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Full Paper

A water-soluble Cu complex as molecular catalyst for electrocatalytic CO₂ reduction on graphene based electrodes

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We report that a structurally simple molecular 1,10-phenanthroline-Cu complex on a mesostructured graphene matrix can be active and selective toward CO₂ reduction over H₂ evolution in an aqueous solution. The active sites consisted of Cu(I) center in a

distorted trigonal bipyramidal geometry, which enabled the adsorption of CO₂ with η^1 -COO-like configuration to commence the catalysis, with a turnover frequency of ~ 45 s⁻¹ at -1 V vs reversible hydrogen electrode. Using in-situ infrared spectroelectrochemical investigation, we demonstrated that the Cu complex was reversibly heterogenized near graphene surface via potential control. An increase of electron density in the complex was observed as a result of the interaction from the electric field, which further tuned the electron distribution in the neighboring CO₂. It was also found that the mesostructure of graphene matrix favored CO₂ reduction on the Cu center over hydrogen evolution by limiting mass transport from the bulk solution to the electrode surface.

1. Introduction

Electrochemical carbon dioxide reduction from the utilization of intermittent and renewable electrical energies is regarded as a potential strategy for the production of chemical fuels or feedstock compounds.^[1] This strategy could help alleviate our dependence on fossil fuels and at the same time balance the atmospheric CO₂ concentration.^[2] For instance, carbon monoxide (CO) and formic acid are two primary and potentially profitable products from carbon dioxide reduction reaction (CO₂RR).^[3] CO is used as a reactant in the Fischer-Tropsch process for the manufacture of hydrocarbons and their oxygen derivatives.^[4] Formic acid has a wide application in textile industries, food chemicals and fuel cells.^[5] However, CO₂ is a structurally stable and fully oxidized molecule. Its reduction is a thermodynamically uphill process, which

involves multiple elemental steps with generation of highly energetic intermediates. This is further complicated by the competing hydrogen evolution reaction (HER) in an aqueous solution. It is imperative to develop efficient and selective catalysts to promote the kinetics of CO₂RR over HER in the presence of water at mild conditions.

Molecular catalysts, represented by transition metal complexes, offer an attractive option to promote selective CO₂RR catalysis. These catalysts contain versatile structures that can be systematically tuned via ligands' screening in order to optimize their catalytic performance. Molecular catalysts are also considered as appropriate platforms for gaining mechanistic insights into catalysis because their active sites are well-defined and uniform. The representative molecular catalysts for CO₂RR include Re(bpy)(CO)₃Cl (bpy=2,2'-bipyridine),^[6] Ru(bpy)(CO)₂Cl₂,^[7] Ir pincer complexes,^[8] [Ni(cyclam)]²⁺ (cyclam=1,4,8,11-tetraazacyclotetradecane),^[9] porphyrins and their derivatives with coordinated Fe or Co sites^[10]. Most molecular catalysts function well in nonaqueous aprotic solvents (or blending with a certain fraction of H₂O), while few of them exhibited sufficient activity and selectivity in fully aqueous solutions.^[9, 11] In this context, there are several recent works suggesting that Cu complexes might serve as potential CO₂RR catalysts.^[12] For instance, Bouwman et al.^[13] reported a dinuclear Cu complex that selectively reduced CO₂, rather than O₂, from air to generate oxalate. The mechanistic study showed that CO₂ reacted with Cu(I) sites to derive a tetranuclear Cu structure as a critical reacting intermediate. An analogous catalytic process was later also discovered on

a single macrocyclic complex based on the Cu(I) active sites in DMF.^[14] More recently, Wang et al.^[15] deposited a water-insoluble Cu-porphyrin complex onto carbon nanoparticles, which enabled catalysis being conducted at heterogeneous surfaces in an aqueous solution. The hybrid structure afforded high reaction rates to reduce CO₂ into hydrocarbons.

Besides active sites, the CO₂RR electrocatalysis is also dependent on the mesostructures of electrode surfaces. The surface roughness affects mass transport from the bulk solutions to the electrode, which exhibits different impacts on the reaction rates of the CO₂RR and the competing HER as observed on porous metallic electrodes.^[16]

Herein, we report that a Cu complex, made of 1,10-phenanthroline (phen) ligands and Cu²⁺ ions, can operate as a simple but efficient molecular catalyst for CO₂RR after immobilization onto mesoporous graphene electrode. In 0.1 M KHCO₃, the phen-Cu complex exhibited higher selectivity over HER to reduce CO₂ into CO, formate and C₂H₄ (**Scheme 1**). The highest Faradaic efficiency (FE) achieved was around 90% at -0.6 V vs reversible hydrogen electrode (RHE). We identified that CO₂RR catalysis was commenced with Cu(I)-η¹-COO-like geometry. In-situ attenuated total reflection-infrared (ATR-IR) spectroelectrochemical measurements showed that phen-Cu was reversibly heterogenized near graphene surface driven by potential control. The selectivity of the Cu sites enabled catalysis was also related to the mesostructure of graphene surface that the high surface porosity of graphene limited the mass transport from the electrolyte to the

electrode. Such limited mass transfer led to a decrease of HER rate, which enhanced CO₂RR selectivity.

