalysis

To elaborate the photocatalytic mechanism of hybrid Pt/HO-TPA-TiO₂ catalysts, the steady-state photo-luminescence (PL) spectra were measured to monitor the electron transfer from the excited HO-TPA* to TiO₂ for a series of comparable systems as control experiments (Fig. S21). The HO-TPA compound showed an intensive emission peak centered at 566 nm, which was attributable to its strong recombination of excited charge pairs by exciting light ($\lambda = 400$ nm). For comparison, PL spectra of the other three different systems under the same conditions show the decrease of relative fluorescence intensity of HO-TPA, following the order of hybrid HO-TPA-TiO₂ > surface dye-sensitized Gel-TiO₂/HO-TPA > physical-mixing Gel-TiO₂/HO-TPA > HO-TPA. This indicated that the improved excitation dissociation and more efficient charge transport between HO-TPA and TiO_2 interface occurred for HO-TPA-TiO₂ hybrid material, in contrast to the less effective surface dye-sensitized system and physical-mixing system. Meanwhile, slight blue shifts (~24 or 27 nm) of the emission peaks for Gel-TiO₂/HO-TPA or HO-TPA-TiO₂ materials further confirmed the interfacial electron transfer from the sensitized HO-TPA* to the TiO2. Therefore, it was

reasonable to assume that, in the hybrid system, the electron could transfer from excited **HO-TPA**^{*} to TiO₂ through the coordination Ti-O-TPA linkage on atomic level, and finally to Pt NPs surface to produce H₂. Meanwhile, the HO-TPA^{*} became oxidized HO-TPA⁺ and then it was reduced back to HO-TPA by sacrificial reagent triethanolamine (TEOA). Moreover, holes in TiO₂ could travel in the opposite direction from the more positive VB of TiO₂ to HO-TPA⁺, leading to all-round efficient charge separation and enhanced photocatalytic activity (Fig. 7).



Fig. 7 Proposed mechanism of photocatalytic H_2 production over Pt/HO-TPA-TiO₂.

3.5. Photocatalytic CO₂ Reduction

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Dispersions of ReP/HO-TPA-TiO₂ (5.0 wt%) particles (10 mg with 0.041 µmol ReP adsorbed) in 10 mL CO₂-saturated DMF containing BIH (134 mg) were irradiated at > 420 nm using a xenon lamp. The amounts of CO evolved in the overhead space of the reaction cell were determined by gas chromatography, whereas the liquid phase after irradiation was analysed by HPLC. It was confirmed that the exclusive product is CO accompanied by a trace amount of H₂, while formic acid was not detected at all. Fig. 8 shows plots of turnover numbers TON_{co} (representing mole numbers of CO formed relative to unit mole of the Re complex used) for CO formation versus irradiation time for the ReP/HO-TPA-TiO₂ system, in which the CO formation steadily continued up to ~25 h with no significant levelingoff tendency, giving a high TON_{CO} of 300. The apparent quantum yields on photocatalytic CO production were determined to be 0.37% at 420 nm, 0.13% at 450 nm and 0.047% at 500 nm for ReP/HO-TPA-TiO₂ (Table S5).

The hybrid system exhibited inherent capability for the twoelectron CO₂ reduction under steady supply of electrons through TiO₂ due to the energetic match between **HO-TPA**^{*}, ReP⁻ and CB of TiO₂. The lower rate of photocatalytic CO₂ reduction with the surface dyesensitized ReP/Gel-TiO₂/HO-TPA system compared to the coordinative ReP/HO-TPA-TiO₂ (5.0 wt%) system suggested that the robust coordination linkage between organic and inorganic components in nanoscale was more conducive to the electron transfer from **HO-TPA** to ReP through the TiO₂. For comparison, ReP/Gel-TiO₂ without anchoring **HO-TPA** was much less efficient for formation of CO, confirming incorporation of **HO-TPA** into TiO₂ was indispensable for the efficient reduction of CO₂.



Fig. 8 Plot of CO formation versus time for 10 mg ReP/HO-TPA-TIO₂ (5.0 wt%), ReP/Gel-TiO₂, ReP, and ReP/Gel-TiO₂/HO-TPA (5.0 wt%) in 5 mL CO₂-saturated DMF with 134 mg BIH as electron donor under visible light irradiation ($\lambda > 420$ nm).

