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High-turnover visible-light photoreduction of CO_2 by a Re(I) complex stabilized on dye-sensitized TiO_2†

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Hybrid systems prepared by fixing a Re(I) complex and a dye on three types of TiO_2 nanoparticles in two different ways commonly revealed persistent photocatalysis of the CO_2 reduction to CO with no levelling-off tendency under visible-light irradiation in DMF, giving a turnover number of ≥435.

The visible-light photoreduction of CO_2 has been receiving considerable interest not only from environmental and long-term energy-security viewpoints,[1] but also as a crucial scientific issue in ''artificial photosynthesis''.[2,3] An essential requirement for CO_2 reduction in artificial photosynthesis is to couple the visible-light-driven flow of electrons with multiple-electron chemical processes that can lead to the formation C–H and C–C bonds and can cleave C–O bonds. Such processes require suitable catalysts, among which transition-metal complexes have been regarded as a potential candidate in artificial photosynthesis[4] as well as in electrochemistry,[5] due to the easy tuning of redox potentials, the trapping of CO_2 *via* its coordination to the metal centre, and the valence jump of the metal oxidation state in response to the multiple-electron reduction processes.

Among a variety of metal complexes investigated,[2–5] the (bpy)$Re^I(CO)_3Cl$ (bpy = 2,2′-bipyridine) complex reported by Lehn and his coworkers in 1983 is of particular interest because of the highly selective photoreduction of CO_2 to CO in a relatively high quantum yield.[6] Since then, related Re(I) complexes have been extensively applied to photochemical[7] and electrochemical[8] reductions of CO_2. However, a serious drawback of the Re(I) complexes in the homogeneous-solution photocatalysis is their short durability, as revealed by leveling-off tendencies in the CO formation at a relatively early stage[7,9] due to degradation of the Re(I) complexes.[10] However, the degradation might not arise from the inherent properties of the Re(I) complexes, since high turnover numbers were reported for particular systems using sensitizer-bridged Re(I) supramolecules[11] or a sensitizer of cyclic Re(I) trimer and a Re(I) catalyst.[12] In homogeneous solutions, various intermediates[9,13] involving long-lived reactive species are unintentionally distributed to undergo intermolecular interactions associated with the degradation of the starting complex. It can therefore be expected that the fixing of a Re(I) complex on dye-sensitized semiconductors might allow each Re(I) molecule to work as an intrinsic catalyst under visible-light sensitization by the dye. An additional benefit of utilizing such semiconductor-based hybrid systems would derive from the potential capability of semiconductor materials in multiple-electron deposition and transfer to a catalyst site.[3,14] This communication reports that hybrid systems prepared by immobilizing the Re(I) complex **ReC** on dye-loaded TiO_2 nanoparticles reveal persistent behaviour in the photoreduction of CO_2 to CO under visible-light irradiation in the presence of an electron donor (SD) (Fig. 1), and some interesting findings from this work are presented.

The organic dye (Dye), Re(I) catalysts (**ReC** and ReE) and electron donor (SD) shown in Fig. 1 were prepared according to known methods (see ESI†). The TiO_2 materials used include

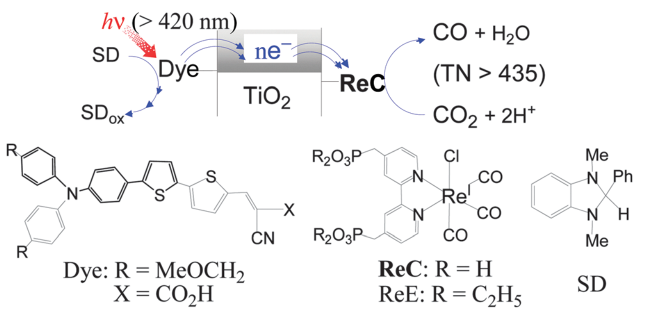

Fig. 1 Conceptual representation for the reaction system (top) and the compounds used in this work (bottom).