2. Results and Discussion

2.1. CO₂RR Measurements

The phen ligand is known as a very common and cheap ligand for various metal ions,^[17] and the formation of complexes with these ions allows convenient preparation at mild conditions. The phen-Cu complex was synthesized from an assembly of CuCl₂ and phen in a solvent mixture of CH₃OH/CH₂Cl₂. The phen-Cu complex can be readily isolated from the solution with a molar ratio of 1:2 (Cu : phen,^[18] details are provided in the synthesis of experiments). **Figure 1a** presents the normalized Cu K-edge X-ray absorption spectroscopy (XAS) data of phen-Cu. The inset shows the pre-edge region for 1s→3d electron transition.^[19] The pre-edge peak of phen-Cu exhibited minor shift compared to that of CuCl₂ (+0.2 eV). At 8987.5 eV, CuCl₂ exhibited a shoulder peak that was assigned to a transition of 1s→4p electron with simultaneous ligand-to-metal charge transfer, while such a peak was not observed in phen-Cu. The intensity of the shoulder peak was positively correlated to the covalence of equatorial ligands for Cu center.^[20] Thus, from CuCl₂ to phen-Cu, the diminished shoulder peak signal implied the ligand variation at Cu center. The oxidation state of Cu center of phen-Cu should remain +2 as both the rising edge and pre-edge peak were close to that of CuCl₂. This was also supported by electron paramagnetic resonance (EPR, Figure S3) spectra, showing that the

phen-Cu was EPR active. The local environments of Cu centers were investigated by the Fourier transformed data of extended X-ray absorption fine structure (EXAFS, Figure 1b). The first shell of Cu center in CuCl₂ was observed at 1.51 Å and 1.91 Å for Cu-O (from hydrate) and Cu-Cl distance, respectively.^[21] For comparison, the first shell of Cu center in phen-Cu shifted to 1.58 Å which should indicate the formation of Cu-N bond. It was also noted that the Cu-Cl bonds (1.91 Å) occurred in phen-Cu but was reflected by a relatively weaker shoulder peak comparing to that in CuCl₂. These variations further supported the ligand variation from Cl⁻/H₂O to phen at the Cu center.

For CO₂RR electrocatalysis on the phen-Cu complex, we used a carbon paper as current collector, and covered it with graphene layers (17-18 μg cm⁻²). The synthesis of graphene was realized by hydrothermal treatment of graphene oxides (GO), followed by heat treatment under H₂/Ar atmosphere (details in experiments and Figure S4). In cyclic voltammetry (CV) tests, phen-Cu displayed a pair of well-defined redox peaks at 0.53 V (E^{1/2}) in CO₂ saturated 0.1 M KHCO₃ solution (Figure S5a), assigned to the Cu^{I/II} couple.^[22] The redox currents had a linear correlation with the square root of scan rates, which reflected a diffusion-controlled process of phen-Cu from bulk solution to graphene electrode surface, and it governed the kinetics of metal redox reaction (Figure S5b). The CO₂RR electrocatalysis of phen-Cu/graphene electrode (denoted as phen-Cu/G, Figure S6a) was evaluated by linear sweep voltammetry curves (LSVs). With purging CO₂ into 0.1 M KHCO₃, an increase of the cathodic currents due to CO₂ reduction was observed

compared to the case of Ar purging, while the redox of the Cu sites was retained at higher potentials. The chronoamperometric curve suggested that the cathodic current was durable in continuous measurement (Figure S6b). A Faradaic efficiency ($FE_{CO+HCOO^-}$) of ~83 % was achieved at -0.5 V (Figure 1c). Increasing the potential resulted in moderate change in FEs and a highest value was observed at -0.6 V ($FE_{CO+HCOO^-} \approx 90\%$). The liquid products were analyzed by HPLC and 1H -NMR. Only HCOOH was identified over the entire potential range. The main gas product was analyzed by in-line gas chromatography to be CO, while trace C_2H_4 was produced at -1 V with FE of 2.4 %. To verify that the products came from CO_2 instead of graphene, we conducted the electrocatalysis on phen-Cu/G in 0.1 M PBS buffer (pH = 6.9) under Ar atmosphere. At all potential values tested (-0.7 V, -0.8 V, -0.9 V and -1 V), the possible products of formate, CO and C_2H_4 were not detected and only H_2 was generated from water reduction. The graphene surface structure was investigated after 2 hours' CO_2 RR electrolysis at -1 V. The characters of metallic Cu or CuO structures was not observed by a variety of structural surveys (Figure S7, S8). The UV-visible spectra of $KHCO_3$ solution showed that there was only a very slight decrease of absorbance for the characters of phen-Cu (Figure S9). In addition, after the CO_2 RR electrolysis, the graphene electrode was taken out from the phen-Cu containing electrolyte, put in fresh 0.1 M $KHCO_3$ in the absence of phen-Cu to further perform CO_2 RR electrolysis. It showed a significant drop of FE and current density comparing to the case of phen-Cu/G (Figure S10). To exclude the

possibility of any in-situ formed metallic particles which might be desorbed from the graphene surface in the step of rinsing the graphene electrode with solvents before the further electrolysis^[23], the used rinsing solvents were collected and checked by TEM, and the possible metallic particles were not observed (Figure S11). These results should suggest that Cu or CuO was not deposited onto graphene and molecular phen-Cu served as the main catalytic sites in the CO₂RR electrolysis. To verify the role of ligand, we performed CO₂RR on CuCl₂/G. The data of SEM and XRD verified that without the phen ligands, the Cu²⁺ ions were reduced into metallic Cu at the CO₂RR potential (-1 V) (including some Cu oxides species). Substantial particles and even dendrites-like structures were deposited onto the graphene layers (Figure S12). The phenanthroline ligands could maintain the molecular integrity of phen-Cu at the reduction potentials through the strong Cu-N bonds. The in-situ formed metallic Cu was reported to be active for CO₂RR^[24]. In this case, the electrode exhibited much improved activity for C₂H₄ production (at -1 V, FE= $\sim$ 8.7 %, J_{C₂H₄}=0.39 mA cm⁻² vs $\sim$ 2.4 %, 0.06 mA cm⁻² on phen-Cu/G). However, it also promoted the competing H₂ production with depressed selectivity of CO+HCOO⁻ production (Figure S13). This is further evidence that the catalytic system is molecular with associated phen ligands.

