Substituent-induced electronic localization of nickel phthalocyanine with enhanced electrocatalytic CO₂ reduction

Kejun Chen

Central South University

Maoqi Cao

Central South University

Yiyang Lin

Central South University

Junwei Fu

Central South University

Hanxiao Liao

Central South University

Feng Xie

King Abdullah University of Science and Technology

Yajiao Zhou

Central South University

Baopeng Yang

Central South University

Kang Liu

Central South University

Guozhu Chen

Central South University

HongMei Li

Central South University

Dawang Wu

Qiannan Normal University for Nationalities

Xiaoqing Qiu

College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, China.

Junhua Hu

Zhengzhou University <https://orcid.org/0000-0003-0191-1503>

Xu-Sheng Zheng

University of Science and Technology of China

Mohsen Shakouri

Canadian Light Source <https://orcid.org/0000-0002-8449-9763>

Qunfeng Xiao

Canadian Light Source

Yongfeng Hu

Canadian Light Source (Canada)

Jun Li

University of Toronto

Min Liu (✉ minliu@csu.edu.cn)

Central South University <https://orcid.org/0000-0002-9007-4817>

Article

Keywords: enhanced electrocatalytic CO₂ reduction, catalysts, highly efficient CO₂RR

Posted Date: January 16th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-138056/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Designing efficient catalysts with high activity and selectivity is desirable and challenging for CO₂ reduction reaction (CO₂RR). Nickel phthalocyanine (NiPc) is a promising molecule catalyst for CO₂RR. However, the pristine NiPc suffers from poor CO₂ adsorption and activation due to its electron deficiency of Ni–N₄ site, which leads to inferior activity and stability during CO₂RR. Here, we develop a substituent-induced electronic localization strategy to improve CO₂ adsorption and activation, and thus catalytic performance. Theoretic calculations and experimental results indicate that the electronic localization on the Ni site induced by electron-donating substituents (hydroxyl or amino) of NiPc greatly enhances the CO₂ adsorption and activation, which is positively associated with the electron-donating abilities of substituents. Employing the optimal catalyst of amino-substituted NiPc to catalyze CO₂ into CO in flow cell can achieve an ultrahigh activity and selectivity of 99.8% at the current densities up to 400 mA cm⁻². This work offers a novel strategy to regulate the electronic structure of the active site by introducing substituents for highly efficient CO₂RR.

Introduction

Electrochemical conversion of CO₂ into the value-added energy chemicals using surplus sustainable energy is an appealing route to mitigate environmental issues and energy crisis.¹⁻³ Catalysts are indispensable for the electrocatalytic CO₂ reduction reaction (CO₂RR) to conquer the kinetic barrier of low electron affinity and inherent thermodynamic stability of CO₂.⁴⁻⁷ Molecule catalysts with redox-active sites for CO₂ activation/adsorption have attracted much attention.⁸⁻¹⁰ Among them, nickel phthalocyanine (NiPc) is considered as a promising catalyst for CO₂RR due to its proper active site.¹¹⁻¹⁶ Unfortunately, the pristine NiPc is subjected to inferior activity and stability owing to the poor CO₂ adsorption and activation rooted in the electron-deficient Ni site.¹⁷⁻²¹ The electronic localization of active site with an increased electronic density is able to optimize the CO₂ adsorption/activation in traditional inorganic catalysts.²²⁻²⁶ Inspired by this result, establishing electronic localization on the Ni site is expected as an effective strategy to improve CO₂RR performance in the NiPc system.

The structural flexibility of the phthalocyanine ring enables an adjustable electronic density of Ni site by tuning periphery substituents of NiPc.^{27,28} The electron-donating substituents tend to denote more electrons into the π conjugation system of phthalocyanine ligand, which is beneficial to the electronic localization.^{29,30} The amino and hydroxyl with lone pair electrons from the 2p orbit of N or O exhibit the prominent electron-donating property via p– π conjugation.^{31,32} Compared with the hydroxyl, amino with a low electronegativity of N leads to interior inductive effect and thus shows preferable electron-donating ability.³³ As for the NiPc molecule catalyst, the electronic structure of the active site (Ni–N₄) directly determines the catalysis of electrochemical CO₂ conversion.^{34,35} Modifying NiPc with different electron-

donating substituents can evoke the various degree of electronic localization on the Ni site and simultaneously reveal an inherent law of NiPc-based molecule catalysts for CO₂RR.

In this work, we demonstrate that the periphery substituents of NiPc can arouse the electronic localization on the Ni site, which facilitates the CO₂ adsorption and activation, and thus enhances the activity and stability of NiPc for CO₂RR. Theoretic simulations demonstrate that the electronic localization in the substituted NiPc is positively correlated with the electron-donating capability of substituents in comparison to that of the pristine one. To realize this speculation, the amino and hydroxyl substituted NiPc were synthesized via a facile approach. As expected, the spectra of X-ray photoelectron spectroscopy (XPS) and synchrotron X-ray absorption spectroscopy (XAS) indicate the electronic density of the Ni site in substituted NiPc becomes concentrated by the substituent-induced electronic localization. The amino-modified NiPc shows the superior performance of CO₂RR compared with other NiPc catalysts, which can be attributed to the stronger electron-donating property of amino. NiPc substituted by amino on the gas diffusion layer delivers a remarkable activity and ultrahigh selectivity of CO (>99.8%) for CO₂RR across a current range from -20 to -400 mA cm⁻². The substituents can regulate the electronic structures of molecule catalysts to improve the CO₂ adsorption and activation, which provides a new approach to modulate the electron structure of active site for enhanced CO₂RR performance.

