Design of a Graphene Nitrene Two-Dimensional Catalyst Heterostructure Providing a Well-Defined Site Accommodating 1 to 3 Metals, with Application to CO₂ Reduction Electrocatalysis for the 2 Metal Case

Shiqian Chen, Hao Yuan, Sergey I Morozov, Lei Ge, Li Li, Lai Xu, and William A. Goddard

J. Phys. Chem. Lett., **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcllett.0c00642 • Publication Date (Web): 12 Mar 2020

Downloaded from pubs.acs.org on March 13, 2020

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

Design of a Graphene Nitrene Two-Dimensional Catalyst Heterostructure Providing a Well-Defined Site Accommodating 1 to 3 Metals, with Application to CO₂ Reduction Electrocatalysis for the 2 Metal Case

Shiqian Chen^{#, †}, Hao Yuan^{#, †}, Sergey I. Morozov[‡], Lei Ge[†], Li Li[†], Lai Xu^{*, †}, and William A. Goddard III^{*, §}

[†] Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou, 215123, China

[‡] Department of Physics of Nanoscale systems, South Ural State University, 76 prospect Lenina, Chelyabinsk 454080, Russia

[§] Materials and Process Simulation Center (MSC), California Institute of Technology (Caltech), Pasadena, California 91125, United States

[#] Contributed equally to this work

AUTHOR INFORMATION

Corresponding Author

*E-mail: xulai15@suda.edu.cn (L. X.). ORCID: 0000-0003-2473-3359

*E-mail: wag@caltech.edu (W. A. G.). ORCID:0000-0003-0097-5716

ABSTRACT Recently, CO₂ reduction to fuels has been the subject of great much numerous studies, but selectivity and activity remain inadequate. Progress has been made on single site two-dimensional catalysts based on graphene coupled to a metal and nitrogen for CO₂RR but the product is usually CO and the metal-N environment remains ambiguous. We report a novel 2D graphene-nitrene heterostructure (grafiN₆) providing well-defined active sites (N₆) that can bind 1 to 3 metals for CO₂RR. We find that homo-bimetallic FeFe-grafiN₆ could reduce CO₂ to CH₄ at -0.61 V and to CH₃CH₂OH at -0.68 V vs RHE, with high product selectivity. Moreover, the heteronuclear FeCu-grafiN₆ system may be significantly less affected by HER, while maintaining low limiting potential (-0.68 V) for C1 and C2 mechanisms. Binding metals to one N₆ site but not the other could promote efficient electron transport facilitating some reaction steps. This framework for single multiple metal sites might also provide unique catalytic sites for other catalytic process.

TOC GRAPHICS

The energy crisis looms as an ever-growing threat to continued development and prosperity. In particular excessive consumption of fossil fuels continues to produce huge amounts of carbon dioxide, leading to severe greenhouse effects expected to double current levels by the 2050's,^{1,2} making it urgent to find efficient ways to reduce CO₂ levels. Thus, great efforts are being made to convert carbon dioxide into organic fuels to help to alleviate these greenhouse effects while providing new energy sources.^{3–7} Many catalysts^{3,8–16} have been tested for the CO₂ reduction reaction (CO₂RR) including biocatalysts,¹⁷ electrocatalysts,¹⁸ photocatalysts, and thermochemical catalysts.^{19,20} However, existing CO₂RR catalysts lack satisfactory selectivity or activity.

Electrocatalytic CO₂RR provides both simple operation and low cost. Moreover, the electrocatalytic process can be tuned by adjusting such parameters as electrolyte and applied potential. Existing CO₂RR catalysts suffer from low selectivity, large overpotentials, and low exchange current densities which makes it important to design new CO₂RR electrocatalysts with high selectivity and low overpotential for efficient catalysis while providing high charge transfer efficiency for conductivity.

The best metal for CO₂RR reduction to C1 or C2 organics is bulk Cu metal, but the interaction with CO₂ is weak, which leads to a decrease in the activity of catalyzing CO₂^{21–23}, but the selectivity and activity is not adequate. Reducing the size of the catalyst to a monoatomic dispersion can make full use of metal atoms while improve catalytic selectivity and activity.²⁴ Two-dimensional carbon-based materials can provide unique electronic structure and impressive physical and chemical properties²⁵ with broad application prospects for electrocatalysis based on well-defined metal atom sites.

Recently, many demonstrations of improved catalytic performance have been achieved using transition metal atom doping of 2D graphene derived structures.^{24,26–30} In particular, the catalytic mechanism of Fe species on N-doped carbon was studied by operando spectroscopy. Genovese et al.²⁹ found that the N-Fe (II) site is a monoatomic or polyatomic species that can convert CO₂ to CH₃COOH. Ju et al.³¹ performed experiment to show that metal(X)-CN materials can be used for CO₂RR reduction and used theory to explain the results. In particular, Mn-CN and Fe-CN was found to produce CH₄. It is believed that this may be due to the strong CO adsorption of Mn-CN and Fe-CN so that it can be further hydrogenated.

In addition to the common single metal catalysis, Warner et al.³² successfully prepared graphene-loaded Fe₂ dimers to illustrate the possibility of bimetallic doping of carbon-based materials. This provides more possibilities to design new catalysts.

Most existing researches on two-dimensional catalysts focused on g-C₃N₄ or a nitrogen doped graphene as a substrate. Few studies reported on carbon nitride composite materials as substrates. Qin et al.³³ found that C₃N can be effectively used for CO₂ capture and Cui et al.³⁴ believed that pyridine nitrogen and graphite nitrogen in carbon nitride materials can effectively convert CO₂ to CO.