In the absence of phen-Cu, the pristine graphene electrode at various potentials all exhibited very low FEs for CO₂RR (Figure S14) and afforded insignificant CO₂RR currents compared to that of phen-Cu/G (Figure 1d). From the redox currents of the Cu^{II/I}

sites and the steady CO₂RR currents, the TOFs of Cu sites were estimated using the calculation method previously established,^[25] which derived a fast TOF of ~45 s⁻¹ at -1 V (the catalytic currents after subtracting the background currents were used, details were provided in SI, Figure S15).

2.2. Insights into Cu Active Sites

It was noted that the Cu^{II/I} redox of phen-Cu occurred at 0.53 V, and no further redox feature of Cu centers was observed prior to the onset potential of CO₂RR (**Figure 2a**). Thus, the reduction state of phen-Cu, termed as phen-Cu(I), is believed to be the adsorption sites for CO₂ and responsible for the catalysis. To identify the structure of phen-Cu(I), phen-Cu was reduced in DMF and the single crystals of phen-Cu(I) were isolated by the gradual evaporation of the solvent. The molecular structure of phen-Cu(I) was presented in Figure 2b. Cu center's five-coordinates were occupied by four N ligands and one Cl ligand in a distorted trigonal bipyramidal geometry. The configuration is consistent with the results in previous studies.^[18, 26] At the axial positions, the Cu-N (N5, N6) bond length was 1.98 Å and the bond angle (N3-Cu1-N6) was 99.5°. At the planar positions, bond lengths were relatively longer: 2.10 Å for Cu-N (N3, N4) and 2.37 Å for Cu-Cl, and the bond angle (N3-Cu1-Cl1) was 117.3° (Table S1). It was inferred that CO₂ might adsorb at the planar position of the Cu(I) sites that afforded minimum steric effect. The adsorption configurations of CO₂ at single metal sites were reported previously,

including η^1 -COO, η^2 -COO and η^1 -OCO geometry with 1 equiv CO₂.^[27] These possible structures were considered in the case of Cu(I) sites and were investigated by first-principle calculations. It was found that all the systems were optimized ultimately to one configuration where CO₂ adsorbed onto the Cu(I) sites with C atom as the interacting site, while the interaction was relatively moderate (Figure S16).

The CO₂RR elementary steps were investigated by first-principles calculations based on the optimized Cu(I)-CO₂ configurations. With the adsorption of CO₂, electrocatalysis followed by one-electron reduction as a rate limiting step which agrees with the experimentally observed CO₂RR Tafel slope of 169 mV dec⁻¹ (Figure 2c). Figure 2d presents the free energy diagram for each elementary step of CO₂RR at an equilibrium potential of 0 V, and that of HER steps was included for comparison. It was found that the protonation of C site of the adsorbed CO₂ to form *OCHO intermediate was found to be energetically more favorable than the protonation of O site to form *COOH intermediate. The formation of *OCHO was rate-limiting for generating either CO or HCOOH. The corresponding limiting potential for CO₂RR (-1.13 eV) was lower than that of HER (-1.77 eV), which indicated better intrinsic activity of the Cu(I) complex toward CO₂ reduction. It was also found that the process of CO formation was less endothermic than that of HCOOH. This result, thus, suggested a higher selectivity of CO over HCOOH in the CO₂RR on the Cu(I) site, as reflected in the FE measurements.

2.3. Spectroscopic Investigation

We applied an in-situ ATR-IR spectroelectrochemistry technique to probe the interfacial behavior of the phen-Cu/G under the CO₂RR condition. The setup for the measurement is shown in **Figure 3a**. The G layers were covered onto a ZnSe prism and attached to the potentiostat. The IR detection was conducted at the interface of the G layers and KHCO₃ solution. At an applied potential of -0.9 V, a series of IR signals were continuously collected (Figure 3b). The peaks at 800/823 cm⁻¹ and 1110/1135 cm⁻¹ were assigned to the out-of-plane and in-plane deformation of C-H bonds, respectively, and the peaks between 1380-1510 cm⁻¹ were assigned to the stretching of C=C/C=N bonds in aromatic rings.^[28] These signals can be attributed to the phen ligands, indicating the gradual adsorption of phen-Cu onto G surface. The collection of IR spectra lasted for 60 min. In this period, the IR peaks of phen-Cu did not exhibit any shift, suggesting that the molecular structure of phen-Cu remained stable under the CO₂RR condition.