Results

Theoretic calculations. The structure models of the pristine NiPc and NiPc with substituents of hydroxyl (NiTHPc) and amino (NiTAPc) are illustrated in Fig. 1a. In order to explore the substituent effect on the NiPc system, the electronic density of Ni was analyzed (Supplementary Fig. 1). Hrishfeld and Mulliken charge of Ni (Fig. 1b) indicates that the electron can be localized on Ni atom by the electron-donating substituents of hydroxyl or amino, and NiTAPc exhibits more apparent electronic localization than that of NiTHPc due to the stronger electron-donating ability of amino. The CO₂ adsorption energy of molecules was also examined (Fig. 1c and Supplementary Fig. 2). NiTAPc shows the best CO₂ adsorption ability (0.228 eV) in contrast to those of NiTHPc (0.22 eV) and NiPc (0.218 eV). To understand the CO₂RR performances of those molecule catalysts, the free energies of the CO₂RR pathway were calculated (Fig. 1d). The rate-determining step on all of the molecule catalysts is the step of CO₂ activation to *COOH. The substituted NiPc with an electron-donating substituent of hydroxyl or amino can lower the free energy of *COOH. NiTAPc with the lowest energy barrier for CO₂ activation manifests the rapid process for CO₂RR in comparison to the NiTHPc and NiPc. According to these theoretic results, the electron-donating substituent of hydroxyl or amino-modified NiPc can induce the electronic localization of Ni site and thus enhances CO₂ adsorption and activation to boost CO₂RR.

Molecule catalysts synthesis and characterization. To synthesize the proposed molecule catalysts, a facile solvothermal reaction was conducted by employing the substituted phthalonitrile and nickel acetate as the reactants (see Methods for details). Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) of as-prepared molecule catalysts (Fig. 2a) shows the mass

of molecule ion at 630 and 634 from NiTHPc and NiTAPc, respectively. This result confirms the successful synthesis of the substituted NiPc (Fig. 1a). Fourier transform infrared (FTIR) spectra (Fig. 2b and Supplementary Fig. 3) prove the presence of hydroxyl and amino in NiTHPc and NiTAPc, respectively, without a characteristic peak of phthalonitrile at around 2230 cm^{-1} . Ultraviolet-visible (UV-Vis) spectroscopy was used to characterize the NiPc, NiTHPc and NiTAPc owing to the special optical property of corresponding substituted NiPc. As shown in Fig. 2c, the substituted NiPc exhibits the characteristic Q band absorption at around 600–800 nm and B band absorption,³⁶ without the absorption of nickel acetate (Supplementary Fig. 4). Furthermore, the Q band absorption of $\pi\rightarrow\pi^*$ is attributed to the electron transition from the highest occupied molecule orbital (HOMO) to the lowest occupied molecule orbital (LOMO) of the phthalocyanine ring.³⁷ The Q band absorption without splitting indicates the symmetrical substituent position of the synthesized molecule.³⁸ There is a redshift in the Q band absorption among NiTHPc and NiTAPc due to the increased electron-donating ability of amino,^{39–41} which is highly matches the results of theoretic calculations (Supplementary Fig. 5). X-ray powder diffraction (XRD) patterns (Fig. 2d) show similar signal peaks of all samples below 10° , suggesting an analogous molecule structure of the fabricated samples. Raman spectra of NiPc, NiTHPc and NiTAPc (Supplementary Fig. 6) exhibit the same sensitive band at 1545 cm^{-1} , which can be caused by the Ni interaction with the phthalocyanine ring.^{42,43} Based on the above-mentioned results, we have demonstrated the successful preparation of the target molecule catalysts of NiTHPc and NiTAPc.

To further investigate the structure-dependent electronic effects of molecules, XPS and XAS were measured. From the XPS survey scan and N 1s spectra of NiPc, NiTHPc and NiTAPc in Supplementary Fig. 7 and Supplementary Note 1, the amino and hydroxyl are successfully substituted in NiTHPc and NiTAPc, respectively.²³ The C and N K-edge of molecules were measured (Supplementary Fig. 8 and Supplementary Note 2). The substituents have no measurable effects on the C K-edge spectra of the molecules. The N K-edge spectra of NiTHPc and NiTAPc can be greatly influenced by the electron-donating substituents. The Ni 2p spectra of NiPc, NiTHPc and NiTAPc (Fig. 3a) exhibit similar signal peaks, which can be indexed to the Ni confined to the ring of phthalocyanines. Noticeably, the binding energy of Ni 2p has a negative shift in NiTHPc and NiTAPc compared with that of the pristine NiPc. Accordingly, XAS spectra of Ni L-edge (Fig. 3b) also show a negative shift of absorption peaks at NiTHPc and NiTAPc in contrast to the counterpart of the pristine NiPc. NiTAPc displays a remarkable shift of absorption energy compared with that of NiTHPc owing to the preferable electron-donating ability of amino. To further confirm the electronic localization of the central Ni atom, X-ray absorption near-edge spectra (XANES) were conducted. XANES spectra of Ni K-edge (Fig. 3c) show a negative shift in NiTHPc and NiTAPc compared to that of the traditional NiPc, which demonstrates that the electron of phthalocyanine ligands could be localized on the Ni site by electron-donating substituents. NiTAPc shows the most apparent electronic localization among the NiPc-based molecules, in good agreement with the results of XPS and XAS of Ni L-edge. In addition, extended X-ray absorption fine structure (EXAFS) spectra of Ni K-edge (Fig. 3d) and the wavelet transform plot (Supplementary Fig. 9) demonstrate the same coordination number of Ni in those catalysts. Thus, the electronic localization on the Ni site is

derived from the peripheral substituents rather than the changed coordination number of Ni. These results indicate that the substituents of hydroxyl or amino with electron-donating ability can arouse the electronic localization on the central Ni atom of molecules, and the degree of electronic localization is positively correlated with the electron-donating ability of substituents.

