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COMMUNICATION

The synergistic catalysis effect within a dinuclear nickel complex for efficient and selective electrocatalytic reduction of CO₂ to CO

Received 00th January 20xx, Accepted 00th January 20xx

Li-Ming Cao,^{+a} Hai-Hua Huang,^{+a} Jia-Wei Wang,^a Di-Chang Zhong,^{*b} and Tong-Bu Lu^{*ab}

DOI: 10.1039/x0xx00000x

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Developing cheap and earth-abundant catalysts for efficient and selective reduction of CO₂ is a promising approach to cut down the rising emission of CO2 and obtain valuable fuels/chemicals simultaneously. Here, we present a dinuclear nickel complex, L¹ = 1,2-bis((5,7-dimethyl-1,4,8,11- $[Ni_2L^1](ClO_4)_4$ (1, tetraazacyclotetradecan-6-yl)methyl)benzene), which shows excellent performance for electrocatalytic reduction of CO₂ to CO, with a Faradaic efficiency of 95%, and a turnover number (TON) and turnover frequency (TOF) values of 4.1×10^6 and 190.0 s⁻¹ respectively. Electrochemical experiments and density functional theory (DFT) calculations revealed that the excellent catalytic performance of 1 attributes to the synergistic catalysis effect between two Ni centers within 1.

Carbon dioxide (CO₂), originating from industrial processes and biological activities, is a type of greenhouse gas threatening the sustainable development of humanbeings.¹ In the past several decades, due to the excessive utilization of traditional fossil fuels, the concentration of atmospheric CO₂ has reached a record level and is going up steadily, leading to global warming and sea level rising. Therefore, developing renewable energy and reducing CO₂ emissions are vital to the sustainable development of human beings.²⁻⁸ The electrocatalytic reduction of CO_2 to valuable fuels/chemicals is a promising access to both targets.⁹⁻¹³ However, due to the high thermodynamic stability of CO_2 , the reduction of CO_2 driven by electricity needs a high overpotential.14 To facilitate the appealing CO_2 reduction, the delicate design of electrocatalysts that can lower the overpotential is required.^{1,15-20} Among them, molecular catalysts have

Electronic Supplementary Information (ESI) available: The syntheses and characterization of the catalyst, DFT calculation, supplementary Figures and Tables. See DOI: 10.1039/x0xx00000x



attracted extraordinary attention due to their adjustable structures, remarkable catalytic activities and available

intermediates for mechanism studies.^{13,20} Therefore,

tremendous efforts have been devoted to the design of

molecular catalysts for CO2 reduction, and a large number of

molecular catalysts have been reported, including precious

metal-based catalysts,²¹⁻³⁰ and earth-abundant metal-based

catalysts. $^{31-47}$ Up to now, the reduction of CO₂ to CO has been

garnered particular interest, since the pathway is beneficial for

producing syngas (CO and H₂), which can be applied in

manufacturing various fuels by the Fischer-Tropsch technologies.^{48,49} In addition, CO is also a crucial industrial

feedstock in chemical synthesis.^{50,51} As a consequence, it is

particularly desired to develop applicable electrocatalysts for

To design suitable molecular catalysts for high-performance

CO₂-to-CO conversion, nature has given us inspiration.⁵² A vivid

example in biological system is the carbon monoxide

dehydrogenase (CODH), in which nickel acts as a Lewis base to

transfer a net electron to the CO₂ molecular and the iron

center serves as a Lewis acid to stabilize the negative partial

charges at the oxygen atom, facilitating the effective

transformation between CO2 and CO through the dinuclear

metal synergistic catalysis (DMSC).53,54 Enlightened by this

great observation, many dinuclear complexes with desired

synergistic catalysis effect have been designed and employed

for a variety of molecular activation and conversion

reactions.⁵⁵⁻⁶¹ We have also devoted to the investigation of

molecular recognition and activation by dinuclear metal

complexes during the past decade, ⁵⁹⁻⁶¹ and recently, we

efficiently and selectively reducing CO₂ to CO.

Fig. 1 Molecular structures of 1, 2 and 3.

^a MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, China. E-mail: lutongbu@mail.sysu.edu.cn.

^{b.} Institute for New Energy Materials & Low Carbon Technologies, School of Materials Science & Engineering, Tianjin University of Technology, Tianjin 300384, China. E-mail: zhong_dichang@hotmail.com.

⁺ These two authors contributed equally to this paper.