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† Electronic supplementary information (ESI) available: Experimental details, IR spectra and DRS of **ReC**/H-TiO_2/Dye, plots of TN(CO) *versus* time for the hybrid systems and SEM images of the TiO_2 sources. See DOI: 10.1039/c3cc49744e

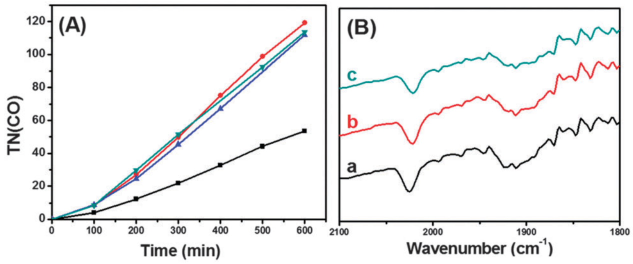

Fig. 2 (A) Plots of CO formation *versus* time in the absence (–■–) and presence of 1.5 M 2,2,2-trifluoroethanol (–●–), 3% (v/v) H_2O (–▲–), and 10% (v/v) H_2O (–▼–) for 10 mg **ReC** (0.1 μmol)/H-TiO_2/Dye (1.5 μmol) in 3 mL DMF containing 0.1 M SD; irradiation at >420 nm. (B) IR spectra of **ReC**/H-TiO_2/Dye in KBr discs (sample: KBr ≈ 1:100) before (a) and after irradiation for 100 min (b) and for 20 h (c).

synthetic nanosheets with exposed [001] facets (S-TiO_2) and two commercially available nanosize powders, Hombikat UV-100 (H-TiO_2) and Degussa P-25 (D-TiO_2), onto which **ReC** and Dye were covalently fixed through the phosphonic or carboxylic acid anchoring group. The hybrid materials are denoted as **ReC**/TiO_2/Dye when prepared by the initial loading of **ReC** followed by fixing of the Dye and as Dye/TiO_2/**ReC**, which was obtained by the reverse sequence of loading. The successful anchoring of **ReC** and Dye on the TiO_2 surface was confirmed by IR and diffuse-reflectance absorption spectroscopy (Fig. S1†). Suspensions of the hybrid materials in CO_2-saturated *N*,*N*-dimethylformamide (DMF) containing SD (0.1 M) were irradiated at >420 nm using a Xenon lamp combined with a glass light filter.

As shown in Fig. 2(A) and Fig. S2† for the plots of TN(CO) (=molar ratio of CO formed/**ReC** used) *versus* irradiation time, CO was steadily formed with no levelling-off tendency; H_2 evolution was only <5% that of CO. Table 1 lists TN(CO) after 10 h of irradiation. In the case of **ReC**/H-TiO_2/Dye, the steady CO formation continued for 20 h with TN(CO) of 160 (Fig. S3†), and no substantial loss in the IR absorption bands of the CO ligands of **ReC** was observed (Fig. 2(B)). Formic acid and oxalic acid as the other possible reduction products were not detected upon HPLC analysis of the liquid phase.

For comparison, the photoreduction of CO_2 in homogeneous DMF solution using a combination of ReE/triethanolamine (TEOA), ReE/SD or $Ru(bpy)_3^{2+}$/ReE/SD was undertaken; the CO formation leveled off within 5 h with TN(CO) of <50 (Fig. S4†). These results clearly demonstrate that **ReC** has been remarkably stabilized by its fixation onto the Dye-loaded TiO_2 nanoparticles. Presumably, two-electron transfers to the **ReC** site would be effectively mediated through TiO_2 to complete the catalytic cycle without significant degradation of **ReC**. On the other hand, in homogeneous solutions, the second electron transfer to a key intermediate following the first one-electron reduction event should proceed under direct interactions with the second electron source(s), typically the one-electron reduced species of the Re(I) catalyst[9] and oxidized donor radicals, so that unfavourable competitive reactions might occur even to a minor extent.