To improve the conductivity of molecules for electrocatalytic CO₂RR, NiPc, NiTHPc and NiTAPc were dispersed onto carbon nanotube to form catalysts of NiPc/CNT, NiTHPc/CNT and NiTAPc/CNT. Scanning electron microscope (SEM) in Supplementary Fig. 10 and the elemental mapping (Supplementary Fig. 11) from high-angle annular dark field-scanning transmission electron microscope (HAADF-STEM) demonstrate that the molecules can be well dispersed by carbon nanotubes. The results of XRD and Raman from the composite catalysts (Supplementary Fig. 12) suggest the presence of carbon.⁴⁴ XANES spectra of Ni K-edge from molecule catalysts and its mixture with the conductive carbon (Supplementary Figs. 13a-c) indicate the stable electronic structure of Ni. Accordingly, EXAFS spectra of Ni K-edge (Supplementary Fig. 13d) manifest the NiPc-like structure of catalysts. It can be concluded that molecule catalysts are well dispersed onto carbon nanotubes, and they maintain the electronic structure of Ni sites in composite catalysts.

CO₂ adsorption measurements. To investigate the CO₂ adsorption ability of different molecule catalysts, the CO₂ adsorption measurement was performed (Supplementary Fig. 14) and normalized by the surface area from N₂ adsorption/desorption analysis (Supplementary Table 1). The pristine NiPc with the electron-deficient Ni site displays negligible CO₂ adsorption (Fig. 4a). On the other hand, NiTHPc and NiTAPc possess the electronic localization of Ni sites that are induced by the electron-donating substituents, and thus both show a significantly enhanced ability of CO₂ adsorption. NiTAPc shows the optimal CO₂ adsorption due to its conspicuous electronic localization among the three of NiPc-based catalysts. Furthermore, the CO₂ adsorption responses of NiPc/CNT, NiTHPc/CNT and NiTAPc/CNT were also explored (Supplementary Fig. 15). N₂ was used as the control gas to study the CO₂ adsorption responses. NiTAPc/CNT exhibits a remarkable response in the CO₂ atmosphere (Fig. 4b), outperforming the moderate response of NiTHPc/CNT and the inferior response of NiPc/CNT. These consequences indicate that the enhanced CO₂ adsorption is enabled by the electronic localization of Ni sites, in accordance well with the results of computational simulations.

CO₂RR performance. To evaluate the catalytic performance of developed catalysts, the electrochemical measurements were carried out in the typical H-cell. Linear sweep voltammetry (LSV) curves in the CO₂ and Ar-saturated 0.5 M KHCO₃ electrolyte (Supplementary Fig. 16) demonstrate the composite catalysts with apparent catalytic activities for CO₂RR. However, the blank carbon nanotube shows no activity for CO₂RR (Supplementary Fig. 17). Electrochemical active surface area (ECSA) measurements (Supplementary Fig. 18) indicate a similar active surface of composite catalysts. Therefore, the catalytic performance results from the intrinsic activity of molecule catalysts. From the LSV in the CO₂-saturated electrolyte (Fig. 3a), the amino-substituted NiPc with superior electronic localization of Ni site exhibits the

best performance of CO₂RR than those of other catalysts. The electron-donating substituents of hydroxyl and amino can greatly improve the catalytic activity of NiPc. To obtain the product distribution at different potentials of catalysts, chronoamperometry measurements (Supplementary Fig. 19) were carried out to detect the products of CO₂RR. Carbon monoxide (CO) can be detected as the only product from the results of gas chromatograph (Supplementary Fig. 20) and ¹HNMR spectroscopy (Supplementary Fig. 21). Fig. 3b shows the faradaic efficiency of CO (FE(CO)). As a byproduct of CO₂RR, the FE of hydrogen (H₂) is also displayed in Supplementary Fig. 22. It can be seen that the FE(CO) of catalysts maintain a level of above 90% in the potential range of 0.58–0.90 V. NiTHPc/CNT and NiTAPc/CNT demonstrates the enhanced selectivity of CO for CO₂RR in comparison to the NiPc/CNT, which can be attributed to electron-donating substituents induced electronic localization of Ni site. Although a high selectivity of CO in NiPc/CNT can be achieved, the stability (Fig. 3c) is much lower than those of NiTHPc/CNT and NiTAPc/CNT, undergoing a fast degradation during the continuous CO₂RR catalysis.