An isotope-labeling experiment was carried out for ReP/HO-TPA-TiO₂ (5.0 wt%) dispersions in ¹³CO₂-saturated DMF-*d*₇ with BIH as the electron donor. As shown in Fig. S22, the ¹³C NMR spectrum of the irradiated sample revealed a signal at δ 185.2 ppm corresponding to the resonance of ¹³CO. In addition, the ¹³C isotope abundance in the CO formed was analyzed by GC-MS to be > 90% (Fig. S23). Moreover, in contrast to TON_{CO} of 114 in CO₂-saturated DMF for 5 h, no obvious CO production for this catalyst was found in Ar-saturated DMF under visible light irradiation, evidently indicating that CO₂ is the source of CO product.

3.6. Effect of TEOA as additive on photoreduction CO₂

It was reported that the photocatalytic activities of the hybrid systems were considerably affected by TEOA additive, because related Re(I) complexes could trap CO₂ in the presence of this amine in the dark to give TEOA-participated Re(I) carbonato complexes.⁴⁰ Therefore, we also explored potential TEOA effect on the photocatalytic activity of ReP/HO-TPA-TiO₂ (Fig. 9), which showed the plots of TON_{CO} versus time for ReP/HO-TPA-TiO₂ (5.0 wt%) in photocatalyzed CO₂ reduction with BIH as the electron donor using different concentrations of TEOA additives. It was found that the photocatalytic activity was significantly enhanced by TEOA at 0.23 M, exhibiting the highest TON_{CO} of 534 for 26 h and TOF_{CO} of 20.5 h⁻¹, which represents, to the best of our knowledge, the highest value for so far reported hybrid catalytic systems. However, the higher concentration of 0.46 M TEOA would deteriorate the activity of the hybrid materials (TON_{c0} = 489 for 26 h). As reported previously,^{40,48} the low-concentration TEOA could enhance the photocatalyzed CO₂ reduction by trapping CO₂ to form TEOA-bound carbonato complex (LRe-OCOO-(CH₂)₂NR₂; $R = (CH_2)_2OH$), and thus accelerate the coordination of CO₂ after the first one-electron reduction of the Re complex, while the high-concentration TEOA would induce an excess negative shift of flat-band potentials (V_{fb}) of TiO₂, unfavorable for the electron injection from dye to TiO₂.

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Fig. 9 Plot of CO formation versus time for 10 mg ReP/HO-TPA-TiO₂ (5.0 wt%) in 5 mL CO₂-saturated DMF with 134 mg BIH as electron donor and 0/0.23/0.46 M TEOA as the additive under visible light irradiation ($\lambda > 420$ nm).

Time / h

3.7. Mechanism of CO_2 photoreduction to CO

A possible outline of the major pathways for the photocatalytic reaction, demonstrates the charge transfer processes of the hybrid materials ReP/HO-TPA-TiO₂ in selective reduction of CO₂ to CO with considerably high turnover numbers (Fig. 10). The excited-state oxidation potential (E^*) of **HO-TPA** (-1.53 V vs. Ag/AgCl) was much more negative than the flat-band potential (V_{fb}) of Gel-TiO₂ (-1.43 V vs. Ag/AgCl) in DMF solution, which allows the ultrafast electron injection under visible light irradiation. The TiO₂ in the hybrid system worked as electron reservoir, which might be easily to transfer electrons in dynamics to the ReP sites for the reduction of CO_2 to CO.⁴⁹ The injected electron from the TiO₂ flowed to the ReP complex to motivate the two-electron catalytic reduction of CO₂ on the ReP sites, where the $V_{\rm fb}$ of TiO₂ should be more negative than $E_{1/2}^{\rm red}$ of ReP (-0.83 V vs. Ag/AgCl) (Fig. S16). However, the mechanistic details of CO₂ reduction catalyzed by PReX have not yet been fully understood (Fig. S24). In principle, a 17-electron species (PRe*) formed from the one-electron reduced state (PReX*-) has been generally accepted for the coordination of CO₂ in equilibrium with the coordination of a solvent molecule (DMF),⁵⁰ which resulted in complicated intermediates, such as, CO2-bridged dimer complex (LRe-COOReL),⁵¹ CO₂-coordinated complex,⁵² metallocarboxylic acid or TEOA-bound carbonato complex by the introduction of H₂O or TEOA.49 Among them, the CO₂-bridged dimer complex was unfavorable to the catalytic activity of CO₂ photoreduction to CO. In our system, the phosphonated ReP complex was immobilize onto the hybrid nanoparticle (HO-TPA-TiO₂) surface at extremely low mass percentage (0.26%), which avoided forming the inactive ReP complex dimers, therefore improving the TON_{CO} value in comparison to the homogeneous ReP complex.³⁹ Furthermore, the CO-formation from CO₂ by Re catalyst was a second-reduction step accompanied by a multi-electron process, involving the generation of a higheroxidation state Re complex, which must be reduced by the second electron transfer to regenerate the starting-state complex, PReX. In present hybrid system, the second-reduction step could occur with the electrons "pooled" in TiO2, which might be long-lived enough to