We propose here the design of a novel two-dimensional graphene-nitrene heterostructure (grafiN₆) aimed at providing well defined active sites that can bind 1 to 3 metals to enable selective catalysis to specific products. Conceptually our grafiN₆ catalyst can be thought as a heterojunction between the C₂N and C₃N two-dimensional (2D) materials. The grafiN₆ structure has a high concentration of isolated sites, each providing a hexagonal cavity with six sp² N atoms available to bond two metals. Since our grafiN₆ heterostructure is conceptually similar to the C-ring-C₃N₄ heterostructure prepared experimentally by Che et al.,³⁵ we expect that preparation of the grafiN₆ heterostructure is feasible. C₂N is a semiconductor,³⁶ (Figure S1) and we predict that C₂N-C₃N becomes a conductor after forming a heterojunction. Thus grafiN₆ provides a continuous electrically conductive surface ideal for electrocatalysis. Indeed the heterostructure might improve charge transport efficiency.³⁷

We considered 15 pairwise combinations of 5 metals to predict that the best two for CO₂RR are FeFe-grafiN₆ and FeCu-grafiN₆. The FeFe-grafiN₆ could produce C1 products at -0.61 V vs RHE, and C2 products such as ethanol and ethane at -0.68 V vs RHE. Moreover, FeCu-grafiN₆ might greatly reduce the competing HER. Due to the different affinities of Fe and Cu for O, the Fe-Cu system may prefer to follow the formate reaction path that generates C1 and C2 products at a limiting potential of -0.68 V. Depending on the application, selectively producing C1 or C2 products are both important.

In this paper, we deployed the spin-polarized density functional theory (DFT) as implemented in the Vienna Ab-initio Simulation Package (VASP) software to optimize the structures of these two dimensional catalysts and to calculate electronic properties.³⁸ We used the Perdew-Burke-Ernzerhof (PBE) flavor of the GGA Exchange-correlation energy, with the van der Waals interaction between atoms corrected using D₃.³⁹ We set the plane-wave cut-off energy at 450 eV. We used 10⁻⁵ eV as the convergence criterion for electronic structure iterations and 0.05 eV/Å as the convergence criteria for force on each atom. Based on the lattice parameter, the K point grid was set to 2 × 5 × 1. We corrected for solvation by water using the VASPsol model as compiled by Mathew and Henning for solvation correction.^{40,41}

The adsorption energy $\Delta E_{\text{ads(A)}}$ was calculated by the following equation:

$$\Delta E_{\text{ads(A)}} = E_{\text{(A-S)}} - E_{\text{S}} - E_{\text{A}}$$

where $E_{\text{(A-S)}}$, E_{S} and E_{A} are the total energy of the adsorbate- substrate (A-S), the substrate (S) and the adsorbate (A), respectively. Free energies of each state were obtained by:⁴²

$$\Delta G = \Delta E + \text{ZPE} - T\Delta S + \Delta G_{\text{pH}} + \Delta G_{\text{U}},$$

where zero-point energies (ZPE) and entropy corrections ($T\Delta S$) were calculated based on vibration analysis obtained by standard methods. All free energies are at 298.15 K. ΔG_{pH} represents the influence of the pH of the solution on the Gibbs free energy and $\Delta G_{\text{pH}} = 2.303 \cdot k_{\text{B}} T \cdot \text{pH}$. In this work, we assume that the reaction is in an acidic medium with pH = 0. $\Delta G_{\text{U}} = -neU$, where n is the number of electrons transferred, e is the amount of charge and U is the applied potential. For the full reaction path study, we used the computational hydrogen electrode (CHE) method⁴³ based on:

$U_L = -\Delta G_{\max} / ne$, where $\Delta G_{\max}$ is the free energy difference of the rate-determining step, U_L is the limiting potential.

For QM based MD calculations (AIMD), we use the PBE-D3 flavor of DFT, including the D3 empirical London Dispersion terms. The energy cutoff for the plane-wave basis expansion was chosen at 500 eV, which was verified to provide converged forces by a test calculation using 600 eV. For the bulk Brillouin zone integration, a Γ -centered k-point mesh was used in all DFT-MD simulations within the supercell. A conjugate gradient algorithm was employed to relax the ion positions to obtain initial optimized structures. The initial velocities to start the DFT-MD were chosen from the Maxwell-Boltzmann distribution with a temperature of 20 K. The temperature during DFT-MD was maintained using the Nose-Hoover thermostat. We increased the temperature from 20 to 1000 K within 10 ps, then decreased it to 300 K within 7 ps, and finally kept the temperature constant at 300 K within 3 ps. The integration time step was 1 fs. Our results were visualized with the help of OVITO.⁴⁴

Structural Characteristics of Bimetal-doped GrafiN₆ The structure of grafiN₆ is shown in Figure 1a. Its design is based on discussions in Xu et al.,³⁷ in which the C₂N unit and the C₃N unit are connected by π -conjugated interactions. The rectangular unit cell contains 36 C atoms and 16 N atoms with two N₆ sites for binding metals.