NiTAPc/CNT shows a high activity of -12.2 mA cm^{-2} at -0.58 V and remarkable CO selectivity of almost 100%, exceeding the other molecule catalysts and even the most performances of representative in literatures (Supplementary Table 2). The electrochemical impedance spectrum (EIS) was employed to explore the reaction dynamics of catalysts during CO₂RR. As exhibited in Fig. 3d, the charge transfer resistance of catalysts is ranked as the order: NiPc/CNT > NiTHPc/CNT > NiTAPc/CNT, which demonstrates the fastest reaction dynamics of NiTAPc/CNT. The substituted NiPc with electron-donating groups encourages the electronic localization of the Ni atom and therefore promotes CO₂RR performance in terms of activity, selectivity and stability.

To study CO₂RR performances at high current density, the composite molecule catalysts were supported on the gas diffusion layer (GDL) to form gas diffusion electrodes. In this way, a fast CO₂ diffusion can be obtained via the gas phase to the catalytic sites, which overcomes the limited mass transfer in H-cell. The schematic illustration of the flow cell is displayed in Supplementary Fig. 23. The pristine NiPc/CNT loaded on the GDL shows the stable CO₂RR performance from LSV measurements in CO₂, but this catalyst suffers from serious degeneration during LSV tests in the Ar without CO₂ atmosphere (Supplementary Fig. 24a). Furthermore, NiPc/CNT with adequate CO₂ in the flow cell displays a stable potential at a low current density of -60 mA cm^{-2} (Supplementary Fig. 24b). When the current density increased at -200 mA cm^{-2} , the performance of NiPc/CNT is dramatically declined due to limited CO₂ adsorption (Fig. 4a). Thus, the inferior stability of the pristine NiPc is rooted in the poor CO₂ adsorption of the active site. The GDL coated with NiTAPc/CNT or NiTHPc/CNT can be operated at the current densities from -20 to -500 mA cm^{-2} at applied potentials less than -0.80 V vs. RHE (Fig. 4a). An ultrahigh current density of -500 mA cm^{-2} can be obtained from NiTAPc/CNT with the FE(CO) of 94.6%. NiTAPc/CNT displays a remarkable performance with high FE(CO) > 99.8% between the current densities from -20 to -400 mA cm^{-2} (Fig. 4b), which is much better than the counterparts of other NiPc catalysts and even the reported catalysts (Supplementary Table 3). Accordingly, the turnover frequency of CO (TOF_{CO}) from

various catalysts (Fig. 6c) is calculated according to the results of inductively coupled plasma-optical emission spectrometry (ICP-OES) in Supplementary Table 4. The optimal catalyst of NiTAPc/CNT can achieve a remarkable TOF_{CO} of 41.9 s^{-1} , outperforming that of NiTHPc/CNT (28.0 s^{-1}) and NiPc/CNT (10.0 s^{-1}). To obtain the stability measurement of NiTAPc/CNT, the CO_2RR performance was conducted at -150 mA cm^{-2} . The catalysts can maintain 12,000 s with the selectivity of CO over 99.8% (Fig. 6d). On the basis of these electrochemical data, the NiTAPc/CNT delivers most superb performance for CO_2RR among the molecule catalysts.

To further verify the significance of the electronic localization of Ni site for CO_2RR , the tert-butyl, a typical electron-withdraw substituent in the phthalocyanine,^{29,45} to substituted NiPc (NiTBPc) was synthesized (Supplementary Fig. 25). MALDI-TOF MS spectrum, FTIR spectra, UV-Vis spectrum and Raman spectrum of NiTBPc (Supplementary Fig. 26) prove the successful preparation of NiTBPc. SEM and HAADF-STEM characterizations (Supplementary Fig. 27) suggest that NiTBPc can be well dispersed onto the carbon nanotubes. NiTBPc possesses an interior electron-withdraw ability of tert-butyl without an obvious shift in the binding energy of Ni 2p and the absorption energy of Ni L-edge (Supplementary Figs. 28a and b). However, XANES spectra of Ni K-edge in NiTBPc (Supplementary Fig. 28c) show a positive shift of near-edge absorption compared with that of NiPc, and this shift can be more obvious (Supplementary Fig. 28d) after dispersing the molecule catalysts onto carbon nanotubes, indicating that there is an electronic delocalization on the Ni site in NiTBPc/CNT when compare to NiPc/CNT. EXAFS spectrum and wavelet transform plot of NiTBPc (Supplementary Figs. 29) demonstrate the similar structures of NiPc. As expected, from the H-cell performance of CO_2RR , NiTBPc/CNT with poor stability exhibits low activity and selectivity in contrast to NiPc/CNT (Supplementary Fig. 30). In flow cell, the activity and selectivity of NiTBPc/CNT are lower than the counterparts of NiPc/CNT (Supplementary Fig. 31) due to its electron-withdraw substituent of tert-butyl. Thus, the electron-withdraw substituent that induces the electronic delocalization of Ni site can inhibit the catalytic activity of NiPc for CO_2RR . These conclusions further demonstrate that the electronic localization of the Ni site plays a significant role in boosting CO_2RR .

Discussion

In summary, we developed the electron-donating substituents induced electronic localization strategy to regulate the electronic density of the catalytic site in NiPc system. XPS and XAS results demonstrated the electronic localization of Ni site induced by tailoring the peripheral substituent of the phthalocyanine ring. When the electron-donating capabilities of substituents were increased, the electron of Ni in substituted NiPc became more localized than that of the pristine NiPc. The electron localized Ni site of NiPc helps to enhance CO_2 adsorption/activation and thus to improve the activity and stability of NiPc for CO_2RR . Conversely, the electron-withdraw substituent triggers the electronic delocalization of the Ni site, resulting in the worse performance for CO_2RR . NiTAPc/CNT with a significant electronic localization of the Ni site in GDL delivered an ultrahigh activity and selectivity, which achieved at 99.8% even at a high current density of -400 mA cm^{-2} . This work offered a new approach to tune electronic localization of catalytic

site for enhanced catalytic performances and it presented valuable guidance to develop efficient molecule catalysts for future electrochemical techniques.

