

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

High-turnover visible-light photoreduction of CO₂ by a Re(I) complex stabilized on dye-sensitized TiO₂

Cite this: DOI: 10.1039/x0xx00000x

Eun-Gyeong Ha,^a Jeong-Ah Chang,^a Sung-Min Byun,^a Chyongjin Pac,^{b,*} Dong-Myung Jang,^a Jeunghye Park^{a,*} and Sang Ook Kang^{a,*}Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Hybrid systems prepared by fixing a Re(I) complex and a dye on three types of TiO₂ nanoparticles in two different ways commonly revealed persistent photocatalysis of the CO₂ 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 CO₂ has been receiving increasingly 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 CO₂ reduction in artificial photosynthesis is to couple the visible-light-driven flow of electrons with multiple-electron chemical processes that can make 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 photosynthesis⁴ as well as in electrochemistry,⁵ due to the easy tuning of redox potentials, the trapping of CO₂ by 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 CO₂ to CO in a relatively high quantum yield.⁶ Since then, related Re(I) complexes have been extensively applied to photochemical⁷ and electrochemical⁸ reductions of CO₂. 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 degradations 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) supramolecules¹¹ 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 in 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.^{3,13} This communication reports that hybrid systems prepared by immobilizing the Re(I) complex **ReC** on dye-loaded TiO₂ nanoparticles reveal persistent behaviour in the photoreduction of CO₂ 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.

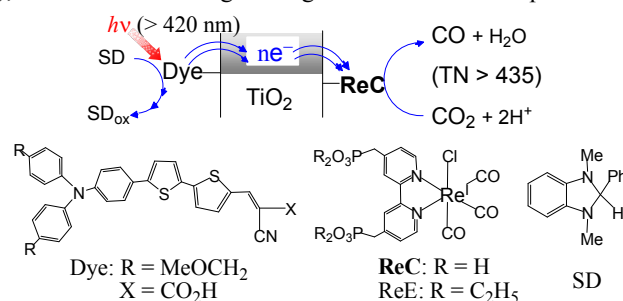


Fig. 1 Conceptual representation for the reaction system (top) and the compounds used in this work (bottom).

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 TiO₂ materials used include synthetic nanosheets with exposed [001] facets (S-TiO₂) and two commercially available nanosize powders, Hombikat UV-100 (H-TiO₂) and Degussa P-25 (D-TiO₂), onto which **ReC** and Dye were covalently fixed through the phosphonic or carboxylic acid anchoring group. The hybrid materials are denoted as **ReC**/TiO₂/Dye when prepared by the initial loading of **ReC** followed by fixing of the Dye and as Dye/TiO₂/**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.

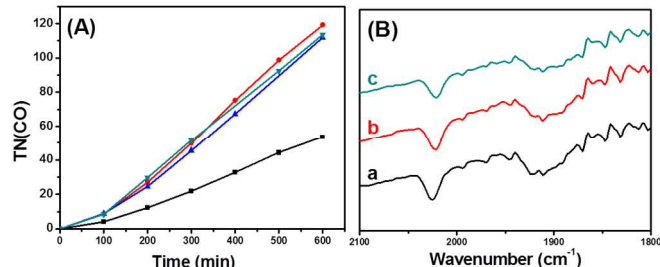


Fig. 2 (A) Plots of CO formation versus time in the absence (-■-) and presence of 1.5 M 2,2,2-trifluoroethanol (-●-), 3%(v/v) H_2O (-▲-), and 10%(v/v) H_2O (-▼-) for 10 mg **ReC** (0.1 μmol)/H- TiO_2 /Dye (1.5 μmol) in 3 mL DMF containing 0.1 M SD; irradiation at > 420 nm. (B) IR spectra of **ReC**/H-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

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.

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 irradiation. In the case of **ReC**/H- TiO_2 /Dye, the steady CO formation continued by 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 by 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 $\text{Ru}(\text{bpy})_3^{2+}$ /**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 on 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 degradations 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)** catalyst⁹ and oxidized donor radicals, so that unfavourable competitive reactions might occur even to a minor extent.

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 $\text{Fc}^{+/0}$),¹⁵ which is 0.42 eV more negative than the oxidation potential of excited-singlet Dye ($^1\text{Dye}^*$).¹⁶ If this were the case, the electron injection from $^1\text{Dye}^*$ into the conduction band of TiO_2 would hardly compete with the decay of $^1\text{Dye}^*$ ($\tau \approx 1$ 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 $^1\text{Dye}^*$ (≈ -2 V versus $\text{Fc}^{+/0}$)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 $^1\text{Dye}^*$ 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 \times 5 nm thickness) with $\approx 90\%$ [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 $^1\text{Dye}^*$ 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}

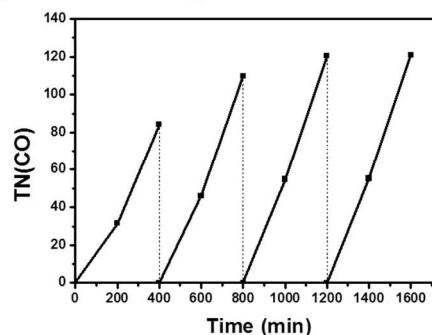


Fig. 3 Formation of CO in 4-cycle repetition of irradiation at > 420 nm for 400 min after CO_2 bubbling for 30 min in the dark; 10 mg Dye/S- TiO_2 /**ReC** with 0.1 μmol **ReC** and 1.5 μmol Dye in the presence of 0.1 M SD and 10%(v/v) H_2O .

In order to confirm the catalytic persistency of the hybrids, we carried out repetitive irradiation experiments. As shown in Fig. 3 for Dye/H-TiO₂/ReC, no leveling-off tendency was observed in each cycle and the efficiency of CO formation increased with the increase of the cycle from TN(CO) of 84 in the 1st run to 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 Figs. 2, 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 TiO₂^{17,19} have been sequentially filled with trapped electrons.

The present investigation has demonstrated that the ReC catalyst immobilized on Dye-sensitized TiO₂ particles works as a persistent catalyst for the reduction of CO₂ 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, directing to couple the CO₂ reduction hybrid with a water-oxidation system.

Acknowledgements. This research was supported by a Korea University Grant.

Notes and references

^a Department of Advanced Materials Chemistry, Korea University, 2511 Sejong-ro, Sejong-city 339-700, Korea, E-mail: parkjh@korea.ac.kr; sangok@korea.ac.kr.

^b Yulchon Research Center, Korea University, Sejong-ro 2511, Sejong-city 339-700, Korea, E-mail: jipac@korea.ac.kr.

† Electronic Supplementary Information (ESI) available: [Experimental details, IR spectra and DRS of ReC/H-TiO₂/Dye, Plots of TN(CO) versus time for the hybrid systems and SEM images of the TiO₂ sources]. See DOI: 10.1039/c000000x/

- 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. Rauchfuss, 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. Mat. 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. Constantin, 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** and *Helv. Chim. Acta*, 1986, **69**, 1990.
- 7 H. Takeda, K. Koike, T. Morimoto, H. Inumaru and O. Ishitani, *Adv. in Inorg. Chem.*, 2011, **63**, 137. H. M. Sung-Suh, D. S. Kim, C. W. Kim, C. W. Lee and S.-E. Park, *Appl. Organometal. 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.