Preliminary Screening of the Catalyst and Initial Activation of Carbon Dioxide To rationally design the transition metal doped grafiN₆ heterostructures, we selected five common metal elements (Fe, Co, Ni, Cu, Pd) and paired them into 15 systems in one N₆ site of the grafiN₆ framework as shown in Figure 1b. First we tested the CO₂ adsorption step including both physisorption as linear CO₂ and chemisorption as bent CO₂⁻⁴⁵ on the grafiN₆ framework (See the supporting information for the specific process in Figure S2 and Figure S3.) We found that the main active site in the catalyst is the bimetal with the chemisorption mode favorable for further catalysis. Since HER is the main competing reaction, we screened these 15 systems by comparing CO₂RR and HER catalytic performance and selectivity based on the screening standard proposed by Yang et al.⁴⁶⁻⁴⁸ that the smaller the ΔG of the first step of CO₂RR is, the more favorable the CO₂RR is to occur over HER. Figure 1c shows that the reaction free energy of CO₂ reduction to COOH* in the Fe-Fe system is slightly higher than that of HER. Furthermore, we found that for the Fe-Fe and Fe-Cu systems, the initial CO₂ adsorption is -0.46 eV and -0.93 eV, respectively, while the corresponding HER adsorption energies are -0.68 eV and 0.04 eV, respectively. According to the research of Wang et al.,⁴⁹ if CO₂ adsorption is strong enough, it can occupy the reaction site to keep H from binding, thereby avoiding the HER reaction. The adsorption of CO₂ for the Fe-Cu system is stronger than that of H; while for the Fe-Fe system, the adsorptions of CO₂ and H are close. Therefore, Fe-Cu has likely better CRR selectivity than Fe-Fe. However, other experimental factors including pH, CO₂ partial pressure, and temperature must be considered to predict the HER side reaction.⁵⁰ Therefore, the competing HER process has likely little effect on the Fe-Fe and Fe-Cu systems under experimental conditions. Consequently, we selected these two systems for further calculations.

Figure 1. (a) Conceptual synthesis of the grafiN₆ heterostructure from C₂N and C₃N. (b) Top view and side view of bimetallic FeFe-grafiN₆ heterojunction. (c) The Gibbs free energy changes for the first step of CO₂RR: $\text{CO}_2 \rightarrow \text{COOH}^*$ or HCOO^* compared with the hydrogen evolution reaction (ΔG_{H^*})

We used QM to calculate the Bader charge of the metal atoms, the grafiN₆ substrate, and the CO₂ in both systems with and without CO₂ adsorption. The changes in the charges upon CO₂ absorption are shown in Figure S4. For FeFe-grafiN₆, the bent CO₂⁻ molecule receives 0.714 |e| after being adsorbed onto the metal atom, where the metal atoms provide 0.309 |e| and the substrate provides 0.405 |e|. For FeCu-grafiN₆, the bent CO₂⁻ molecule receives 0.679 |e|, where the metal contributes 0.355 |e| and the substrate charge provides 0.324 |e|. These results demonstrate that grafiN₆ aids the metal in the initial capture of CO₂, indicating synergy with the bimetals in promoting CO₂ activation.

QM MD (AIMD) Validation of the Structural Stability of the New Bimetallic Doped GrafiN₆ Catalysts From the QM MD results shown in Videos S1-S6, we see that the metal atoms fluctuate at higher temperatures, but remain strong bonding. Upon heating from 20 K to 1000K over 10 ps, the two Fe of the Fe-Fe system fluctuate from bonding to pairs of N on opposite sides of the N₆ binding site (Figure S5a and Figure S6abcd) to occasionally having one Fe bonded to only one N (Figure S5b and Figure S6e) and sometimes having each Fe bonded to two N but with all four N sequential. At higher temperature there are dramatic motions of the grafiN₆ plane but the overall structure remains stable. After cooling to 300 K over 7 ps and holding for 3 ps, the two Fe of the Fe-Fe system fluctuate from bonding to pairs of N on opposite sides of the 6N binding site at the higher temperatures as in Figure S7bcd, to occasionally having one Fe bonded to only one N as in Figure S7a and other structures with each Fe bonded to two N but with all four N sequential.

For the Fe-Cu system, the bonding to the Cu fluctuates at the higher temperatures from bonding to pairs of N on opposite sides of the N₆ binding site (Figure S5d and Figure S8abcd) to occasionally having Cu bonding to only one N as in Figure S5e and Figure S8e. For Fe-Cu system, at higher temperatures the Cu can fluctuate from bonding to a pair of N on opposite sides of the 6N binding site to the Fe as in Figure S9abc to occasionally having one Cu bonded to only N.

In summary, the grafiN₆ design gives a very stable platform for designing new single site catalysts with 2 metals in the 6N binding site. The structural fluctuations in the range of 300 to 500K might promote unique catalytic properties.

Figure 2. The Gibbs free energy changes for CO₂ reduction to CH₃OH (blue) and CH₄ (red) for (a) FeFe-grafiN₆ and (b) FeCu-grafiN₆. The red line is the best overall reaction path for generating CH₄, and the blue line is the best overall reaction path for generating CH₃OH. (The specific values of each step of the reaction are shown in Table S4.)

C1 Reaction Path We adopted the well-established CO₂ reduction reaction path towards C1 products^{13,51} to obtain the reaction free energy for both systems as shown in Figure 2. Based on previous studies,⁵¹ the hydrogenation of CO₂ to generate the *OCOH or *HC(O)O intermediates is usually the first step of CO₂RR. For the Fe-Fe system, the *HC(O)O intermediate is more stable which may be because the electron affinity of O atom is greater than C atom and in turn is greater than for Cu or Fe so the two O atoms of the *HC(O)O intermediate adsorb more tightly on the two metal atoms, as shown in Figure S10. However, further protonation of *HC(O)O to form formate, *HC(O)OH, is endoergic by 0.88 eV which may be because the strong binding of O to Fe hinders hydrogenation of O. While the reduction of *OCOH to *CO plus one molecule of water remains exothermic. Therefore, the FeFe-grafiN₆ system is more suitable for the C1 reaction along the *OCOH path to form *CO (Figure 2). According to Asthagiri et al.,⁴⁷ the next protonation step to form *CHO/*COH is the most important step in the reaction process, with free energy increases of 0.55 eV and 0.43 eV, respectively. Both intermediates are further reduced to *HCOH (Figure 3) with a free energy increase of 0.40 eV and 0.52 eV, respectively. Methanol is produced after two additional exothermic steps. However, the *CH₃OH (Figure 3) is bound to the site so strongly, an adsorption energy of -1.16 eV (Table S5), that catalysis may terminate at this step. Methane can also be generated along the *HCOH path, but the final step of *CH₃ + H⁺ → *CH₄ is endothermic by 0.93 eV, making it unfavorable.