The adsorption kinetics was depicted by the peak intensity at 1510 cm⁻¹ vs time. The coverage of phen-Cu increased rapidly in the first 10 min, afterwards it came to a plateau (Figure 3b inset). This feature was fitted to the typical behavior of interfacial interaction,^[29] and demonstrated that phen-Cu was heterogenized near G surface. After the adsorption of phen-Cu reached equilibrium, the applied potential was removed. For the convenience of IR signals analysis, we directly set the spectrum obtained on the surface after adsorbing phen-Cu for 60 min as the background, and continued to collect

the IR data after the removal of the potential control. The IR peaks gradually turned negative, which was attributed to the desorption of phen-Cu from the G surface (Figure 3c). The desorption kinetics was analogous to that of adsorption (Figure S17). Besides, using density functional theory (DFT) study, we investigated if possible electronic interaction occurred between the Cu sites and graphene surface. The calculation results (Table S2) indicated that the electronic interaction between them was relatively weak and of typical van der Waals type. The graphene surface hardly altered the electronic or geometric structures of the Cu sites, being similar to the cases of C₆₀ adsorption on MoS₂/WS₂ and other van der Waals heterostructures^[30]. In addition, phen-Cu was directly reacted with G surface in DMF at 80 °C for 12 h. XPS survey did not show the Cu signals on the G surface (Figure S18). Taken together, these results indicated that the heterogenization process of phen-Cu was driven by the applied electric field as a relatively long-range interaction^[31], and such a process was observed to be reversible. In addition, the negative peaks exhibited red shift compared to the positive ones. It is believed that under the CO₂RR condition, the reduction potential led to an increased electron density of phen ligands and resulted in the red shift. In the meantime, the CO₂ vibration occurred between 2300-2400 cm⁻¹, corresponding to the antisymmetric stretch of C=O bonds coupled with the rotational movement of CO₂ (Figure 3d). From the open circuit to turnover condition (@-0.9V), R branch of the vibration shifted from 2336.5 to 2342.2 cm⁻¹ as a result of the increased electron density in CO₂ (blue/red curves). In

contrast, in the absence of phen-Cu, the vibration shifted from 2336.4 cm^{-1} (green curve) to a higher position of 2343.2 cm^{-1} with a clearly narrowed peak (orange curve). This further reflects the efficient electronic interaction between phen-Cu and CO_2 near the graphene surface that the electron density of CO_2 was tuned by phen-Cu to a relatively continuous distribution state under the catalytic condition.

2.4. CO_2RR catalysis at phen-Cu/G-2

The ATR-IR measurements showed that phen-Cu was heterogenized near G surface under the CO_2RR condition. Despite the DFT calculation suggested the G surface cannot alter the electronic structure of phen-Cu to tune its intrinsic CO_2RR activity (Table S2), we suspected that the surface structure of G might determine the high selectivity of CO_2RR through tuning the mass transport near the electrode surface.^[16] In a control experiment, we synthesized a graphene sample (G-2) only by hydrothermal reduction of GO (Figure S19), and applied G-2 as another electrode material to support the CO_2RR catalysis in the presence of phen-Cu (denoted as phen-Cu/G-2). As compared by SEM images, the G surface showed high roughness, exposing substantial graphene edges, resulting in the high porosity. In contrast, G-2 exhibited a flat surface with graphene layers aligning tightly (**Figure 4a**, S20). The Brunauer-Emmett-Teller (BET) specific areas of G and G-2 were measured to be $131.4\text{ m}^2\text{ g}^{-1}$ and $46.9\text{ m}^2\text{ g}^{-1}$, respectively (Figure S21 and Table S3). With this structural evolution, the wettability by water

improved from G to G-2 surface. The contact angle (CA) of a water droplet on G was 152° due to its superhydrophobic nature, while CA decreased to 112.5° on G-2 (Figure S22), which was consistent with Cassie's and Wenzel's theories, reflecting the high porosity of G surface.^[32]

It was observed that, from phen-Cu/G to phen-Cu/G-2, the FEs of CO₂RR decreased over the entire potential range, although the reaction products remained to be CO, HCO₂H and a small fraction of C₂H₄ collected at -1 V (Figure 4b). The remaining product was measured to be H₂ from water reduction (Figure S23). In the absence of phen-Cu, both the CO₂RR and HER currents on pristine G-2 electrode were less significant than those on phen-Cu/G-2 but were almost the same as those on pristine G electrode (Figure S24). However, the different surface morphologies of graphene electrodes, with the accompanied variation of hydrophobicity, suggested that in the aqueous solution, the mass transport from the electrolyte to graphene surface during the catalysis could be tuned. This has been demonstrated as a determinant to the catalytic selectivity on CO₂RR and HER.^[16a, 16b]

We investigated the capacitance of G and G-2 in a non-Faradaic range in 0.1 M KHCO₃. The capacitive currents of G-2 were much higher than those of G (Figure S25a, b), in spite of its lower BET surface area. In the Nyquist plot, G-2 showed a smaller solution resistance in the high frequency range that was attributed to the contact among solution, graphene layers and current collectors (Figure S25c).^[33] At the low frequencies,

G-2 revealed a more vertical line than that of G. It suggested an ideal capacitive behavior of G-2, where ions' transport from solution to electrode was fast, while the ions' transport to G was relatively slow.^[34] To further verify the tuned mass transport, we used molecular dynamics (MD) simulations to examine the diffusion of KHCO_3 aqueous solution near different graphene surfaces. As G surface exposed substantial edges of graphene sheets, the MD results showed that it was relatively difficult for KHCO_3 solution to accumulate near such a surface. For comparison, the basal plane of graphene exhibited an improved affinity to KHCO_3 solution, and near this surface, the concentration of KHCO_3 solution was higher than the case of graphene edges, indicating the facilitated mass transport (Figure S26). Therefore, both the experiments and simulations indicated that the porous G surface limited the mass transport from the electrolyte to the electrode. However, from the results of catalytic measurements, such a limitation only decreased the HER currents, while the CO_2RR currents were barely influenced (Figure 4c). This was consistent with the previous report, showing that HER is strongly dependent on proton donor environment while CO_2RR was not. Therefore, a higher selectivity is expected on a porous electrode with amplified proton depletion effects.^[16a, 16b, 35]