Methods

Synthesis of substituted NiPc. 4 mmol of 4-Aminophthalonitrile and 1 mmol of nickel acetate tetrahydrate were dissolved into 30 mL of ethanol with the help of ultrasonic treatment. The reaction mixture was transferred into a 50 mL Teflon-lined stainless-steel autoclave and then heated at 160 °C for 6 h. The obtained sample was washed with hot ethanol and the 1 M hydrogen chloride solution for several times. After that, a black sample of NiTAPc was dried in a vacuum oven at 60 °C for 10 h. NiTHPc and NiTBPC were synthesized by employing 4-tert-Butylphthalonitrile and 4-Hydroxyphthalonitrile to replace 4-Aminophthalonitrile in a similar fashion, respectively.

Preparation of carbon nanotube supported molecule catalysts. NiPc was obtained from Alfa Aesar. Carbon nanotube (Tanfeng Tech. Inc.) was treated with the concentrated nitric acid at 90 °C overnight to remove the nickel nanoparticles. The purified carbon nanotube was obtained after washing with the water and drying at 60 °C for 12 h. Molecule catalysts (0.01 mmol) including the NiPc, NiTBPC, NiTHPc and NiTAPc were dispersed into 50 mL of DMF, respectively. The prepared suspension was sonicated for 30 min, and then 100 mg of purified carbon nanotube was added. The mixed suspension was further sonicated for another 30 min and stirred for 24 h at room temperature. Finally, the carbon nanotube supported molecule catalysts (NiPc/CNT, NiTBPC/CNT, NiTHPc/CNT and NiTAPc/CNT) was obtained by suction filtration and dried in a vacuum oven at 80 °C for 10 h.

Materials characterizations. UV-Vis spectra were measured by Shimadzu UV-2600. MALDI-TOF-MS of substituted NiPc were analyzed by AB SCIEX MALDI-TOF/TOF 5800. FTIR spectra were measured by Thermo iS50. Powder XRD patterns were carried out on a RIGAKU Rint-2000 X-ray diffractometer equipped with graphite monochromatized Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$). Raman spectra were performed by a Laser Micro-Raman Spectrometer (Renishaw InVia, UK). Inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out on PerkinElmer Optima 8300. The CO₂ adsorption and Brunauer–Emmett–Teller specific surface areas of samples were carried out by using Micromeritics ASAP 2020. XPS was tested by Thermo ESCALAB 250XI. SEM was conducted by TESCAN MAIA3. HAADF-STEM experiments were conducted on a Cs-corrected FEI Titan Cube transmission electron microscope at an acceleration voltage of 300 kV.

Electrochemical measurements. All the electrochemical tests were implemented on an electrochemical station of Auto Lab at room temperature.

In the H-type cell, two chambers were separated by the proton exchange membrane of Nafion 117. The three-electrode system consisted of a modified carbon paper (Toray, TGP-H-060) as a working electrode, a platinum plate as a counter electrode and an Ag/AgCl filled with saturated KCl electrode as a reference electrode. To prepare the working electrode, 4 mg of catalyst was dispersed into 1 mL of aqueous alcohol

(50 vol%) and 60 μL of Nafion (5 wt%) was employed as the binder. The prepared ink was dropped onto carbon paper with a loading of 0.4 mg cm^{-2} . The 0.5 M KHCO_3 saturated with high-purity CO_2 (99.999%) was used as the electrolyte for electrocatalytic CO_2 reduction. The flow rate of high-purity CO_2 was set at 20 sccm. The potentials in H-cell were transformed to the RHE with iR compensations by the equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0592 \times \text{PH} + 0.197 - iR_u \quad (1)$$

where i is the current and R_u is the solution resistance.

The products of CO_2 RR in cathodic were analyzed by an on-line gas chromatograph (Shimadzu, 2014C) and ^1H NMR. High-purity N_2 (99.999%) was used as the carrier gas. A thermal conductivity detector was employed to measure the H_2 fraction and a flame ionization detector was equipped with a nickel conversion furnace to analyze the CO fraction. The faradaic efficiency of products was calculated from gas chromatograph chromatogram peak according to the flowing equation:

$$FE_{\text{CO or H}_2} = x \times V \times \frac{2FP_0}{iRT} \quad (2)$$

where x is the fraction, V is the flow rate of CO_2 , F is faraday constant (96485 C mol^{-1}), P_0 is the normal atmosphere (101325 Pa), i is the applied current, R is the gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) and T is the room temperature (298 K).

The flow cell measurements were performed on a home-made cell including sandwich of flow frames, gaskets and an anion-exchange membrane (Selemion DSVN). The window for electrolysis is set at 0.52 cm^2 . 6 mg of carbon nanotube supported molecule catalysts can be dispersed into 2 mL ethanol with 100 μL of Nafion (5 wt%), forming a homogenous suspension. A 13 cm^2 gas diffusion layer (GDL, SGL29BC) with a catalyst loading of 1 mg cm^{-2} was used as the working electrode, The IrO_2 -coating titanium sheet was employed as the counter electrode and an Ag/AgCl (with saturated KCl) electrode as a reference electrode. The flow rate of the electrolyte (1 M KHCO_3) was set at 10 mL min^{-1} in both of cathodic and anodic chambers. The potentials in flow-cell were transformed to the RHE with iR compensations (resistance of $\sim 4 \Omega$).

