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COMMUNICATION

A copper(1) dye-sensitised TiO_2 -based system for efficient light harvesting and photoconversion of CO_2 into hydrocarbon fuel[†]

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A new copper(1) complex with the ability to bind to TiO_2 was synthesised and successfully employed as a solar cell sensitizer. Furthermore, we demonstrated that the copper(1) dyesensitised TiO_2 -based photocatalyst exhibits impressive effectiveness for the selective photoreduction of CO_2 to CH_4 under visible light.

The alarming climate-change issue triggered by global warming has generated great interest in the exploration of effective and clean approaches to holding and reducing greenhouse-gas emissions, especially carbon dioxide induced by the extensive use of fossil fuels.¹ Among the advances developed thus far, the lightdriven reduction of carbon dioxide directly into a high-energycontent fuel is attractive because it is emerging as a promising form of artificial photosynthesis that converts solar energy into stored chemical energy.² The catalysts typically used to achieve such a demanding task are semiconductor metal oxide particles, such as TiO₂ and some non-titanates with the frequent use of metallic clusters that contain Cu, Pt or Rh as active sites. These materials are popular because of their ability to assist in the photoreduction of carbon dioxide into various hydrocarbons.^{3,4} However, most of the previously developed catalysts rely on ultraviolet light for excitation, which mainly concerns the conversion efficiency and selective chemistry of the reactions and therefore limits their potential number of applications. The creation of new low-cost photocatalysts that can function with visible light, facilitate the complicated multielectron reaction and achieve high efficiency and selectivity has proven challenging. Toward this end, spectral sensitisation of wide-band-gap semiconductor oxides, such as TiO₂, allows the use of the main visible-light range of the solar spectrum via photoinduced interfacial electron transfer.⁵ In this manner, hybrid materials based on the preferred TiO₂ nanoparticles combine the dissimilar physical and chemical potentials of organic-inorganic species while eliminating or reducing their particular individual limitations. With respect to the cost and environmental demand of the

^bState Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, P.R. China commonly used rare heavy-metal (poly-)pyridine complexes,⁶ efforts have been focused on exploration of hybrid systems based exclusively on earth-abundant elements for the conversion of solar energy into electricity (dye-sensitised solar cells, DSSCs);⁷ however, such photo collectors that are capable of efficient charge separation are still relatively scarce, particularly those capable of CO₂ photoconversion.

An alternative pathway toward the conversion of CO2 involves the use of transition-metal complexes as molecular photocatalysts,⁸ although most of these important systems suffer from a tendency to promote only partial reduction to CO. One of the main reasons behind this shortcoming is that the selective formation of CH₄ from CO₂ is significantly more difficult than the CO2-to-CO conversion process, which involves the participation of only two electrons.⁹ The tailoring of a metal complex that contains a low-cost, environmentally benign and abundant metal as an alternative functional species to the more precious and less-abundant systems for CO₂ photoreduction is highly desirable. Copper(I) complexes represent a good choice of catalyst in this respect. As an electrocatalyst, copper complexes have been shown to be capable of the reductive coupling of CO2 to oxalate.¹⁰ Because of their d¹⁰ configuration, copper(1) complexes, particularly the copper(1) bis(phenanthroline)-type complexes, exhibit a long-lived photoexcited state compared to those of other redox-active first-row-transition-metal analogues. This long-lived excited state represents a set of key electrochemical and photophysical properties that render such materials suitable for application in a solar-energy-conversion scheme.¹¹ However, a copper(1)-phenanthroline derivative was found to exhibit low efficiency when used as a sensitiser.^{11d} Recent work on copper(I)-bipyridine complexes has shown that the photosensitising behaviour of these complexes makes them strong candidates for DSSC applications.¹² These complexes provide an exciting prospect for the use of Cu(I) sensitisers to drive electron-transfer processes in CO₂ photoreduction.

In the course of our search for efficient components for solar energy conversion,^{9a} we designed and synthesised an air-stable copper(1) complex 1 to serve as a photosensitiser for TiO₂. The $1/\text{TiO}_2$ hybrid system provides a good platform to promote the photoreduction of CO₂ with high efficiency and selectivity under visible-light irradiation. The structure of 1 is depicted in Fig. 1. The methyl groups are appended at the 6- and 6'-position of 2,2'-bipyridine (bpy) to provide protection around the labile metal copper(1), and the presence of these groups is believed to increase the excited-state lifetime of the cuprous complex.¹²

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Fig. 1 Chemical structure of cationic copper(I) complex 1.

The cyanoacetic acid moieties at the end position act as anchoring groups to ensure their grafting onto the semiconductor surface, which has been extensively adopted as an efficient acceptor unit for the construction of metal-free dye sensitisers with high molar extinction coefficients for DSSCs; such semiconductor surfaces thereby achieve directional electron transport for the implementation of efficient light-harvesting devices.