Table 1 Turnover number of CO formation (TN(CO))[a]

ReC/TiO_2/Dye			Dye/TiO_2/**ReC**		
S-TiO_2	H-TiO_2	D-TiO_2	S-TiO_2	H-TiO_2	D-TiO_2
70 (85)	53 (113)	51 (84)	111 (118)	55 (116)	93 (n.d.[b])

[a] Average values after 10 h irradiation. In parenthesis are the values for the reactions in the presence of 10% (v/v) H_2O. [b] Not determined.

While the electron flow in the CO_2 reduction should follow the scheme shown in Fig. 1, the relative energy levels of the components need to be referred to. The flat-band potential of a fused-particle TiO_2 electrode in DMF was reported to lie at −2.04 V *versus* SCE (−2.42 V *versus* $Fc^{+/0}$),[15] which is 0.42 eV more negative than the oxidation potential of excited-singlet Dye (^{1}Dye*).[16] If this were the case, the electron injection from ^{1}Dye* into the conduction band of TiO_2 would hardly compete with the decay of ^{1}Dye* ($\tau \approx 1$ ns).[16] Furthermore, the electron transfer to **ReC** through TiO_2 should be exergonic enough to compete with fast charge recombination.[17] Therefore, the conduction-band minimum of our TiO_2 materials in DMF might be located between the oxidation potential of ^{1}Dye* (≈−2 V *versus* $Fc^{+/0}$)[17] and the reduction potential of **ReC** (−1.67 V). The oxidation potential of SD (−0.185 V) is much more negative than that of Dye (0.50 V) so that the Dye radical cation left after electron injection from ^{1}Dye* into TiO_2 might be efficiently reduced by SD.

Some interesting features from the present observations should be noted. (1) The photocatalytic efficiencies significantly depend on the TiO_2 sources (Table 1), probably related, at least in part, to the different morphologies and crystal phases of the nanoparticles (Fig. S5 and S6†). S-TiO_2 has an anatase nanosheet morphology (20 nm length × 5 nm thickness) with ≈90% [001] facets, whereas H-TiO_2 (pure anatase) and D-TiO_2 (75% anatase and 25% rutile) are spherical nanoparticles of 5 nm and 18 nm diameter, respectively. The agglomerates of the different nanoparticles should have different distributions of surface states/trap sites and grain boundaries associated with the catalytic properties. (2) In the cases of S- and D-TiO_2, the initial loading of Dye resulted in considerably higher catalytic activity than the initial loading of **ReC**, whereas such a loading-sequence effect was not clear in the case of H-TiO_2 (Table 1 and Fig. S1†). A possible assumption is that the surfaces of larger-size S- and D-TiO_2 would have local distributions with different activities in the electron injection from ^{1}Dye* and/or electron transfer to **ReC**, while the surface of smaller-size pure anatase H-TiO_2 would be relatively homogeneous. (3) The reaction efficiencies were considerably enhanced on addition of 1.5 M 2,2,2-trifluoroethanol or 3–10% (v/v) H_2O, particularly in the cases of the hybrids based on H-TiO_2 and D-TiO_2 (Table 1). This observation is reminiscent of the Brønsted acid effect on electrochemical CO_2 reduction.[18] Such an effect was minor, but appreciable, for the S-TiO_2 hybrids. (4) The CO_2 reduction was almost completely retarded by 1.2 M TEOA, unlike homogeneous-solution CO_2 reduction which is more or less assisted by TEOA coexisting with a real electron donor.[11,12]

In order to confirm the catalytic persistency of the hybrids, we carried out repetitive irradiation experiments. As shown in

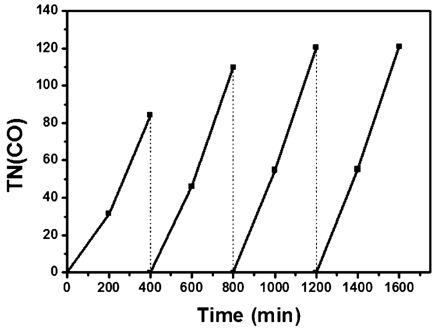

Fig. 3 Formation of CO in a 4-cycle repetition of irradiation at >420 nm for 400 min after CO_2 bubbling for 30 min in the dark; 10 mg Dye/S-TiO_2/**ReC** with 0.1 μmol **ReC** and 1.5 μmol Dye in the presence of 0.1 M SD and 10% (v/v) H_2O.