3. Conclusion

In summary, we reported that a structurally simple phen-Cu complex was an active and selective CO_2RR catalyst on graphene-based electrode in a fully aqueous solution. The

Cu center of phen-Cu was redox active, which had a well-defined five-coordination with a distorted trigonal bipyramidal geometry to commence the CO₂RR catalysis. By ATR-IR investigations, phen-Cu was found to be reversibly heterogenized near graphene surfaces by potential control, and led to the increased electron density under the catalytic condition. The electronic interaction between CO₂ and phen-Cu was also demonstrated to be efficient by IR signals, in which the catalyst tuned the electron distribution of CO₂ during catalysis. The surface structure of graphene electrode was involved to affect the CO₂RR catalysis sustained by phen-Cu. The high surface porosity of graphene limited the mass transport from bulk solution to graphene electrode. This feature greatly improved CO₂RR selectivity by inhibiting HER, while CO₂RR was barely influenced. These results highlighted the importance of both the molecular Cu active sites and surface property of graphene electrode to achieve high CO₂RR selectivity.

4. Experimental Section

Chemical: Graphite powders, 1,10-phenanthroline, CuCl₂, K₂S₂O₈, P₂O₅, KMnO₄ and KHCO₃ were purchased from Sigma Aldrich and were used as received. All organic solvents were of analytical grade and were used without further purification. Carbon papers treated with PTFE were purchased from Fuelcellstore. All aqueous solutions were prepared using Millipore water of 18 MΩ•cm electrical resistance.

Synthesis of Cu-1,10-phenanthroline Complex and Graphene: The Cu complex was synthesized as following: briefly, CuCl₂ and 1,10-phenanthroline were mixed with a molar ratio of 1:2.2 in CH₃OH/CH₂Cl₂, and heat-treated at 60 °C for 12 h. Afterwards, the solvent was removed by rotary evaporation. The remaining solid was washed by

CH_2Cl_2 and water successively. The resultant precipitate was re-crystallized in CH_3OH to be collected as the final product.

Graphene oxides (GOs) were synthesized following a modified Hummers' method as previously established,^[36] which was applied as the precursors to synthesize graphene. Briefly, graphite (6 g), P_2O_5 (2 g) and $\text{K}_2\text{S}_2\text{O}_8$ (2 g) were mixed in concentrated H_2SO_4 (98 %) to be heated at 80 °C for 10 h. Afterwards, the solid product (2 g) was continued to react with KMnO_4 (6 g) in concentrated H_2SO_4 (98 %) at 40 °C for 2 h to generate GO. Before using GO, the dispersion solution of GO was dialyzed by copious amount of water for 2-3 weeks. To achieve graphene, i) GO aqueous solution (1 mg mL^{-1}) was sealed into a Teflon-lined stainless autoclave. The autoclave was heated at 150 °C for 3 h to generate hydro-treated graphene. The product was freeze dried to remove residual water and was pyrolyzed under H_2 (5%)/Ar (95%) atmosphere at 850 °C for 1 h, resulting in hydrogen treated graphene.

Electrocatalytic Measurements: Graphene was dispersed in isopropanol (2 mg mL^{-1}), and casted onto carbon paper at a mass loading of 17-18 $\mu\text{g cm}^{-2}$. In a typical three-electrode setup, the modified carbon paper was used as the working electrode, an Ag/AgCl electrode was used as the reference electrode and a Pt mesh (2.25 cm^2) was used as the counter electrode. Aqueous solution of 0.1 M KHCO_3 was applied as the electrolyte. Under the CO_2 electrocatalytic condition, the copper complex (35 μM) was added into 0.1 M KHCO_3 under CO_2 atmosphere. The catalytic measurements were

conducted on a CHI 1140 potentiostat. The electrochemical impedance was conducted on an Autolab PGSTAT302 potentiostat. The electrochemical cell was a typical H-type with anode (containing Pt mesh) and cathode (containing Ag/AgCl, and graphene coated carbon paper) separated by a Nafion membrane. The Ag/AgCl wire was stored in saturated KCl solution, and regularly refreshed to counteract the contamination from electrolytes. The electrode potential was converted to reversible hydrogen electrode (RHE) scale based on $E(\text{versus RHE}) = E(\text{versus Ag/AgCl}) + 0.197 + 0.059(\text{pH})$.

During the electrolysis, CO₂ was continuously sparged into cathodic chamber with a flow rate of 2 sccm. The generated gases were directly injected into gas chromatography (GC) for quantitative analysis. Hydrocarbon products (i.e., C₂H₄) were identified by a flame ionization detector, and CO and H₂ were identified by thermal conductivity detector, respectively. N₂ is used as the carrier gas. Each collection of GC spectrum took around 15 min. A representative GC spectrum was shown in Figure S1. At the end of electrolysis, the liquid products were analyzed by high performance liquid chromatography (HPLC). A representative HPLC spectrum was shown in Figure S2. The nature of liquid products was further confirmed by nuclear magnetic resonance (NMR) spectroscopy and only formic acid was detected.