This desired complex $[Cu(bpy)_2]^+$ was easily synthesised in good yield through the metalation of the functionalised bpy ligand with one-half equivalent of [Cu(CH₃CN)₄]PF₆ in $CH_3OH-CH_2Cl_2$ (1:1, v/v) and was characterised using conventional spectroscopic and analytical methods (ESI⁺). Complex 1 is stable in solution and in the solid state in air, which indicated that modification of the bpy ligand with methyl groups effectively stabilises the Cu(I) species. In terms of the electronic absorption properties, similar to those of bipyridyl complexes of copper(I), complex 1 in MeOH produces an intense characteristic band in the UV region with an absorption maximum centred at 310 nm (extinction coefficient $\varepsilon = 5.54 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) that was assigned to ligand-based $\pi \to \pi^*$ transitions. The expected metal-to-ligand charge transfer (MLCT) absorption for 1 typically appears in the visible region centred at 496 nm with ε 8033 M^{-1} cm⁻¹ (Fig. S2[†]), which accounts for the dark red appearance of the complex.¹² When the complex is bound to the surface of titania (Degussa P-25), as verified using IR spectroscopy, the particles are rendered dark red, and the original MLCT bands appear at approximately the same wavelength as the band of the complex in solution. The solid-state absorption bands are, however, broader and red-shifted compared to those in the solution spectra, which is related to π - π stacking or aggregation in the solid state. Two strong bands appear in the IR spectrum of 1 at 1389 and 1628 cm^{-1} , in accordance with the characteristic symmetric and asymmetric stretching frequencies of the carboxylate group (Fig. S3[†]). After being adsorbed onto TiO₂, the complex exhibits two related bands at 1418 and 1631 cm⁻¹. Complex 1 is non-emissive in air-saturated MeOH solution (the only common solvent in which it is slightly soluble) at room temperature, which may be due to the presence of some quenchers (most likely MeOH) or due to the excitedstate structural dynamics of 1.¹³ The complex is also non-emissive in the solid state, most likely because of the aggregation effect. Although a few copper(1)-bipyridine complexes have been previously employed as sensitisers in DSSC applications, the photophysical characterisation for the excited state has been less extensively investigated.¹² This is unfortunate for sensitisers because the performance of solar conversion devices relies on both the MLCT absorption profile and the excited-state properties. We have tried to determine the excited-state lifetime with the help of a pulsed Nd:YAG laser; however, no information



Fig. 2 Photocurrent density–voltage (J-V) characteristic curves for DSSC device with 1 recorded under illumination of simulated solar light (AM 1.5G, 100 mW cm⁻²). Inset: photograph of a 1-coated TiO₂ film on FTO.

could be extracted, which indicated that the electrons do not stay in the excited state for an expected prolonged time in **1**. The decrease in rigidity of the bpy fragment compared to that of the phenanthroline should promote deterioration of the excited-state properties of the bipyridine-type complex.¹⁴

To determine the identity of the lower-energy MLCT band in 1, density functional theory (DFT) calculations were performed on the cation of 1 using the B3LYP method with the LANL2DZ basis set (Figs. S4-S6[†]). The HOMO is populated over the Cu d_{π} orbitals and partially on the pyridine rings of the ligand whereas the lowest unoccupied molecular orbital (LUMO) resides primarily on the π system of the bpy moieties and on the anchoring units, which serve as an acceptor through which the excited electrons of the complex are directionally injected into TiO₂. The presence of the LUMO on the ligand, especially on the aromatic rings of the ligand, may facilitate electron injection because it provides electronic mixing between the bpy π^* orbital into which the electron is excited and the TiO₂ acceptor orbitals. The good separation of the frontier molecular orbitals is beneficial for the charge migration on the electron excitation from the HOMO level to the LUMO level.

The light-harvesting property of complex 1 on a nanocrystalline TiO₂ electrode was initially confirmed through the demonstration of a typical DSSC device. Complex 1 achieved efficient sensitisation of nanocrystalline TiO2, as illustrated in Fig. 2. The photovoltaic performance of the solar cell was measured under standard AM 1.5G conditions at a light intensity of 100 mW cm⁻². The cell yielded a short-circuit current (J_{sc}) of 4.69 mA cm⁻² an open-circuit voltage ($V_{\rm oc}$) of 570 mV and a fill factor (FF) of 78.8%, and achieved an overall energy conversion efficiency (η) of 2.2%, which is slightly lower than the previous value reported for the copper(I)-based DSSCs (2.3% with higher J_{sc} of 5.9 mA cm⁻²).¹² For purposes of comparison, a cell with the art ruthenium dye of N719 was also fabricated under the same conditions, and it gave a η value of 7.8%. The results clearly imply that complex 1 works properly for harvesting light in the cell and that the injected electrons are effectively transported, which results in the generation of electricity. The photon-to-current conversion mechanism, which is similar to the photosynthesis mechanism of plants, is well understood.^{12a} In DSSCs, the sensitiser captures sunlight, which results in the injection of an electron into the conduction band of the semiconductor TiO₂. The injected electrons diffuse through the nanoparticle porous