Fig. 3 for Dye/H-TiO_2/**ReC**, no leveling-off tendency was observed in each cycle and the efficiency of CO formation increased with the increase of the cycle from a TN(CO) of 84 in the 1st run to a TN(CO) of 121 in the 4th run. The total TN(CO) reached 435. The other hybrids also revealed similar behaviour as well (Fig. S8†). This unique phenomenon appears to be in line with the appearance of induction periods in Fig. 2, Fig. S2–S4, S7, and S8.† While investigations are now being performed on the mechanistic origin, we tentatively assume that the electron transfer to **ReC** would progressively prevail over electron trapping as various electron-trapping sites distributed in TiO_2[17,19] have been sequentially filled with trapped electrons.

The present investigation has demonstrated that the **ReC** catalyst immobilized on Dye-sensitized TiO_2 particles works as a persistent catalyst for the reduction of CO_2 to CO with high TN(CO) under visible-light irradiation. It is implied that the convenient methodology reported here might provide a possible way for manifesting the "inherent" catalytic ability of particular transition-metal complexes that would be masked in homogeneous-solution catalysis. A further attempt is currently being made to find stable hybrid systems that can efficiently work in water, directed at coupling the CO_2 reduction hybrid with a water–oxidation system.

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Notes and references

1 S. Styring, *Faraday Discuss.*, 2012, **155**, 357; A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. Dubois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. Kenis, C. A. Kerfeld, R. H. Morris, C. H. Peden, A. R. Portis, S. R. Ragasdale, T. B. Rauchfues, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer and G. L. Waldrop, *Chem. Rev.*, 2013, **113**, 6621.
2 T. Yui, Y. Tamaki, K. Sekigawa and O. Ishitani, *Top. Curr. Chem.*, 2011, **303**, 151.
3 L. Alibabai, H. Luo, R. L. House, P. G. Hoeltz, R. Lopez and T. J. Meyer, *J. Mater. Chem. A*, 2013, **1**, 4133.
4 A. J. Morris, G. J. Meyer and E. Fujita, *Acc. Chem. Res.*, 2009, **42**, 1983; J. Schneider, H. Jia, J. T. Muckerman and E. Fujita, *Chem. Soc. Rev.*, 2012, **41**, 2036.
5 K. Tanaka and D. Ooyama, *Coord. Chem. Rev.*, 2002, **226**, 211; J.-M. Savéant, *Chem. Rev.*, 2008, **108**, 2348; E. E. Benson, C. P. Kubiak, A. J. Sathrum and J. M. Smieja, *Chem. Soc. Rev.*, 2009, **38**, 89; C. Constentin, M. Robert and J.-M. Savéant, *Chem. Soc. Rev.*, 2013, **42**, 2423.
6 J. Hawecker, J.-M. Lehn and R. Ziessel, *J. Chem. Soc., Chem. Commun.*, 1983, 536; J. Hawecker, J.-M. Lehn and R. Ziessel, *Helv. Chim. Acta*, 1986, **69**, 1990.