Computational methods. All density functional theory calculations on nickel phthalocyanines in this work were conducted by using the Gaussian 09 program.⁴⁶ A PBE0 functional with D3 correction (Becke–Johnson damping) was employed for the dispersion and robustness corrections,⁴⁷ which can achieve the proper function to investigate the reactions of transition nickel complexes. The double- ξ valence basis set and Stuttgart–Dresden pseudopotential were used for nickel atom. The all-electron 6–31G* basis set was used for the other elements (C, H, O, N).^{48–50} The geometry optimization and frequencies calculations

were performed. Kohn–Sham molecular orbital analysis and atomic charge analysis by Mulliken atom population and Hirshfeld atomic charge were carried out via using Multiwfn 3.8 software.⁵¹⁻⁵⁴ The 3D models of all the reaction intermediates were visualized by using the VMD 1.9 program.⁵⁵

The pathways for reduction of CO₂ into CO are listed as the following elementary steps:

where * is the active site of the catalyst surface and * and * were two key intermediates during CO₂RR. The computational hydrogen electrode (CHE) model was used to describe the free energy of proton-electron pairs in the proton-electron transfer steps by using the free energy of hydrogen at the potential of 0 V. The effect of applied bias on a proton-electron transfer step is represented by adding a $-eU$ term to the standard .

Declarations

Data availability

The data that support the findings of this study are available from the corresponding author on reasonable request.

Acknowledgements

The authors gratefully thank the International Science and Technology Cooperation Program (Grant No. 2017YFE0127800 and 2018YFE0203400), Natural Science Foundation of China (Grant No. 21872174 and U1932148), Hunan Provincial Science and Technology Program (No.2017XK2026), Shenzhen Science and Technology Innovation Project (Grant No. JCYJ20180307151313532). Natural Science Foundation of Education Department of Guizhou Province ([2016]110, [2015]342).

Author contributions

M.L., and H.M. L. conceived the project; K. C. and M. L. designed the experiments and analyzed the results. K. C., H.X. L., B. Y., G. C. and Y. Z. synthesized the samples and performed the electrochemical experiments and analyzed the results. M. C., J. F., and K. L. carried out the simulations and wrote the corresponding section. Y. L., X. Z., M. S., Q. X., Y. H. and J. L. conducted the XAS measurements. F. X., J. H., X.Q. and J. F. carried out the electron microscope measurements. All authors read and commented on the manuscript.

Competing interests

The authors declare no competing interests.

References

1. Gu, J., Hsu, C.-S., Bai, L., Chen, H.M. & Hu, X. Atomically dispersed Fe^{3+} sites catalyze efficient CO_2 electroreduction to CO. *Science* **364**, 1091-1094 (2019).
2. Ma, W., *et al.* Electrocatalytic reduction of CO_2 to ethylene and ethanol through hydrogen-assisted C–C coupling over fluorine-modified copper. *Nat. Catal.*, 1-10 (2020).
3. Zheng, T., *et al.* Large-scale and highly selective CO_2 electrocatalytic reduction on nickel single-atom catalyst. *Joule* **3**, 265-278 (2019).
4. Liu, M., *et al.* Enhanced electrocatalytic CO_2 reduction via field-induced reagent concentration. *Nature* **537**, 382-386 (2016).
5. Lin, L., *et al.* Synergistic Catalysis over Iron-Nitrogen Sites Anchored with Cobalt Phthalocyanine for Efficient CO_2 Electroreduction. *Adv. Mater.* **31**, 1903470 (2019).
6. Yang, H.B., *et al.* Atomically dispersed Ni (I) as the active site for electrochemical CO_2 reduction. *Nat. Energy* **3**, 140-147 (2018).
7. Fu, J., *et al.* Graphitic carbon nitride based single-atom photocatalysts. *Front. Phys.* **15**, 33201 (2020).
8. Lv, F., *et al.* Transition metal macrocycles for heterogeneous electrochemical CO_2 reduction. *Coord. Chem. Rev.* **422**, 213435 (2020).
9. Ren, S., *et al.* Molecular electrocatalysts can mediate fast, selective CO_2 reduction in a flow cell. *Science* **365**, 367-369 (2019).
10. Zhu, M., Ye, R., Jin, K., Lazouski, N. & Manthiram, K. Elucidating the Reactivity and Mechanism of CO_2 Electroreduction at Highly Dispersed Cobalt Phthalocyanine. *ACS Energy Lett.* **3**, 1381-1386 (2018).
11. Wang, M., *et al.* CO_2 electrochemical catalytic reduction with a highly active cobalt phthalocyanine. *Nat. Commun.* **10**, 1-8 (2019).
12. Zhu, M., *et al.* Cobalt phthalocyanine coordinated to pyridine-functionalized carbon nanotubes with enhanced CO_2 electroreduction. *Appl. Catal. B. Environ.* **251**, 112-118 (2019).
13. Wu, Y., Jiang, Z., Lu, X., Liang, Y. & Wang, H. Domino electroreduction of CO_2 to methanol on a molecular catalyst. *Nature* **575**, 639-642 (2019).
14. Gounden, D., Nombona, N. & van Zyl, W.E. Recent advances in phthalocyanines for chemical sensor, non-linear optics (NLO) and energy storage applications. *Coord. Chem. Rev.* **420**, 213359 (2020).
15. Chen, K., *et al.* Iron phthalocyanine with coordination induced electronic localization to boost oxygen reduction reaction. *Nat. Commun.* **11**, 1-8 (2020).