ATR-IR Analysis: The Reflection plane of ZnSe hemispherical prism was cleaned by polishing with 1 mm alumina slurries for 10 min, and sonicating in ethanol and water for 10 min, respectively. The graphene suspension was casted onto the surface of ZnSe prism

to form graphene film that was connected to a potentiostat for ATR-IR study under electrocatalytic conditions. A homemade glass cell was covered over the graphene film for carrying electrolytes (15 mL), as well as Ag/AgCl reference electrode and Pt counter electrode. The diameter of cell for IR detection was 1 cm. To obtain spectra, background signals were collected on the graphene film with or without applying constant potential with the testing solution of N₂ saturated 0.1 M KHCO₃, and the solution was balanced on the graphene films for 2 h. In Figure 3b, the IR signals were collected for 60 min at -0.9 V. Afterwards, the surface was set as the background to further collect IR signals at the condition of without applying -0.9 V, which described the negative signals in Figure 3c. Unpolarized IR radiation was totally reflected at the interface of graphene film loaded ZnSe prism and aqueous solutions with an incident angle of 70° and was detected by a liquid N₂-cooled MCT detector. The spectral range was 4000 cm⁻¹ to 650 cm⁻¹ with a resolution of 4 cm⁻¹, and the limit of noise signals was ±0.0002 unit.

First-Principles Calculations: The study was performed using the Vienna Ab-Initio Simulation Package with spin-polarized Perdew-Burke-Ernzerhof exchange correlation functional including van der Waals corrections (DFT-D3 method).^[37] A cutoff energy of 500 eV was used for the plane-wave expansion.^[38] The geometry was optimized until all residual forces were less than 0.01 eV/Å.

According to the previous studies,^[39] the electroreduction of CO₂ to CO was studied as followings,

the conversion of CO_2 to HCOOH was studied as followings,

the hydrogen evolution was described simply as followings,^[40]

in the above equations, the asterisk (*) denotes a site on the catalyst. For the adsorption of intermediate $*\text{COOH}$, $*\text{CO}$ and $*\text{H}$, a series of possible adsorption configurations with the molecular catalyst were considered. The free energy for each intermediate state was calculated as $G = E + \text{ZPE} - TS$ with ZPE and S being the zero-point energy and entropy, respectively. T is the temperature and equals to 298 K. For gas phase, the ZPE and TS_0 were taken from standard tables.^[41] For the liquid water and formic acid (HCOOH), the TS s were calculated based on gas phase with a fugacity of 3530 and 19 Pa for H_2O (pure water) and HCOOH (1 M HCOOH),^[42] respectively, through the equation:

$$TS = TS_0 + k_{\text{B}}T \ln(p/p_0) \quad (7)$$

where p is partial pressure and p_0 is the standard state pressure (101,325 Pa). ZPE and TS were neglected for the catalyst due to effective cancellation, while the ZPEs and entropies

of adsorbates were calculated from the vibrational frequencies.^[43] The adsorbate solvation effects were estimated according to previous studies: intermediates of *COOH/*OCHO and *CO were stabilized by 0.25 and 0.10 eV, respectively.^[42] A correction of -0.51 eV was made to the energetic gas-phase due to the Perdew-Burke-Ernzerhof functional.^[39a] Following the previous study, the proton-electron pair was assumed and the corresponding free energy was calculated relative to the reversible hydrogen electron (RHE).

Molecular Dynamics (MD) Simulations: To examine the diffusion of water molecules on graphene layers in KHCO₃ aqueous solution (mole ratio of KHCO₃ : H₂O set to be 4:125), molecular dynamics simulations were performed by using Universal force field as implemented in Forcite package in Materials Studio 7.0. We conducted several simulations with specified sites for the graphene layers exposed to the solution at room temperature (ca. 300 K). The simulation cell contained six graphene layers whose initial configurations were taken from the experimentally obtained crystalline graphite. The five-layer water molecules taken from ice (*P6₃/mmc* symmetry) together with four KHCO₃ molecules were put above the graphene layers.

The MD simulations (MD) were performed under NVT ensemble with a 0.1 fs time step for up to 500 ps. The van der Waals interactions are described by the Lennard-Jones potential. The electrostatic interactions are described by atomic monopoles and a screened (distance-dependent) Coulombic term. In all simulations, the initial structures

were taken from the experimental structure and then optimized to the energy minimum structures by the Universal force field. The MD simulations were conducted at 300 K to allow the full relaxation of the solution on the graphene layers.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Scheme 1. A phen-Cu complex applied as CO₂RR molecular catalyst on mesoporous graphene electrode in CO₂ saturated 0.1 M KHCO₃. A representative SEM image of the graphene surface is included.

Figure 1. (a) Normalized Cu K-edge XAS spectra of CuCl_2 and phen-Cu. Inset shows the pre-edge region. (b) Fourier transformed EXAFS curves collected at Cu-K edge. (c) FEs of CO_2RR catalyzed by phen-Cu/G at different potentials in CO_2 saturated 0.1 M KHCO_3 (each data point was collected after electrolysis for about 2 h, the concentration of phen-Cu in the electrolyte was set as 35 μM). (d) The steady-state current densities of CO_2RR at phen-Cu/G with the TOF analysis based on Cu sites.

Figure 2. (a) Typical CV polarization curves of phen-Cu on graphene electrode, and they showed the clear Cu^{II} to Cu^I conversion prior to CO₂RR, scan rate: 20 mV s⁻¹, 0.1 M KHCO₃. To eliminate the influence from oxygen reduction, the tests were performed under Ar atmosphere. (b) Crystal structure of phen-Cu(I), [Cu^I(phen)₂Cl], derived from the DMF treatment of phen-Cu. H atoms are removed for clarity. (c) Tafel plot. (d) The free energy diagram of CO₂RR with CO (red) and HCOOH (black) as main products, and HER (blue) under an equilibrium potential of 0 V vs. RHE. Insets show respective *OCHO, *CO and *H intermediate state. Gray, green, brown, red and white spheres represent Cu, Cl, C, O and H atoms. The adsorption of *H on the Cu site is highlighted by a red circle.