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reported a dinuclear cobalt complex $[Co_2(OH)L^1](CIO_4)_3$ ($L^1 = N[(CH_2)_2NHCH_2(m-C_6H_4)CH_2NH(CH_2)_2]_3N)$, which displays much high selectivity and efficiency for the photocatalytic reduction of CO₂ to CO in CH₃CN/H₂O ($\nu/\nu = 4:1$), with CO₂ to CO selectivity reaching as high as 98%, and turnover number (TON) and turnover frequency (TOF) reaching as high as 16896 and 0.47 s⁻¹, respectively.⁵⁵

To further make use of the DMSC effect for boosting the CO₂-to-CO conversion, herein, we designed and synthesized a dinuclear nickel complex, $[Ni_2L^1](CIO_4)_4$ (**1**, $L^1 = 1,2$ -bis((5,7-dimethyl-1,4,8,11-tetraazacyclotetradecan-6-

yl)methyl)benzene, Fig. 1). 1 was selected as electrocatalyst for CO₂ reduction is based on the following two considerations: (1) The mononuclear $[Ni(cyclam)]^{2+}$ (cyclam = 1,4,8,11tetraazacyclotetradecane) possesses good eletrocatalytic activity for the reduction of CO_2 to CO_2^{44} 1 with two [Ni(cyclam)]²⁺ connected by phenyl group may exhibit DMSC effect beneficial for electrocatalytic CO₂-to-CO conversion. (2) The separation between two catalytic centers of 1 is suitable for the generation of synergistic catalysis effect, which may greatly boost the electrochemical CO₂-to-CO conversion. Based on the above considerations, 1 was synthesized and estimated as a catalyst for electrochemical CO₂ reduction. For comparison, a mononuclear Ni^{II}-macrocycle complex, $[NiL^{2}](ClO_{4})_{4}$ (2, L^{2} = 6-benzyl-5,7-dimethyl-1,4,8,11tetraazacyclotetradecane, Fig. 1) and another dinuclear Ni^{II}macrocycle complex, $[Ni_2L^3](ClO_4)_4$ (3, $L^3 = 1,4$ -bis((5,7dimethyl-1,4,8,11-tetraazacyclotetradecan-6-

yl)methyl)benzene, Fig. 1) with a farther separation between two Ni^{II} catalytic centers were synthesized. As expected, **1** shows excellent catalytic activity and selectivity for electrocatalytic reduction of CO₂ to CO in CH₃CN/H₂O (v/v =4:1) solution, with Faradaic efficiency of 95%, and turnover number (TON) and turnover frequency (TOF) values of 4.1 × 10⁶ and 190.0 s⁻¹, respectively. These values are much higher than those of **2** and **3** under the same conditions. The experimental observations, coupled with the DFT calculations demonstrated that the DMSC effect between two Ni^{II} catalytic centers in **1** contributes to its high catalytic activity for electrochemical CO₂-to-CO conversion.

1-3 were synthesized according to the literature methods.⁶² Except as otherwise noted, all potentials are referenced to the normal hydrogen electrode (NHE). Cyclic voltammograms (CVs) of 1 (0.5 mM) measured in anhydrous acetonitrile using a glassy carbon electrode (GCE) show a quasi-reversible reduction peak at $E_{1/2}$ = -1.18 V under an argon atmosphere, corresponding to the Ni^{II/I} reduction (Fig. S1). Further controlled-potential electrolysis (CPE) experiment at -1.21 V exhibits the charge reaching a plateau at 0.96 Coulombs after a 3 h of CPE with 0.5 mM 1 (Fig. S2), indicating that the reversible redox couple of 1 is a 2e reduction/oxidation process.⁶³ This result illustrates that two Ni^{II} centers can be simultaneously reduced to Ni^l state. On the basis of the 2e $Ni^{II/I}$ couple, the diffusion coefficient (D) of **1** can be calculated by the Randles-Sevcik equation (Fig. S3).⁶⁴ The calculated value of D is 1.3×10^{-6} cm²/s. Under a CO₂ atmosphere, the CV of **1** (0.5 mM) exhibits two irreversible reduction waves at -1.08 V

and -1.37 V, respectively (Fig. S1). The former is attributed to the Ni^{II/I} reduction, with the reduction potential positively shifting in contrast to the one in Ar (-1.18 V), which suggests the binding of CO2 to the Ni^I species of 1.⁶⁵ The latter, a newly-appeared wave, may result from a quick, irreversible chemical step following the binding of CO₂.⁶⁵