16. Zhang, X., *et al.* Molecular engineering of dispersed nickel phthalocyanines on carbon nanotubes for selective CO₂ reduction. *Nat. Energy* **5**, 684-692 (2020).
17. Pan, Y., *et al.* Design of single-atom Co–N₅ catalytic site: a robust electrocatalyst for CO₂ reduction with nearly 100% CO selectivity and remarkable stability. *J. Am. Chem. Soc.* **140**, 4218-4221 (2018).
18. Jiang, Z., *et al.* Revealing the hidden performance of metal phthalocyanines for CO₂ reduction electrocatalysis by hybridization with carbon nanotubes. *Nano Res.* **12**, 2330-2334 (2019).
19. Zhang, Z., *et al.* Reaction Mechanisms of Well-Defined Metal–N₄ Sites in Electrocatalytic CO₂ Reduction. *Angew. Chem. Int. Ed.* **57**, 16339-16342 (2018).
20. Yang, X., Cheng, J., Xuan, X., Liu, N. & Liu, J. Boosting Defective Carbon by Anchoring Well-Defined Atomically Dispersed Ni–N₄ Sites for Electrocatalytic CO₂ Reduction. *ACS Sustain. Chem. Eng.* **8**, 10536-10543 (2020).
21. Ma, D.-D., *et al.* Remarkable electrocatalytic CO₂ reduction with ultrahigh CO/H₂ ratio over single-molecularly immobilized pyrrolidinonyl nickel phthalocyanine. *Appl. Catal. B Environ.* **264**, 118530 (2020).
22. Zhang, J., Yin, R., Shao, Q., Zhu, T. & Huang, X. Oxygen Vacancies in Amorphous InO_x Nanoribbons Enhance CO₂ Adsorption and Activation for CO₂ Electroreduction. *Angew. Chem. Int. Ed.* **58**, 5609-5613 (2019).
23. Fu, J., *et al.* Graphitic carbon nitride with dopant induced charge localization for enhanced photoreduction of CO₂ to CH₄. *Adv. Sci.* **6**, 1900796 (2019).
24. Dong, H., *et al.* Abundant Ce³⁺ Ions in Au-CeO_x Nanosheets to Enhance CO₂ Electroreduction Performance. *Small* **15**, 1900289 (2019).
25. Gao, S., *et al.* Atomic layer confined vacancies for atomic-level insights into carbon dioxide electroreduction. *Nat. Commun.* **8**, 1-9 (2017).
26. Zhou, Y., *et al.* Dopant-induced electron localization drives CO₂ reduction to C₂ hydrocarbons. *Nat. Chem* **10**, 974-980 (2018).
27. Corbin, N., Zeng, J., Williams, K. & Manthiram, K. Heterogeneous molecular catalysts for electrocatalytic CO₂ reduction. *Nano Res.* **12**, 2093-2125 (2019).
28. Henari, F., Davey, A., Blau, W., Haisch, P. & Hanack, M. The electronic and non-linear optical properties of oxo-titanium phthalocyanines. *J. Porphyrins Phthalocyanines* **3**, 331-338 (1999).
29. Li, R., *et al.* Electron-Donating or -Withdrawing Nature of Substituents Revealed by the Electrochemistry of Metal-Free Phthalocyanines. *Inorg. Chem.* **45**, 2327-2334 (2006).
30. Boutin, E., *et al.* Molecular catalysis of CO₂ reduction: recent advances and perspectives in electrochemical and light-driven processes with selected Fe, Ni and Co aza macrocyclic and polypyridine complexes. *Chem. Soc. Rev.* **49**, 5772-5809 (2020).
31. Zhang, X., Chen, S., Han, Q. & Ding, M. Preparation and retention mechanism study of graphene and graphene oxide bonded silica microspheres as stationary phases for high performance liquid