Figure 3. (a) Schematic illustration of an in-situ ATR-IR cell with internal reflection mode. (b) A series of IR spectra versus time in 0.1 M KHCO₃ (CO₂ saturated, 0.6 mM phen-Cu) collected on G surface at -0.9 V. Inset presents the adsorption kinetics of phen-Cu. (c) IR spectra of phen-Cu on G surface with and without applying -0.9 V. (d) IR spectra of CO₂ under different conditions.

Figure 4. (a) Comparison of the morphologies of G and G-2 surfaces by SEM images. (b) The FEs and (c) current densities for CO₂RR and HER at phen-Cu/G and phen-Cu/G-2.

Molecular 1,10-phenanthroline-Cu complex is an active and selective CO₂RR catalyst on a mesostructured graphene based electrode in aqueous solution. The Cu(I) site has trigonal bipyramidal geometry, and is reversibly heterogenized near graphene surfaces with potential control to commence catalysis. The mesostructure of graphene surface suppresses HER by limiting mass transport from the bulk solution to the electrode surface, while CO₂RR is not sensitive to this variation.

Molecular catalysis, carbon dioxide reduction, graphene, in-situ infrared spectroscopy, mechanism

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A water-soluble Cu complex as molecular catalyst for electrocatalytic CO₂ reduction on graphene based electrodes

Supporting Information

Water-soluble Cu complex as molecular catalyst for electrocatalytic CO₂ reduction on graphene based electrodes

*Jiong Wang, Liyong Gan, Qianwen Zhang, Vikas Reddu, Yuecheng Peng, Zhichao Liu, Xinghua Xia, Cheng Wang and Xin Wang**

Figure S1. (a) A representative GC spectrum for the detection of CO and C₂H₄ products of CO₂RR electrocatalyzed by phen-Cu/G electrode in CO₂ saturated 0.1 M KHCO₃. The GC data of (b) 100% (v/v) H₂, (b) 10% (v/v) CO and 5% (v/v) C₂H₄ and 5 % (v/v) C₂H₆.

Figure S2. (a) A representative HPLC spectrum for the detection of formate product of CO₂RR electrocatalyzed by phen-Cu/G electrode in CO₂ saturated 0.1 M KHCO₃. (b) The HPLC calibration curve for formic acid.

Figure S3. EPR spectra of CuCl_2 and phen-Cu powders collected at room temperature.

Figure S4. TEM images of graphene (G) collected at different magnifications.

Figure S5. (a) CVs of phen-Cu/G with scan rates of 5, 10, 20, 30, 40, 50, 60, 80 and 100 mV s^{-1} , 0.1 M KHCO_3 under Ar atmosphere. (b) The redox peak currents densities versus square root of scan rates.

Figure S6. (a) Linear sweep voltammetry curves of phen-Cu/G acquired in Ar and CO₂ atmosphere, respectively, 0.1 M KHCO₃, scan rate: 20 mV s⁻¹. Inset shows the redox of Cu sites before and after undergoing 20 polarization cycles from 0 V to -1 V in CO₂ saturated 0.1 M KHCO₃. (b) Chronoamperometric curve of CO₂RR on phen-Cu/G at -0.8 V in CO₂ saturated 0.1 M KHCO₃.

Figure S7. SEM images of G loaded on carbon paper after running CO₂RR for 2 h in 0.1 M KHCO₃ in the presence of phen-Cu (35 μM) at -1 V.

Figure S8. (a) XRD pattern and (b, c) TEM images of G electrode after running CO₂ reduction electrocatalysis for 2 h in the presence of phen-Cu (35 μM) at -1 V. (d) The dark field TEM image of graphene after supporting the phen-Cu based CO₂RR, and (e) the corresponding elemental analysis by EDX. The measurement was conducted on Mo-grid. (f) Raman spectra of graphene electrode before and after supporting the phen-Cu based CO₂RR. (g) XPS Cu 2p survey of graphene electrode after supporting the phen-Cu based CO₂RR.

Figure S9. UV-visible spectra of phen-Cu contained in 0.1 M KHCO₃ solution before and after CO₂ electrolysis at -1 V for 2 h.

Figure S10. FEs and current densities of CO₂RR on phen-Cu/G, pristine graphene and a control sample at -1 V in CO₂ saturated 0.1 M KHCO₃. The control sample was achieved as following: the CO₂RR reduction was conducted in phen-Cu/G at -1 V for 2 h. Afterwards, the graphene electrode was taken out of the electrolyte. It was washed with water and dried at ambient condition to serve as the control sample to further perform CO₂RR in the absence of phen-Cu.

After running phen-Cu/G at -1 V for 2 h, the graphene electrode (size: 2 cm²) was rinsed by 100 uL water repeatedly. The rinsing water was checked by TEM (Figure S11).

Figure S11. TEM images of rinsing solution, which was used to wash graphene with running CO₂RR at -1 V for 2 h in the presence of phen-Cu.

Figure S12. SEM images of G electrode after running CO₂RR in the presence of CuCl₂ (35 μM) at -1 V for 1 h (a) and 2 h (b, c), respectively. (d) XRD of CuCl₂/G after running CO₂RR for 2 h.

Figure S13. Comparison of FEs and current densities of C₂H₄ production on CuCl₂/G and phen-Cu/G, 0.1 M KHCO₃, CO₂ atmosphere, -1 V. Inset shows the overall FE for CO₂RR and HER on CuCl₂/G.

Figure S14. FEs of CO₂RR on the pristine graphene electrode in the absence of phen-Cu at different potentials, performed in CO₂ saturated 0.1 M KHCO₃.