As shown in Fig. S1, in anhydrous acetonitrile, the CVs of 1 show no obvious catalytic current density enhancement under CO_2 compared with that under Ar, suggesting that the CO_2 reduction in the absence of a proton reagent is unfavorable.⁶² Therefore, we tentatively added water as proton source to the system to improve the catalytic performance. It was noticed that with the increase of H_2O , the reduction wave of Ni^{II/I} shows a marked current enhancement with a positive shifting (Fig. 2), indicative of a proton-dependent electron transfer process.^{65,66} This result indicates that CH₃CN/H₂O mixture is a good solvent system for electrocatalytic reduction CO2 to CO by 1, where CH₃CN with a wide electrochemical window can serves as a solvent for absorbing enough carbon dioxide for the subsequent CO_2 reduction, and H_2O can acts as a proton source to improve the catalytic performance of 1. When the concentration of H₂O increases to 14 M (corresponding to the 4:1 volume ratio of CH₃CN/H₂O), the current density reaches the largest value of 2.2 mA/cm² and the reduction potential of Ni^{II/I} couple positively shifts to the largest value of -1.00 V (Fig. 2). These observations indicate that the 4:1 CH₃CN/H₂O (v/v) is the most appropriate solvent system where 1 can exhibit the best electrocatalytic property. Therefore, the 4:1 CH₃CN/H₂O (v/v) solvent system was employed as a catalytic medium in the subsequent electrochemical analysis. Further control experiments showed that without 1 or CO₂, the CVs display no current enhancement, indicating that the catalytic activity originates from 1 rather than the blank GCE or proton reduction (Fig. S4). To well understand the catalysis of 1 for



Fig. 2 CVs of 0.5 mM 1 in a 0.1 M TBAPF₆ MeCN solution under CO_2 in the presence of different concentration of H_2O (scan rate: 100 mV/s).

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Fig. 3 CVs of 0.5 mM **1**, 1.0 mM **2** and 0.5 mM **3** in 0.1 M TBAPF₆ CH₃CN/H₂O (v:v = 4:1) under Ar and CO₂ atmosphere, respectively (scan rate: 100 mV/s).

 CO_2 reduction, the correlation between the catalytic currents and the concentrations of **1** was investigated. As shown in Fig. S5, the catalytic current density is enhanced linearly with the concentrations of catalyst, indicating that the electrocatalytic CO_2 reduction by **1** is a first order reaction.

The electrochemical properties of **2** (1.0 mM) and **3** (0.5 mM) were also investigated in CH₃CN/H₂O ($\nu/\nu = 4:1$) solvent system under Ar or CO₂. As shown in Fig. 3, for both **2** and **3**, the current densities show an obvious enhancement in CO₂ compared with that in Ar, and the reduction potentials of the Ni^{II/I} couple in CO₂ also exhibit an obvious positive-shift in contrast to that in Ar. These observations suggest that the Ni^I species of **2** and **3** can also bind with CO₂, and **2** and **3** are potential electrocatalysts for CO₂ reduction. In contrast to **1**, the reduction potentials of Ni^{II/I} couple of **2** and **3** appear at - 1.08 and -1.10 V in CO₂ atmosphere, respectively, more negative than that of **1** (-1.00 V) under the same conditions (Fig. 3), which suggests that the Ni^{II/I} reduction is easier in **1** than those in **2** and **3**, and **1** may possess better electrocatalytic activity for CO₂ reduction than **2** and **3**.

The CPE experiment of 0.5 mM 1 was carried out in a 20 mL CH_3CN/H_2O (v/v = 4:1) containing 0.1 M TBAPF₆ under a CO_2 atmosphere. After electrolyzed at -1.16 V for 6 h, 18.8 coulombs of charge were accumulated at a relatively stable current density of 0.60 mA/cm² (Fig. S6). The gas chromatography (GC) analyses revealed that the amounts of generated gas products were 92.6 μ mol for CO and 4.9 μ mol for H₂, corresponding to a Faradaic efficiency of 95% for CO and 5% for H_2 (Table 1, and Fig. S7). The total TON (mol_{co}/mol_{cat}) was calculated as 9.26. This value is significantly undervalued due to limited catalyst molecules interacting with the surface of the electrode.⁶⁷ Based on the catalyst molecules in the diffusion layer of the cathode, an intrinsic catalytic rate (k_{cat}) of 603.0 s⁻¹, a remarkable TON of 4.1 × 10⁶ and a noticeable TOF of 190.0 s⁻¹ were obtained (see the details in the SI).^{68,69} The CPE analyses for 2 (1.0 mM) and 3 (0.5 mM) were also performed under the same conditions as those of 1. For 2, 42.0 µmol of CO was obtained, corresponding to a Faradaic efficiency of 62% and a TON value of 1.1×10^{5} for CO (Table 1; Fig. S8); For 3, 16.2 µmol of CO was afforded, corresponding to a Faradaic efficiency of 25% and a TON value of 9.2 \times 10 4 for CO (Table 1; Fig. S8). Obviously, the Faradaic efficiency of 1 (95%) is much higher than those of 2 (62%) and 3 (25%), and the TON value of 1 is also much higher than those