- chromatography. *J. Chromatogr. A* **1307**, 135-143 (2013).
32. Arokiyanathan, A.L. & Lakshmipathi, S. Impact of functional groups substitution on the molecular properties of magnesium and scandium phthalocyanines. *Inorg. Chim. Acta* **483**, 203-210 (2018).
 33. Zegkinoglou, I., *et al.* Spectroscopy of Donor- π -Acceptor Porphyrins for Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **117**, 13357-13364 (2013).
 34. Liu, S., *et al.* Elucidating the Electrocatalytic CO₂ Reduction Reaction over a Model Single-Atom Nickel Catalyst. *Angew. Chem. Int. Ed.* **59**, 798-803 (2020).
 35. Zhang, T., *et al.* Atomically Dispersed Nickel(I) on an Alloy-Encapsulated Nitrogen-Doped Carbon Nanotube Array for High-Performance Electrochemical CO₂ Reduction Reaction. *Angew. Chem. Int. Ed.* **59**, 12055-12061 (2020).
 36. Peng, J., *et al.* The synthesis of graphene oxide covalently linked with nickel tetraamino phthalocyanine: A photoelectrochemical sensor for the analysis of rifampicin irradiated with blue light. *J. Chin. Chem. Soc.* **66**, 1311-1317 (2019).
 37. Ağırtaş, M.S. Highly soluble phthalocyanines with hexadeca tert-butyl substituents. *Dyes Pigments* **79**, 247-251 (2008).
 38. Zhang, L., Qi, D., Zhao, L., Bian, Y. & Li, W. Substituent effects on the structure–property relationship of unsymmetrical methyloxy and methoxycarbonyl phthalocyanines: DFT and TDDFT theoretical studies. *J. Mol. Graph. Model.* **35**, 57-65 (2012).
 39. Lokesh, K.S. & Adriaens, A. Synthesis and characterization of tetra-substituted palladium phthalocyanine complexes. *Dyes Pigments* **96**, 269-277 (2013).
 40. Liu, Y. & McCrory, C.C. Modulating the mechanism of electrocatalytic CO₂ reduction by cobalt phthalocyanine through polymer coordination and encapsulation. *Nat. Commun.* **10**, 1-10 (2019).
 41. Nyokong, T. Electronic spectral and electrochemical behavior of near infrared absorbing metallophthalocyanines. in *Functional Phthalocyanine Molecular Materials* 45-87 (Springer, 2010).
 42. Khene, S., Lobb, K. & Nyokong, T. Characterization of nickel tetrahydroxy phthalocyanine complexes and the electrocatalytic oxidation of 4-chlorophenol: Correlation of theory with experiments. *Inorg. Chim. Acta* **362**, 5055-5063 (2009).
 43. Madhuri, K.P. & John, N.S. Supercapacitor application of nickel phthalocyanine nanofibres and its composite with reduced graphene oxide. *Appl. Surf. Sci.* **449**, 528-536 (2018).
 44. Chen, K., *et al.* Untying thioether bond structures enabled by “voltage-scissors” for stable room temperature sodium–sulfur batteries. *Nanoscale* **11**, 5967-5973 (2019).
 45. Brauman, J.I. & Blair, L.K. Gas-phase acidities of alcohols. Effects of alkyl groups. *J. Am. Chem. Soc.* **90**, 6561-6562 (1968).
 46. Frisch, M. J. *et al.* Gaussian 09 (Gaussian, 2009).
 47. Adamo, C. & Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **110**, 6158-6170 (1999).

48. Hariharan, P.C. & Pople, J.A. The influence of polarization functions on molecular orbital hydrogenation energies. *Theoretica chimica acta* **28**, 213-222 (1973).
49. Gordon, M.S. The isomers of silacyclopropane. *Chem. Phys. Lett.* **76**, 163-168 (1980).
50. Binning Jr, R.C. & Curtiss, L.A. Compact contracted basis sets for third-row atoms: Ga–Kr. *J. Comput. Chem.* **11**, 1206-1216 (1990).
51. Hirshfeld, F.L. Bonded-atom fragments for describing molecular charge densities. *Theoretica chimica acta* **44**, 129-138 (1977).
52. Tian, L. & Feiwu, C. Calculation of molecular orbital composition. *Acta Chim. Sinica* **69**, 2393–2406 (2011).
53. Mayer, I. Charge, bond order and valence in the AB initio SCF theory. *Chem. Phys. Lett.* **97**, 270-274 (1983).
54. Lu, T. & Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **33**, 580-592 (2012).
55. Buck, D. & Collins, A. Persistence of Vision Raytracer 3.6 (Persistence of Vision, 2004).

Figures

Figure 1

Theoretic calculations. a Molecular structure models. b Hirshfeld and Mulliken charge of Ni atom in NiPc, NiTHPc and NiTAPc. c The CO₂ adsorption energies of NiPc, NiTHPc and NiTAPc. d Free energy diagrams of NiPc, NiTHPc and NiTAPc for CO₂RR at -0.11 V versus reversible hydrogen electrode (RHE).

Figure 2

Characterizations of NiPc, NiTHPc and NiTAPc. a MALDI-TOF MS spectra. b FTIR spectra. c UV-Vis spectra in dimethyl formamide. d XRD patterns.

Figure 3

Electronic localization characterizations. a High-resolution XPS of Ni 2p spectra. b XAS spectra of Ni L-edge. c XANES spectra of Ni K-edge. d EXAFS spectra of Ni K-edge.

Figure 4

CO₂ adsorption ability. a The CO₂ adsorption isotherms of NiPc, NiTHPc and NiTAPc normalized by the surface area from the N₂ adsorption/desorption analysis. b The CO₂ adsorption responses of NiPc/CNT, NiTHPc/CNT and NiTAPc/CNT at varied potential.

Figure 5

CO₂RR performance of catalysts in H-cell. a LSV profiles in 0.5 M CO₂-saturated KHCO₃ electrolyte. b FE(CO) of catalysts at different potentials. c Chronoamperometry of NiPc/CNT at -0.68 V, NiTHPc/CNT at -0.61 V and NiTAPc/CNT at -0.58 V. d EIS spectra of catalysts at applied potential of 0.6 V vs. RHE.

Figure 6

CO₂RR performance of catalysts in GDL. a Current densities of NiPc/CNT, NiTHPc/CNT and NiTAPc/CNT at different potentials in 1 M KHCO₃ electrolyte. b FE(CO) of NiPc/CNT, NiTHPc/CNT and NiTAPc/CNT. c TOFCO comparison of different catalysts. d The CO₂RR electrolysis at the current density of -150 mA cm⁻².

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupplementaryInformation.docx](#)