be transferred to the PReX site. At last, the catalytic cycle cathbe completed after the recovery of HO-TPA by the reduction of HO-TPA by the reduction of HO-TPA with BIH as the electron donors.





4. Conclusions

We present an unprecedented strategy to design and prepare a robust porous hybrid material (HO-TPA-TiO₂) with combination of TiO_2 and calixarene dye **HO-TPA** containing four D- π -A units through a sol-gel method, offering efficient and persistent dual-function photocatalytic activities when loaded with Pt nanoparticles or ReP as co-catalysts. For comparison, the coordination binding Pt/HO-TPA-TiO₂ with 0.6 wt% of Pt loading exhibits much higher H₂ production activity and more excellent stability than analogous Pt/Gel-TiO₂/HO-TPA system under the similar photocatalytic conditions. The enhancement in H₂ evolution efficiency and stability could be ascribed to stable Ti-O-TPA linkage and more efficient electron transfer between calixarene dye and TiO₂. On the other hand, the HO-TPA-TiO₂ hybrid system loading 0.26 wt% ReP complex works as a stable photocatalyst for the selective reduction of CO₂ to CO in DMF in the presence of an electron donor BIH, of which the photocatalytic activities can be tuned by TEOA additives. A remarkable TON_{co} of 534 (2.19 mmol g⁻¹ based on the mass of hybrids or 854.4 mmol g⁻¹ based on ReP mass) has been achieved via a single-run photoreaction of Re/HO-TPA-TiO₂ in the presence of 0.23 M TEOA with no leveling-off tendency for 26 h, which represents one of the highest among all the reported heterogeneous catalytic systems under visible-light. The convenient methodology reported here might provide a potential approach to develop highly active, robust and multi-functional organic-inorganic hybrid systems for the efficient photocatalysis.

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Conflicts of interest

There are no conflicts to declare.

Appendix A. Supplementary data

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXX.