Figure 3. Some reaction pathways for CO₂ reduction to C1 and C2 products with the Gibbs free energy changes for FeFe-grafinN₆. (The energy in the figure is the free energy difference of each step, red represents an increase, and green represents a decrease)

Alternatively, methane can be generated through the *CH₂O intermediate with successive hydrogenation on the C atom. The key to this path is that after the CH₄ molecule desorbs, the remaining O atom must be further hydrogenated to a water molecule, which has a rate-determining barrier of 0.61 eV at the final step, to prevent subsequent reactions from being affected. In summary, the CHE mechanism suggests that CH₄ could be produced with a limiting potential of -0.61 V for the FeFe-grafinN₆ catalyst.

For FeCu-grafinN₆ we examined the same reaction pathways. By comparison, the free energy changes of *HC(O)O reduction to *HCOOH and *OH reduction to *H₂O are both less favorable for FeCu-grafinN₆ than for FeFe-grafinN₆. This may arise from the weaker adsorption of O atom after one Fe is replaced by Cu, so the O atom is hydrogenated more easily. In contrast, the adsorption of *CO for the Fe-Cu system is stronger, leading to a large free energy increase for its protonation. Therefore, the whole reaction process follows the *HC(O)O path.

For CH₄ production using FeCu-grafinN₆, the final step that convert O atom into water molecule requires 0.48 eV. In contrast, the free energy increase of the final step forming methanol is only 0.08 eV. Like the Fe-Fe system, the adsorption energy of CH₃OH in the Fe-Cu system is too large (-1.12 eV, Table S5) impeding further reduction.

In summary, the optimal path for generating CH₄ for the Fe-Fe system is *CO₂ → *COOH → *CO + H₂O → *CHO → *CH₂O → *CH₃O → *O + CH₄ → *OH → *H₂O; while the optimal path for generating CH₄ for the Fe-Cu system is *CO₂ → *HCOO → *HCOOH → *CHO + H₂O

→ *CH₂O → *CH₃O → *O + CH₄ → *OH → *H₂O. Although CH₃OH is formed easily following the blue path in Figure 2, the difficulty in CH₃OH desorption requires more energy to obtain CH₃OH, so CH₄ remains the preferred product. To further understand the difference between the Fe-Fe and Fe-Cu system for the C1 reaction path, we calculated and analyzed the differential electron density and LPDOS (Figure S11 and Figure S12), as described in the Supporting Information.

Figure 4. (a) Free energy for CO₂ reduction to CH₃CH₂OH and CH₂CH₂ on the FeFe-grafin₆ catalyst. (The specific values of each step of the reaction are shown in Table S6.) (b) The IS, TS, and FS structure diagrams and energy changes involved in the reaction process *CO + *COH → *COCO for FeFe-grafin₆.

C2 Reaction Path There are several comprehensive studies on forming C1 products, but few on the C2 mechanism. Typically, the metal atoms of a single atom catalyst are too far apart for C-C coupling to form multi-carbon products.^{26,51,52} In contrast, the two metal atoms in FeFe-grafin₆ and FeCu-grafin₆ are bonded, providing the opportunity for generating multi-carbon products.

Previous studies^{51,53} indicate that CO can be coupled with COH to form a CO-COH product, which shares the COH intermediate with C1 production. Indeed Figure S13 shows that it is feasible to reduce another molecule of CO₂ to CO based on adsorbing one molecule of CO. We find that *CO+*COH→*HOCCO has an energy barrier of 0.64 eV for Fe-Fe system (Figure 4b) and 0.80 eV for Fe-Cu system (Figure S14). We examined the total energy changes and reaction energy barriers for CC-coupling of the Fe-Fe system for various charges. As shown in Figures S15 and S16, we found that the energy barriers are reduced compared to the linear change trend. Here we consider neutral conditions.

As shown in Figure 3 and 4a, the Fe-Fe system can easily adsorb an additional CO to be coupled with *COH that requires only 0.68 eV of free energy, much easier than direct coupling of the CO dimer (1.06 eV, Figure S17). Further protonation steps of the *HOCCO intermediate (Figure 3) are less consuming. According to research reported by Lum et al.,⁵⁴ ethylene generation follows the *HOCCOH → *HOCC → *HOCCH → *CCH → *CCH₂ → *HCCH₂ → *H₂CCH₂ path while ethanol generation follows the *HOCCH → *HO(CH)CH → *HO(CH)CH₂ → *HO(CH)CH₃ → *HO(CH₂)CH₃ pathway. For our catalyst, the further hydrogenation to *CCH from *CHCOH requires free energy of 0.28 eV, while the free energy change of hydrogenation to *CHCHOH is -0.83 eV. The energy required by three subsequent electron transfer steps are all

less than 0.28 eV. Alternatively, the two steps after the formation of $^*\text{CH}_2\text{CHOH}$ require less energy than the rate limiting step $^*\text{CO} + ^*\text{COH} \rightarrow ^*\text{HOCCO}$ (0.68 eV). Therefore, both ethanol and ethylene can be generated at an external potential of -0.68 V. Considering that the energy required for $^*\text{CCH}$ formation is higher than $^*\text{HOCHCH}$, ethanol product may be favored in this system.