of 2 and 3, with 38 and 45-fold, respectively. In addition, the catalytic current density of 1 (0.60 mA/cm²) is larger than those of 2 and 3 (0.42 and 0.4 mA/cm², respectively, Fig. S9 and S10). These results reveal that 1 possesses much higher catalytic performance than 2 and 3. Actually, to our knowledge, the catalytic performance of 1 for CO2-to-CO conversion is also better than most reported electrocatalysts with mononuclear metal catalytic centers (Table S1), 38,44,66,70-74 including those state-of-the-art ones.^{38,44,66,70} The advantage of 1 over mononuclear metal molecular catalyst for the CO2-to-CO conversion may be the synergistic catalysis effect between two Ni centers, where one Ni center could act as a Lewis base to transfer electron to the CO₂ molecule and the other could serve as a Lewis acid to stabilize the partial negative charges at the O atom, increasing the kinetics of the reduction reaction and facilitating the effective transformation from CO_2 to CO_2

Considering the excellent catalytic activity of 1 for CO₂-to-CO conversion in CH_3CN/H_2O (v/v = 4:1) mixture, we further evaluated the catalytic performance of 1 in pure H₂O. As shown in Fig. S11, although not as high as in CH_3CN/H_2O (v/v =4:1), the catalytic current density of 1 in H₂O also clearly enhanced under CO₂ in contrast to that under Ar, indicating that 1 may also possess good catalytic activity for CO₂-to-CO conversion in H₂O. This speculation was confirmed by the CPE result. The CPE experiment of 0.5 mM 1 carried out in a 20 mL H₂O solvent containing 0.1 M KCl under a CO₂ atmosphere at -1.16 V showed that after electrolyzed for 6 h, 9.6 coulombs of charge were accumulated at a relatively stable current density of 0.32 mA/cm². 43.1 µmol of CO was obtained, corresponding to a Faradaic efficiency of 87% (Fig. S12). The remarkable Faradaic efficiency suggests that 1 also possesses good electrocatalytic performance for reduction of CO₂ to CO in pure H₂O solvent system.

Energy dispersive X-ray spectroscopy (EDX) measurements for the GCEs after CPE showed that there was no nickel residue on the surface of GCEs (Fig. S13), indicating that all the electrocatalytic reactions of CO₂ reduction by **1**, **2** and **3** are homogeneous, and these catalysts have perfect durability during the catalytic process of CO₂-to-CO conversion. The robustness, together with the high selectivity and efficiency reveal that **1** is a potential electrocatalyst for CO₂-to-CO

Table 1 The results of electrocatalytic reduction of CO₂ by **1-3**^a

						- 2 - 1 -
Cat.	Q(C)	n(CO)	n(H ₂)	F(CO)	TOF(CO)	TON
		(µmol)	(µmol)	(%)	(s ⁻¹) ^b	(CO) ^b
1	18.8	92.6	4.9	95	190.0	4.1×10^{6}
2	13.0	42.0	11.5	62	5.0	1.1 × 10 ⁵
3	12.3	16.2	24.2	25	4.2	9.2 × 10 ⁴

^aCPE experiments were operated with 0.5 mM **1**, 1.0 mM **2**, and 0.5 mM **3** in a 0.1 M TBAPF₆ CH₃CN/H₂O (v/v = 4:1) solution at E_{cat} = -1.16 V vs NHE for 6 h under CO₂ atmosphere. ^bThe TON and TOF values were calculated based on the number of the catalyst molecules in the diffusion layer.