Reference

- L. Shen, S. Liang, W. Wu, R. Liang, L. Wu, *Dalton Trans.*, 2013, 42, 13649.
- [2] S. Sato, T. Morikawa, S. Saeki, T. Kajino, T. Motohiro, Angew Chem Int Edit., 2010, 122, 5227.
- [3] Y. Ji, Y. Luo, J. Am. Chem. Soc., 2016, **138**, 15896.
- [4] H. Park, H.-I. Kim, G.-H. Moon, W. Choi, *Energy. Environ. Sci.*, 2016, 9, 411.
- [5] S. N. Habisreutinger, L. Schmidt-Mende, J. K. Stolarczyk, Angew. Chem. Int. Ed., 2013, 52, 7372.
- [6] L. Wei, C. Yu, Q. Zhang, H. Liu, Y. Wang, J. Mater. Chem. A, 2018, 6, 22411.
- [7] M. Gao, L. Zhu, W. Ong, J. Wang, G. W. Ho, *Catal. Sci. Technol.*, 2015, 5, 4703-4726.
- [8] Q. Xiang, J. Yu, M. Jaroniec, J. Am. Chem. Soc., 2012, **134**, 6575.
- [9] J. Sato, N. Saito, Y. Yamada, K. Maeda, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen, Y. Inoue, *J. Am, Chem. Soc.*, 2005, **127**, 4150.
- [10] S. Nakamura, Solid State Commum., 1997, **102**, 237.
- [11] M. Shibata, A. Kudo, A. Tanaka, K. Domen, K. Maruya, T. Onishi, *Chem. Lett.*, 1987, **16**, 1017.
- [12] Y.-N. Liu, C.-C. Shen, N. Jiang, Z.-W. Zhao, X. Zhou, S.-J. Zhao, A.W. Xu, ACS Catal., 2017, 7, 8228.
- [13] J. F. Guayaquil-Sosa, A. Calzada, B. Serrano, S. Escobedo, H. D. Lasa, Catal., 2017, 7, 324.
- [14] M. Luo, W. Yao, C. Huang, Q. Wu, Q. Xu, RSC Adv., 2015, 5, 40892.
- [15] D. Wang, L. Huang, Z. Guo, X. Han, C. Liu, W. Wang, W. Yuan, *Appl. Surf. Sci.*, 2018, **456**, 871.
- [16] S. Ida, P. Wilson, B. Neppolian, M. Sathish, P. Karthik, P. Ravi.P, Ultrason. Sonochem., 2019, 57, 62.
- [17] W. X. Zeng, Y. Bian, S. Cao, A. Q. Zhu, L. L. Qiao, Y. J. Ma, P. F. Tan, Q. Y. Ma, R. Dong, J. Pan, *Appl. Surf. Sci.*, 2019, **478**, 334.
- [18] Q. Q. Liu, J. Y. Shen, X. H. Yu, X. F. Yang, W. Liu, J. Yang, H. Tang, H. Xu, H. M. Li, Y. Y. Li, J. S. Xu, *Appl. Catal. B.*, 2019, **248**, 84.
- [19] X. Zhang, T. Peng, S. Song. J. Mater. Chem. A, 2016, 4, 2365.
- M. Watanabe, S. Sun, T. Ishihara, T. Kamimura, M. Nishimura, F. Tani, *Appl. Energy. Mater.*, 2018, 1, 6072.
 M. D. Bardy, P. N. G. Statis, and J. S. Sun, J. Su
- [21] M. D. Brady, R. N. Sampaio, D. Wang, T. J. Meyer, G. J. Meyer, J. Am. Chem. Soc., 2017, 139, 15612.
- [22] A. Kruth, A. Quade, V. Brüser, K.-D. Weltmann, J. Phys. Chem. C, 2013, 117, 3804.
- [23] N. Mattias, L. Sten, P. Petter, O. Lars, Surf. Sci., 2005, 582, 49.
- Y.-F. Chen, L.-L. Tan, J.-M. Liu, S. Qin, Z.-Q. Xie, J.-F. Huang, Y. W. Xu, L.-M. Xiao, C.-Y. Su, *Appl. Catal. B.*, 2017, **206**, 426.
- [25] Y.-L. Chen, S.-L. Lo, H.-L. Chang, H.-M. Yeh, L. P. Sun, C. Oiu, Water Sci. Technol., 2015, 73, 1667.
- [26] Z. Jiang, D. Jiang, Z. Yan, D. Liu, K. Qian, J. Xie, Appl. Catal. B-Environ., 2015, 170, 195.
- [27] A. Schmid, S. Fujii, S.P. Armes, C.A. Leite, F. Galembeck, H. Minami, N. Saito, M. Okubo, *Chem. Mater.*, 2007, **19**, 2435.
- [28] H. Xie, Y. Li, H. Li, Y. Xu, X. Chen, J. Mater. Sci., 2019, 54, 10836.