Figure 5. (a) Free energy for CO_2 reduction to $\text{CH}_3\text{CH}_2\text{OH}$ and CH_2CH_2 for the FeCu-grafin₆ catalyst. (The specific values of each step of the reaction are shown in Table S7.) (b) The IS, TS, and FS structure diagrams and energy changes involved in the reaction process $^*\text{CO} + ^*\text{CH}_2 \rightarrow ^*\text{COCH}_2$ for FeCu-grafin₆. The top views are shown below the side view.

Because C2 and C1 share the intermediate $^*\text{COH}$ through this path, it is likely to compete with C1. Figure 3 shows that after formation of COH, further hydrogenation to CHOH requires additional energy of 0.52 eV, while the free energy decreases by 0.52 eV when forming $\text{COH}^* + \text{CO}^*$. And it was found in Figure S18 that the kinetic energy barrier for $^*\text{COH} + ^*\text{H} \rightarrow ^*\text{CHOH}$ is 0.93 eV, which is greater than the required energy barrier for $^*\text{COH} + ^*\text{CO} \rightarrow$

*COHCO (which is 0.64 eV). Thus, C2 path is more likely to occur with COH-CO coupling dominating the limiting potential of -0.68 V. In summary the Fe-Fe system starts to produce C2 products, mainly CH₃CH₂OH, at an applied potential of U= -0.68 V. The same coupling process was compared for Fe-Cu in Figure S14 (see Supporting Information for details) where *CO + H⁺ → *COH in Fe-Cu requires 0.92 eV of free energy, so instead we consider the path involving the *CH₂CO intermediate.

Figure 6. Some pathways for CO₂ reduction to C1/C2 products with the Gibbs free energy changes for FeCu-grafin₆. (The energy involved in the figure is the free energy difference of each step, red represents an increase, and green represents a decrease)

For the Fe-Cu system, the reaction energy barrier for forming *CH₂CO (0.44 eV, Figure 5b) is lower than that for forming *HOCCO (0.80 eV, Figure S14). Furthermore, the smaller C-C distance (2.66 Å) indicates that the metal atoms barely move in the Fe-Cu system during the transformation process which may lead to lower energy barrier. After formation of the *CH₂ intermediate, the energy change for each subsequent step (Figure 5) is lower than the rate-determining step of the C1 path (0.68 eV). Therefore, the Fe-Cu system could produce CH₃CH₂OH and CH₂CH₂ with an applied potential of -0.68 V, where CH₃CH₂OH is more favored. Figure 6 reveals that after formation of CH₂ along the C1 path, it is easy to continue hydrogenation to CH₃ whereas adding additional CO requires additional energy. However, in Figure S19, the kinetic energy barrier of *CH₂ + *H → *CH₃ is 0.79 eV, which is larger than that of C-C coupling. Therefore, like the Fe-Fe system, the Fe-Cu system is also more likely to produce C2 products with a limiting potential of -0.68 V.

The above analysis indicates that the Fe-Cu system may generate C-C coupling products under an applied potential of -0.68 V without strong HER. However, combining the results for the C1 path, we find the selectivity of Fe-Fe to be superior over Fe-Cu for generating CH₄ under -0.61 V and C2 products under -0.68 V. Thus, heteronuclear dimers are not necessarily more advantageous for catalysis than homonuclear dimers. Compared with other CO₂RR catalysts reported experimentally,^{55,56} our bimetallic system more readily reduces CO₂ under lower potential.

We reported here a novel 2D graphene-nitrene heterostructure material (denoted grafiN₆) that provides a framework for single site multimetal catalysis. It contains two isolated N₆ rings per periodic cell, each of which can accommodate two transition metals. We considered 15 cases for CO₂RR and concluded that FeFe and FeCu doping leads to potentially favorable catalytic processes. The application to CO₂RR suggests that

- the grafiN₆ with homonuclear bimetal Fe-Fe could greatly lower the limiting potential of CO₂RR to -0.61 V vs RHE for producing CH₄.
- C2 products including ethylene and ethanol may be obtained with a limiting potential of -0.68 V vs RHE, leading to product richness and selectivity.
- substituting one Fe atom with Cu atom to form the heteronuclear bimetallic Fe-Cu system makes competing HER side reactions more difficult, while the CO₂RR catalytic performance for both C1 and C2 mechanisms are barely affected.
- the grafiN₆ substrate provides a flexible multimetal single site to assist the CO₂ reduction processes.

These examples illustrate some possibilities for rational design of bimetallic CO₂RR catalysts to achieve selectivity with lower limiting potentials. The heteronuclear and homonuclear systems each have advantages.

Looking beyond these results, we note that the grafiN₆ framework can coordinate up to three transition metal atoms to provide novel catalytic processes. We expect that suitable two or three metal systems might provide single site catalysts useful for OER, HER, N₂RR, and ORR. We anticipate that these single layer 2D catalysts would adhere to standard conductive carbon supports.

ASSOCIATED CONTENT

Supporting Information Available: Thermodynamic data, adsorption energies, reaction free energies, density of states, snapshots of molecular dynamics, adsorption patterns. (PDF)

Videos of molecular dynamics. (MP4)

These materials are available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

We acknowledge financial support from the National Natural Science Foundation of China (Grant No. 91961120), Innovative and Entrepreneurial Doctor (World-Famous Universities) in Jiangsu Province, Talent in Demand in the city of Suzhou, and the Scientific Research Startup Funding from the Institute of Functional Nano & Soft Materials (FUNSOM) in Soochow University. This project is also funded by the collaborative Innovation Center of Suzhou Nano Science & Technology, the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), the 111 Project, and Joint International Research Laboratory of Carbon-based Functional Materials and Devices.