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DOI: 10.1039/C7GC03451B Journal Name



Fig. 4 Proposed mechanism for CO_2 to CO conversion catalyzed by a dinuclear nickel complex 1.

conversion. The higher catalytic performance of **1** with dinuclear Ni(II) catalytic centers than **2** with mononulcear catalytic center, together with the much higher catalytic performance of **1** with the close Ni…Ni separation than **3** with far Ni…Ni separation, solidly evidenced that there is synergistic catalysis effect between two Ni^{II} catalytic centers within **1**, which endows **1** with excellent catalytic performance in electrochemical CO₂ reduction.

The synergistic catalysis effect between two Ni centers in 1 for CO₂-to-CO conversion has been further studied by the DFT calculations. Combined with the experimental observations and previous mechanism investigation on CO2-to-CO conversion by molecular catalysts,⁷⁵ a reasonable catalytic mechanism has been proposed. As shown in Fig. 4, firstly, 1 with $Ni_2^{II,II}$ undergoes a 2e⁻ reduction to generate **1a** with Ni_2^{I} according to the electrochemical results. The calculated redox potential for Ni^{1,II}/Ni^{1,I} is -1.15 V vs. NHE, consistent with the experimental result (-1.18 V). Secondly, 1a binds with a CO₂ molecule to yield 1b. The bonded CO₂ undergoes a 2e reduction to obtain 1c through transition state TS1-1. The total energy barrier calculated is 8.6 kcal/mol. In this process, the transition state and intermediate may be stabilized by through-space interactions between the partial negative charge on the COO species bound to one Ni and the positive charges of the other Ni.⁷⁶ Thirdly, 1c is protonated to form 1d with a comproportionation process. Finally, the C-OH bond within **1d** is cleaved with the assistance of H_3O^+ to yield **1e**. After the release of CO, 1 is regenerated and the catalytic cycle restarts. The pathway for the reduction of CO₂ to CO catalyzed by 2 was also investigated by the DFT calculations. As shown in Fig. S14, firstly, the Ni^{II} in **2** is reduced to Ni^I (**2a**). Then a molecular CO₂ bonds to 2a and undergoes a 2e⁻ reduction by Ni['] via transition state TS1-2 to generate 2b, with the total calculated energy barrier of 11.7 kcal/mol. The resulted 2b undergoes a proton-coupled electron transfer (PCET) process to form **2c**, and the C-OH bond in **2c** is cleaved assisted by H_3O^{\dagger} to generate 2d. After the release of CO, 2 is regenerated and the catalytic cycle restarts.

The results of DFT calculations have illustrated that the electrocatalytic reduction of CO2 to CO by either dinuclear complex of 1 or mononuclear complex of 2 is feasible, consistent with the experimental observations. Moreover, the energy barriers of rate-determining CO₂ reduction step for 1 (8.6 kcal/mol) is much lower than that for 2 (11.7 kcal/mol), indicating that the reduction of CO_2 to CO by 1 is much more favored in comparison with 2. This result solidly evidenced the experimental result, that is, 1 with a dinuclear catalytic center shows much higher electrocatalytic activity for CO2-to-CO conversion than 2 with a single catalytic center. The dramatic decrease of the energy barriers by 1 in contrast to 2 clearly reveals that there is really a synergistic catalysis effect between two Ni^{II} within **1**. The significant enhancement of the electrocatalytic activity of 1, together with the excellent photocatalytic performance for CO₂-to-CO conversion of our previously reported dinuclear Co^{III} complex,⁵⁵ clearly demonstrates that dinuclear molecular catalysts with DMSC effect are beneficial for CO₂ reduction.

Conclusions

In summary, we report a dinuclear nickel complex which can serve as a highly efficient and selective catalyst for electrochemical CO₂-to-CO conversion. The TON and TOF values reach as high as 4.1×10^6 and 190.0 s^{-1} , respectively, and the Faradaic efficiency reaches as high as 95%. The experimental studies and theoretical calculations reveal that the synergistic catalytic effect between two Ni centers plays a key role in enhancing the catalytic activity and selectivity for CO₂-to-CO conversion. The presented studies may provide new insights for designing of high-performance electrocatalysts for CO₂-to-CO conversion.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful for the financial support by the 973 program of China (2014CB845602), the NSFC (21331007,,21401026), and the NSF of Guangdong Province (S2012030006240).

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A dinuclear nickel complex was found to be excellent catalyst for electrocatalytic reduction of CO_2 to CO. This excellent catalytic performance can be attributed to the synergistic catalysis effect between two Ni centers.