7 H. Takeda, K. Koike, T. Morimoto, H. Inumaru and O. Ishitani, *Adv. Inorg. Chem.*, 2011, **63**, 137; H. M. Sung-Suh, D. S. Kim, C. W. Kim, C. W. Lee and S.-E. Park, *Appl. Organomet. Chem.*, 2000, **14**, 826; P. Kurz, B. Probst, B. Spingler and R. Alberto, *Eur. J. Inorg. Chem.*, 2006, 2966; C. Wang, Z. Xie, K. E. deKrafft and W. Lin, *J. Am. Chem. Soc.*, 2011, **133**, 13445; C. Liu, K. D. Dubois, M. E. Lois, A. S. Vorushilov and G. Li, *ACS Catal.*, 2013, **3**, 655; G. A. Andrade, A. J. Pistner, G. P. A. Yap, G. A. Lutterman and J. Rosenthal, *ACS Catal.*, 2013, **3**, 1685.
8 J. Hawecker, J.-M. Lehn and R. Ziessel, *J. Chem. Soc., Chem. Commun.*, 1984, 328; J. R. O'toole, L. D. Margelum, T. D. Westmoreland, W. J. Vining, R. W. Murray and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, 1985, 1416; B. K. Kumar, J. M. Smieja, A. F. Sasayama and C. P. Kubiak, *Chem. Commun.*, 2012, **48**, 272.
9 H. Takeda, K. Koike, H. Inoue and O. Ishitani, *J. Am. Chem. Soc.*, 2008, **130**, 2023.
10 C. Kutal, M. A. Weber, G. Ferraudi and G. Geiger, *Organometallics*, 1985, **4**, 2161; C. Kutal, A. J. Corbin and G. Ferraudi, *Organometallics*, 1987, **6**, 553; O. Ishitani, I. Namura, S. Yanagida and C. Pac, *J. Chem. Soc., Chem. Commun.*, 1987, 1153.
11 B. Gholamkhass, H. Mametsuka, K. Koike, T. Tanabe, M. Furue and O. Ishitani, *Inorg. Chem.*, 2005, **44**, 2326; Z.-Y. Bian, K. Sumi, M. Furue, S. Sato, K. Koike and O. Ishitani, *Dalton Trans.*, 2009, 983; Y. Tamaki, K. Watanabe, K. Koike, H. Inoue and O. Ishitani, *Faraday Discuss.*, 2012, **155**, 115; Y. Tamaki, K. Koike, T. Morimoto and O. Ishitani, *J. Catal.*, 2013, **304**, 22.
12 T. Morimoto, C. Nishiura, M. Tanaka, J. Rohacova, Y. Nakagawa, Y. Funada, K. Koike, Y. Yamamoto, S. Shishido, T. Kojima, T. Saeki, T. Ozeki and O. Ishitani, *J. Am. Chem. Soc.*, 2013, **135**, 13266.
13 B. P. Sullivan and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, 1984, 1244; B. P. Sullivan, C. M. Bolinger, D. Conrad, W. J. Vining and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, 1985, 1414; D. H. Gibson, X. Yin, H. He and M. S. Mashuta, *Organometallics*, 2003, **22**, 337; Y. Hayashi, S. Kita, B. S. Brunschwig and E. Fujita, *J. Am. Chem. Soc.*, 2003, **125**, 11976; K. D. Dubois, A. Petushkov, E. G. Cardona, S. C. Larsen and G. Li, *J. Phys. Chem. Lett.*, 2012, **3**, 486.
14 T. W. Woolerton, S. Sheard, F. Reisner, E. Pierce, S. W. Ragasdale and F. A. Armstrong, *J. Am. Chem. Soc.*, 2010, **132**, 2123; Y. S. Chaudhary, T. W. Woolerton, C. S. Allen, T. H. Warner, E. Pierce, S. W. Ragasdale and F. A. Armstrong, *Chem. Commun.*, 2012, **48**, 58.
15 G. Redmond and D. F. Fitzmaurice, *J. Phys. Chem.*, 1993, **97**, 1426.
16 S.-H. Lee, Y. Park, K. R. Wee, H. J. Son, D. W. Cho, C. Pac, W. Choi and S. O. Kang, *Org. Lett.*, 2010, **12**, 460.
17 W.-S. Han, K.-R. Wee, H.-Y. Kim, C. Pac, Y. Nabetani, D. Yamamoto, T. Shimada, H. Inoue, H. Choi, K. Cho and S. O. Kang, *Chem. – Eur. J.*, 2012, **18**, 16368.
18 J. M. Smieja and C. P. Kubiak, *Inorg. Chem.*, 2010, **49**, 9283.
19 A. L. Linsebigler, G. Lu and J. T. Yates Jr., *Chem. Rev.*, 1995, **95**, 735; J. R. Durrant, S. A. Haque and J. R. Plomares, *Coord. Chem. Rev.*, 2004, **248**, 1247.