TOF calculation. The calculation was conducted following the equations.

$$i_p = 0.4463 n_p F A C_{\text{cat}} (n_p F v D / RT)^{1/2} \quad (1)$$

$$i_c = n_c F A C_{\text{cat}} (D k_{\text{cat}})^{1/2} \quad (2)$$

$$i_c / i_p = 2.24 n_c n_p^{-3/2} (k_{\text{cat}} RT)^{1/2} (F v)^{-1/2} \quad (3)$$

in these equations (1-3):

i_p = the peak currents of $\text{Cu}^{2+/1+}$ redox collected cyclic voltammetry

i_c = catalytic currents of CO_2RR

n_p = number of electrons transferred in each $\text{Cu}^{2+/1+}$ redox

n_c = number of electrons transferred in each CO_2RR event

F = Faraday constant

A = area of the electrode

C_{cat} = bulk concentration of phen-Cu

v = scan rate

D = diffusion coefficient of phen-Cu

R = ideal gas constant

T = temperature

k_{cat} = catalytic turnover frequency

The equation (3) was applied to obtain k_{cat} , which was considered as the estimation of TOF of Cu sites. The i_p was considered as the average values of anodic peak currents and cathodic peak currents of $\text{Cu}^{2+/1+}$ couple. The i_c was considered with subtracting the background currents (The background currents were the CO_2RR currents acquired on graphene in the absence of phen-Cu, Figure S15).

Figure S15. The i_c/i_p as the function of $v^{-1/2}$ in 0.1 M KHCO_3 .

Table S1. Metrical parameters of phen-Cu(I) structure acquired from the data of single-crystal X-ray diffraction.

bond distance (Å)	
Cu1-N3	2.101
Cu1-N4	2.094
Cu1-Cl1	2.374
Cu1-N5	1.980
Cu1-N6	1.976
bond angle (degree)	
N3-Cu1-N6	99.49
N1-Cu1-N5	81.65
N3-Cu1-Cl1	114.73
N3-Cu1-N4	124.97

Figure S16. (a)-(c) Initial considered CO₂ adsorption configurations: $\eta^1\text{-COO}$, $\eta^2\text{-COO}$ and $\eta^1\text{-OCO}$, respectively.^[1] (d) Optimized CO₂ adsorption configuration including its adsorption energy (E_{ad}) and the C-Cu distance ($d_{\text{C-Cu}}$). Gray, green, brown, red and white spheres represent Cu, Cl, C, O and H atoms, respectively.

Figure S17. (a) A series of IR spectra versus time in 0.1 M KHCO_3 (CO_2 saturated, 0.6 mM phen-Cu) collected on phen-Cu attached G surface without applying potential, it presented the desorption of phen-Cu from G surface. (b) The desorption kinetics of phen-Cu.

Table S2. Properties of phen-Cu(I) adsorption on graphene: Binding energy (E_B);

Distance between Cu atom and graphene plane (D); corrugation (Δ) of graphene. Values in brackets were obtained without consideration of van der Waals correction. The brown, light blue, white and green spheres indicate the C, N, H and Cl atoms. The blue sphere indicates the Cu atom.

Configurations	E_B (eV)	D (Å)	Δ (Å)
A
-1.41 (-0.09)	4.445	0.229

B
-0.71 (-0.02)	4.782	0.240

In the DFT study, we achieved two optimized configurations (A and B) with phen-Cu(I) fully interacted with graphene surface. Their binding strengths were calculated to be -1.41 eV and -0.71 eV, respectively, and the values were substantially weakened to be -0.09 eV and -0.02 eV without the consideration of van der Waals correction. The distance between Cu sites and graphene is calculated to be 4.445 Å (A) and 4.782 Å (B). Upon the adsorption of phen-Cu(I), the planar geometry of graphene remains largely intact with slight corrugations.

Figure S18. XPS survey of Cu 2p core level of G after reacting with phen-Cu in DMF at 80 °C for 12 h.

Figure S19. TEM images of G-2 collected at different magnifications.

Figure S20. SEM images of G-2 loaded on carbon paper at different magnifications.

Figure S21. N₂ adsorption-desorption isotherm curves of G and G-2 performed at 77 K.

Table S3. Structural Parameters of G and G-2.

	G	G-2
BET surface area (m ² g ⁻¹)	131.4	46.9
Pore volume (cm ³ g ⁻¹)	0.234	0.178
Average pore size (nm)	7.13	15.18

G surface: 152°

G-2 surface: 112.5°

Figure S22. The shapes of water droplets on G and G-2 surfaces, respectively.

Figure S23. FEs of H_2 production CO_2RR on phen-Cu/G-2 at various potentials in 0.1 M KHCO_3 .

Figure S24. (a) FEs of CO_2RR on pristine G-2 at various potentials in 0.1 M KHCO_3 . (b) CO_2RR currents on pristine G, G-2 and phen-Cu/G-2. (c) HER currents on pristine G, G-2 and phen-Cu/G-2.

Figure S25. (a) CVs of G and G-2 loaded on the carbon papers, and were collected in CO_2 saturated 0.1 M KHCO_3 in a potential window without any faradaic processes. (b) The corresponding capacitive currents at 0.45 V vs. Ag/AgCl as a function of scan rates. (c) Nyquist plots of G and G-2 electrodes by applying an AC voltage of 5 mV amplitude from 0.1 Hz to 100 kHz.

Figure S26. Models for diffusion of water molecules on the (101, a) and (001, b) surface of a few layers of graphene, respectively. (c) The mean square displacement of water molecules in 500 ps, and (d) the concentration of water along the (101) and (001) surfaces of graphene nanolayers.

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