S. M. is thankful for the support by Act 211 Government of the Russian Federation, under No. 02.A03.21.0011.

WAG is supported by the National Science Foundation (CMMT 18-500, Bob McCabe).

REFERENCES

- (1) Cook, B. I.; Wolkovich, E. M.; Parmesan, C. Divergent Responses to Spring and Winter Warming Drive Community Level Flowering Trends. *Proc. Natl. Acad. Sci.* **2012**, *109*, 9000.
- (2) Cox, P. M.; Betts, R. A.; Jones, C. D.; Spall, S. A.; Totterdell, I. J. Acceleration of Global Warming Due to Carbon-Cycle Feedbacks in a Coupled Climate Model. *Nature* **2000**, *408*, 184–187.
- (3) Lewis, N. S.; Nocera, D. G. Powering the Planet: Chemical Challenges in Solar Energy Utilization. *Proc. Natl. Acad. Sci.* **2006**, *103*, 15729.
- (4) Kuhl, K. P.; Hatsukade, T.; Cave, E. R.; Abram, D. N.; Kibsgaard, J.; Jaramillo, T. F. Electrocatalytic Conversion of Carbon Dioxide to Methane and Methanol on Transition Metal Surfaces. *J. Am. Chem. Soc.* **2014**, *136*, 14107–14113.
- (5) Gao, S.; Lin, Y.; Jiao, X.; Sun, Y.; Luo, Q.; Zhang, W.; Li, D.; Yang, J.; Xie, Y. Partially Oxidized Atomic Cobalt Layers for Carbon Dioxide Electroreduction to Liquid Fuel. *Nature* **2016**, *529*, 68.
- (6) Asadi, M.; Kim, K.; Liu, C.; Addepalli, A. V.; Abbasi, P.; Yasaei, P.; Phillips, P.; Behranginia, A.; Cerrato, J. M.; Haasch, R.; *et al.* Nanostructured Transition Metal Dichalcogenide Electrocatalysts for CO₂ Reduction in Ionic Liquid. *Science* **2016**, *353*, 467.
- (7) Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Nørskov, J. K.; Jaramillo, T. F. Combining Theory and Experiment in Electrocatalysis: Insights into Materials Design. *Science* **2017**, *355*, eaad4998.
- (8) Qu, Y.; Duan, X. Progress, Challenge and Perspective of Heterogeneous Photocatalysts. *Chem. Soc. Rev.* **2013**, *42*, 2568–2580.
- (9) Poh, H. L.; Sofer, Z.; Luxa, J.; Pumera, M. Transition Metal-Depleted Graphenes for Electrochemical Applications via Reduction of CO₂ by Lithium. *Small* **2014**, *10*, 1529–1535.

- (10) Graciani, J.; Mudiyansele, K.; Xu, F.; Baber, A. E.; Evans, J.; Senanayake, S. D.; Stacchiola, D. J.; Liu, P.; Hrbek, J.; Sanz, J. F.; *et al.* Highly Active Copper-Ceria and Copper-Ceria-Titania Catalysts for Methanol Synthesis from CO₂. *Science* **2014**, *345*, 546.
- (11) White, J. L.; Baruch, M. F.; Pander, J. E.; Hu, Y.; Fortmeyer, I. C.; Park, J. E.; Zhang, T.; Liao, K.; Gu, J.; Yan, Y.; *et al.* Light-Driven Heterogeneous Reduction of Carbon Dioxide: Photocatalysts and Photoelectrodes. *Chem. Rev.* **2015**, *115*, 12888–12935.
- (12) Hansen, H. A.; Varley, J. B.; Peterson, A. A.; Nørskov, J. K. Understanding Trends in the Electrocatalytic Activity of Metals and Enzymes for CO₂ Reduction to CO. *J. Phys. Chem. Lett.* **2013**, *4*, 388–392.
- (13) Durand, W. J.; Peterson, A. A.; Studt, F.; Abild-Pedersen, F.; Nørskov, J. K. Structure Effects on the Energetics of the Electrochemical Reduction of CO₂ by Copper Surfaces. *Surf. Sci.* **2011**, *605*, 1354–1359.
- (14) He, S.; Ni, F.; Ji, Y.; Wang, L.; Wen, Y.; Bai, H.; Liu, G.; Zhang, Y.; Li, Y.; Zhang, B.; *et al.* The P-Orbital Delocalization of Main-Group Metals to Boost CO₂ Electroreduction. *Angew. Chem.* **2018**, *130*, 16346–16351.
- (15) Rezayee, N. M.; Huff, C. A.; Sanford, M. S. Tandem Amine and Ruthenium-Catalyzed Hydrogenation of CO₂ to Methanol. *J. Am. Chem. Soc.* **2015**, *137*, 1028–1031.
- (16) Álvarez, A.; Bansode, A.; Urakawa, A.; Bavykina, A. V.; Wezendonk, T. A.; Makkee, M.; Gascon, J.; Kapteijn, F. Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO₂ Hydrogenation Processes. *Chem. Rev.* **2017**, *117*, 9804–9838.
- (17) Shi, J.; Jiang, Y.; Jiang, Z.; Wang, X.; Wang, X.; Zhang, S.; Han, P.; Yang, C. Enzymatic Conversion of Carbon Dioxide. *Chem. Soc. Rev.* **2015**, *44*, 5981–6000.
- (18) Zhu, D. D.; Liu, J. L.; Qiao, S. Z. Recent Advances in Inorganic Heterogeneous Electrocatalysts for Reduction of Carbon Dioxide. *Adv. Mater.* **2016**, *28*, 3423–3452.
- (19) Wang, W.; Wang, S.; Ma, X.; Gong, J. Recent Advances in Catalytic Hydrogenation of Carbon Dioxide. *Chem. Soc. Rev.* **2011**, *40*, 3703–3727.
- (20) Klankermayer, J.; Wesselbaum, S.; Beydoun, K.; Leitner, W. Selective Catalytic Synthesis Using the Combination of Carbon Dioxide and Hydrogen: Catalytic Chess at the Interface of Energy and Chemistry. *Angew. Chem. Int. Ed.* **2016**, *55*, 7296–7343.
- (21) Rodriguez, J. A.; Liu, P.; Stacchiola, D. J.; Senanayake, S. D.; White, M. G.; Chen, J. G. Hydrogenation of CO₂ to Methanol: Importance of Metal–Oxide and Metal–Carbide Interfaces in the Activation of CO₂. *ACS Catal.* **2015**, *5*, 6696–6706.
- (22) Behrens, M.; Studt, F.; Kasatkin, I.; Köhl, S.; Hävecker, M.; Abild-Pedersen, F.; Zander, S.; Girgsdies, F.; Kurr, P.; Kniep, B.-L.; *et al.* The Active Site of Methanol Synthesis over Cu/ZnO/Al₂O₃ Industrial Catalysts. *Science* **2012**, *336*, 893–897.