Fig. 3 CH₄ generation catalyzed by solid 1/P-25 under visible-light irradiation ($\lambda > 420$ nm).

network to the photoanode electrode, where they are collected for powering a load. However, the energy-to-electricity capability is lower than that of N719, which is primarily attributed to the relatively narrow optical absorbance of the copper complex in the visible region and to its relatively short excitedstate lifetime. Like other transition-metal complex sensitisers fixed on the surface of TiO₂ for solar energy conversion,^{7,15} the copper complex exhibits a short-lived excited state may negatively impact the electron-transfer dynamics and, therefore, the performance of the device. Nevertheless, our results strongly indicate that the potential of this copper(1) material is promising and competitive for light-harvesting applications in next-generation devices.

In view of these encouraging energy-conversion results, further investigations were conducted to assess the activity of the system for the photocatalytic conversion of CO₂. Upon irradiation with visible light (radiation $\lambda > 420$ nm), CO₂ photoreduction was established using water vapour as an electron donor over 0.1 g of a solid sample that contained 1/P-25 in a special gas-solid reaction system.^{9a} The reduction product during the experiment was monitored and confirmed by gas chromatography analysis. The results showed that 1/P-25 was active in the selective reduction of CO₂ to only CH₄ as the product over H₂O under these conditions. The amount of CH₄ production increased stepwise with increasing time, until a plateau value of *ca*. 7 μ mol g⁻¹ was reached after 24 h of irradiation (Fig. 3). In the absence of 1, 1/TiO₂ or CO₂, no CH₄ generation was observed under identical gaseous conditions. In addition, the reaction in which 100 mg of pure 1 was used alone showed also no detectable CH₄ production over 10 h. Therefore, the photoreduction of carbon dioxide is involved in the generation of methane. Although the photoreduction of CO2 to methane has been achieved by several Ru(II) complexes,8,9,16 such impressive activity for the clean formation of CH₄ represents a significant advance given that the metal on which the complex is based is inexpensive and abundant. The activity observed in the present reduction of CO₂ is lower than that reported for previous noble-metal-loaded inorganic semiconductor catalysts that require UV irradiation;² however, it is comparable with the iridium-complex sensitiser that was aided by the presence of active Pt sites on a TiO₂ support.^{9a} After the photoreduction process, the absorption spectrum of 1/TiO₂ was almost unchanged from that of the parent compound (Fig. S7[†]), *i.e.*, the compound appears to be stable towards photocatalysis. However,

strong IR bands appeared at lower frequencies of 1392 and 1604 cm⁻¹ for the $1/\text{TiO}_2$ sample after it was used as a photocatalyst, which is attributed to the adsorption of CO₂ or the intermediate products on the surface of the $1/\text{TiO}_2$.

These results demonstrate that electron transfer from the copper complex to CO₂ is effective. The separation of electrons and holes by visible light is also evidenced by the surface photovoltage spectrum of 1-derivatised TiO₂ (Fig. S9⁺), which exhibits an obvious signal in response to visible light ($\lambda > 420$ nm). The occurrence of this signal indicated that the photogenerated electron-hole pairs were effectively separated.¹⁷ This result also suggested that the introduction of complex 1 is beneficial to the separation of the charges in TiO₂ under irradiation from visible light.^{18,19} The formation mechanism of hydrocarbons from CO₂ photoreduction remains to be elucidated. The possible process is shown in the ESI.^{\dagger^{20}} The inactivity of the parent TiO₂ in this reaction revealed that the Cu(I) moiety was responsible for the visible-light activity towards catalytic CO₂ reduction.^{2e,3c} The copper(I) species apparently serves the function of harvesting visible photons to drive rapid electron injection into the conduction band of the TiO_2 , as confirmed by its effective performance in a DSSC device.

In conclusion, we have achieved selective CO_2 visible-light conversion based on the functionalisation of TiO_2 with an artificial light-harvesting copper(I) complex. The results may upgrade copper to the metal of choice in CO_2 reduction catalysts. The superior performance of the copper complexes may be due to a modification of the key structural and electronic features that sustain efficient CO_2 reduction. Further detailed investigations are also needed to obtain an exact mechanistic understanding of the reaction process. We believe that these investigations would contribute significantly to the exploitation of new efficient lightharvesting complexes for the creation of sustainable artificial photosynthesis.

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