- [29] Y. Chen, X. Luo, Y. Luo, P. Xu, J. He, L. Jiang, J. Li, Z. Yuew Anticle Online Nanomaterials., 2019, 9, 698. DOI: 10.1039/C9TA06038C
- [30] C. Bak, H. W. Hyun, C. Lee, D.-Y. Jeong, H. Eom, *Thin Solid Film*, 2019, 678, 32.
- [31] A. Wight, M. Davis, Chem. Chem. Rev., 2002, 102, 3589.
- [32] M. Ge, C. Cao, J. Huang, S. Li, Z. Chen, K.-Q. Zhang, S. S. Al-Deyab, Y. Lai, J. Mater. Chem. A, 2016, 4, 6772.
- [33] Z. Rodolfo, R.-G. V, Arzola, Y.; M.-R. A, ACS Catal. 2012, 2, 1.
- [34] L. Li, S. Xiang, S. Cao, J. Zhang, G. Ouyang, L. Chen, C.-Y. Su, Nat. Commun., 2013, 4, 1774.
- [35] H. J. Kim, M. H. Lee, L. Mutihac, J. Vicens, J.S. Kim, Chem. Soc. Rev., 2012, 41, 1173.
- [36] H. Miyaji, H.-K. Kim, E.-K. Sim, C.-K. Lee, W.-S. Cho, J.L. Sessler, C.-H. Lee, J. Am. Chem. Soc., 2005, 127, 12510.
- [37] T. Kamegawa, S. Matsuura, H. Seto, H. Yamashita, Angew. Chem. Int. Ed., 2013, 52, 916.
- [38] L.-L. Tan, J.-M. Liu, S.-Y. Li, L.-M. Xiao, D.-B. Kuang, C.-Y. Su, ChemSusChem., 2015, 8, 280.
- [39] C. D. Windle, E. Pastor, A. Reynal, A. C. Whitwood, Y. Vaynzof, J. R. Durrant, R. N. Perutz, E. Reisner, *Chem. Eur. J.*, 2015, **21**, 3746.
- [40] D.-I. Won, J.-S. Lee, J.-M. Ji, W.-J. Jung, H.-J. Son, C. Pac, S.O. Kang, J. Am. Chem. Soc., 2015, 137, 13679.
- [41] C. L. Anfuso, R. C. Snoeberger III, A. M. Ricks, W.-M. Liu, D.-Q. Xiao, V. S. Batista, T.-Q. Lian, J. Am. Chem. Soc., 2011, 133, 6922.
- [42] M. Dudic, A. Colombo, F. Sansone, A. Casnati, G. Donofrio, R. Ungaro, *Tetrahedron*, 2004, **60**, 11613.
- [43] T.-E. Clark, M. Makha, A.-N. Sobolev, H. Rohrs, J.-L. Atwood, C. L. Raston, *Chem. Eur. J.*, 2008, **14**, 3931.
- [44] T. A. Kandiel, A. Feldhoff, L. Robben, R. Dillert, D. W. Bahnemann, Chem. Mater., 2010, 22, 2050.
- [45] D. Dung, J. Ramsden, M. Grätzel, J. Am. Chem. Soc., 1982, 104, 2977.
- [46] Y.-F. Chen, L.-L. Tan, J.-M. Liu, S. Qin, Z.-Q. Xie, J.-F. Huang, Y.-W. Xu, L-M. Xiao, C.-Y. Su, *Appl. Catal. B-Environ.*, 2017, 206, 426.
- [47] J.-F. Huang, J.-M. Liu, L.-M. Xiao, Y.-H. Zhong, L. Liu, S. Qin, J. Guo, C.-Y. Su. J. Mater. Chem. A., 2019, 7, 2993.
- [48] T. Morimoto, T. Nakajima, S. Sawa, R. Nakanishi, D. Imori, O. Ishitani, J. Am. Chem. Soc., 2013, 135, 16825.
- [49] M. Abdellah, A. M. El-Zohry, L. J. Antila, C. D. Windle, E. Reisner,
 L. Hammarström, J. Am. Chem. Soc., 2017, 139, 1226.
- [50] Y. Hayashi, S. Kita, B.S. Brunschwig, E. Fujita, J. Am. Chem. Soc., 2003, 125, 11976.
- [51] J. Agarwal, E. Fujita, H. F. Schaefer III, J. T. Muckerman, J. Am. Chem. Soc., 2012, 134, 5180.
- [52] D. H. Gibson, X. Yin, J. Am. Chem. Soc., 1998, **120**, 11200.