- (23) Yang, Y.; Evans, J.; A. Rodriguez, J.; G. White, M.; Liu, P. Fundamental Studies of Methanol Synthesis from CO₂ Hydrogenation on Cu(111), Cu Clusters, and Cu / ZnO(0001[Combining Macron]). *Phys. Chem. Chem. Phys.* **2010**, *12*, 9909–9917.
- (24) Ao, C.; Feng, B.; Qian, S.; Wang, L.; Zhao, W.; Zhai, Y.; Zhang, L. Theoretical Study of Transition Metals Supported on G-C₃N₄ as Electrochemical Catalysts for CO₂ Reduction to CH₃OH and CH₄. *J. CO₂ Util.* **2020**, *36*, 116–123.
- (25) Machado, B. F.; Serp, P. Graphene-Based Materials for Catalysis. *Catal. Sci. Technol.* **2012**, *2*, 54–75.
- (26) Cui, X.; An, W.; Liu, X.; Wang, H.; Men, Y.; Wang, J. C₂N-Graphene Supported Single-Atom Catalysts for CO₂ Electrochemical Reduction Reaction: Mechanistic Insight and Catalyst Screening. *Nanoscale* **2018**, *10*, 15262–15272.
- (27) Zhao, J.; Zhao, J.; Li, F.; Chen, Z. Copper Dimer Supported on a C₂N Layer as an Efficient Electrocatalyst for CO₂ Reduction Reaction: A Computational Study. *J. Phys. Chem. C* **2018**, *122*, 19712–19721.
- (28) Jiao, Y.; Zheng, Y.; Chen, P.; Jaroniec, M.; Qiao, S.-Z. Molecular Scaffolding Strategy with Synergistic Active Centers to Facilitate Electrocatalytic CO₂ Reduction to Hydrocarbon/Alcohol. *J. Am. Chem. Soc.* **2017**, *139*, 18093–18100.
- (29) Genovese, C.; Schuster, M. E.; Gibson, E. K.; Gianolio, D.; Posligua, V.; Grau-Crespo, R.; Cibir, G.; Wells, P. P.; Garai, D.; Solokha, V.; *et al.* Operando Spectroscopy Study of the Carbon Dioxide Electro-Reduction by Iron Species on Nitrogen-Doped Carbon. *Nat. Commun.* **2018**, *9*, 1–12.
- (30) Gao, G.; Jiao, Y.; Wacławik, E. R.; Du, A. Single Atom (Pd/Pt) Supported on Graphitic Carbon Nitride as an Efficient Photocatalyst for Visible-Light Reduction of Carbon Dioxide. *J. Am. Chem. Soc.* **2016**, *138*, 6292–6297.
- (31) Ju, W.; Bagger, A.; Hao, G.-P.; Varela, A. S.; Sinev, I.; Bon, V.; Roldan Cuenya, B.; Kaskel, S.; Rossmeisl, J.; Strasser, P. Understanding Activity and Selectivity of Metal-Nitrogen-Doped Carbon Catalysts for Electrochemical Reduction of CO₂. *Nat. Commun.* **2017**, *8*, 1–9.
- (32) He, Z.; He, K.; Robertson, A. W.; Kirkland, A. I.; Kim, D.; Ihm, J.; Yoon, E.; Lee, G.-D.; Warner, J. H. Atomic Structure and Dynamics of Metal Dopant Pairs in Graphene. *Nano Lett.* **2014**, *14*, 3766–3772.
- (33) Qin, G.; Cui, Q.; Wang, W.; Li, P.; Du, A.; Sun, Q. First-Principles Study of Electrocatalytically Reversible CO₂ Capture on Graphene-like C₃N. *ChemPhysChem* **2018**, *19*, 2788–2795.
- (34) Cui, H.; Guo, Y.; Guo, L.; Wang, L.; Zhou, Z.; Peng, Z. Heteroatom-Doped Carbon Materials and Their Composites as Electrocatalysts for CO₂ Reduction. *J. Mater. Chem. A* **2018**, *6*, 18782–18793.

- (35) Che, W.; Cheng, W.; Yao, T.; Tang, F.; Liu, W.; Su, H.; Huang, Y.; Liu, Q.; Liu, J.; Hu, F.; *et al.* Fast Photoelectron Transfer in (Cring)–C₃N₄ Plane Heterostructural Nanosheets for Overall Water Splitting. *J. Am. Chem. Soc.* **2017**, *139*, 3021–3026.
- (36) Li, X.; Zhong, W.; Cui, P.; Li, J.; Jiang, J. Design of Efficient Catalysts with Double Transition Metal Atoms on C₂N Layer. *J. Phys. Chem. Lett.* **2016**, *7*, 1750–1755.
- (37) Xu, W.; Chen, C.; Tang, C.; Li, Y.; Xu, L. Design of Boron Doped C₂N–C₃N Coplanar Conjugated Heterostructure for Efficient HER Electrocatalysis. *Sci. Rep.* **2018**, *8*, 5661.
- (38) Goedecker, S.; Teter, M.; Hutter, J. Separable Dual-Space Gaussian Pseudopotentials. *Phys. Rev. B* **1996**, *54*, 1703–1710.
- (39) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H–Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
- (40) Mathew, K.; Sundararaman, R.; Letchworth-Weaver, K.; Arias, T. A.; Hennig, R. G. Implicit Solvation Model for Density-Functional Study of Nanocrystal Surfaces and Reaction Pathways. *J. Chem. Phys.* **2014**, *140*, 084106.
- (41) Fishman, M.; Zhuang, H. L.; Mathew, K.; Dirschka, W.; Hennig, R. G. Accuracy of Exchange-Correlation Functionals and Effect of Solvation on the Surface Energy of Copper. *Phys. Rev. B* **2013**, *87*, 245402.
- (42) Henkelman, G.; Jónsson, H. A Dimer Method for Finding Saddle Points on High Dimensional Potential Surfaces Using Only First Derivatives. *J. Chem. Phys.* **1999**, *111*, 7010–7022.
- (43) Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jónsson, H. Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. *J. Phys. Chem. B* **2004**, *108*, 17886–17892.
- (44) Stukowski, A. Visualization and Analysis of Atomistic Simulation Data with OVITO—the Open Visualization Tool. *Modell. Simul. Mater. Sci. Eng.* **2009**, *18*, 015012.
- (45) Wang, L.; Chen, W.; Zhang, D.; Du, Y.; Amal, R.; Qiao, S.; Wu, J.; Yin, Z. Surface Strategies for Catalytic CO₂ Reduction: From Two-Dimensional Materials to Nanoclusters to Single Atoms. *Chem. Soc. Rev.* **2019**, *48*, 5310–5349.
- (46) Peterson, A. A.; Abild-Pedersen, F.; Studt, F.; Rossmeisl, J.; Nørskov, J. K. How Copper Catalyzes the Electroreduction of Carbon Dioxide into Hydrocarbon Fuels. *Energy Environ. Sci.* **2010**, *3*, 1311–1315.
- (47) Nie, X.; Luo, W.; Janik, M. J.; Asthagiri, A. Reaction Mechanisms of CO₂ Electrochemical Reduction on Cu(111) Determined with Density Functional Theory. *J. Catal.* **2014**, *312*, 108–122.
- (48) Liu, J.-H.; Yang, L.-M.; Ganz, E. Electrocatalytic Reduction of CO₂ by Two-Dimensional Transition Metal Porphyrin Sheets. *J. Mater. Chem. A* **2019**, *7*, 11944–11952.

- (49) Ling, C.; Li, Q.; Du, A.; Wang, J. Computation-Aided Design of Single-Atom Catalysts for One-Pot CO₂ Capture, Activation, and Conversion. *ACS Appl. Mater. Interfaces* **2018**, *10*, 36866–36872.
- (50) Shen, H.; Li, Y.; Sun, Q. CO₂ Electroreduction Performance of Phthalocyanine Sheet with Mn Dimer: A Theoretical Study. *J. Phys. Chem. C* **2017**, *121*, 3963–3969.
- (51) Xiao, H.; Cheng, T.; Goddard, W. A. Atomistic Mechanisms Underlying Selectivities in C1 and C2 Products from Electrochemical Reduction of CO on Cu(111). *J. Am. Chem. Soc.* **2017**, *139*, 130–136.
- (52) Calle-Vallejo, F.; Koper, M. T. M. Theoretical Considerations on the Electroreduction of CO to C2 Species on Cu(100) Electrodes. *Angew. Chem. Int. Ed.* **2013**, *52*, 7282–7285.
- (53) Cheng, T.; Xiao, H.; Goddard, W. A. Full Atomistic Reaction Mechanism with Kinetics for CO Reduction on Cu(100) from Ab Initio Molecular Dynamics Free-Energy Calculations at 298 K. *Proc. Natl. Acad. Sci.* **2017**, *114*, 1795.
- (54) Lum, Y.; Cheng, T.; Goddard, W. A.; Ager, J. W. Electrochemical CO Reduction Builds Solvent Water into Oxygenate Products. *J. Am. Chem. Soc.* **2018**, *140*, 9337–9340.
- (55) Pan, F.; Zhang, H.; Liu, K.; Cullen, D.; More, K.; Wang, M.; Feng, Z.; Wang, G.; Wu, G.; Li, Y. Unveiling Active Sites of CO₂ Reduction on Nitrogen-Coordinated and Atomically Dispersed Iron and Cobalt Catalysts. *ACS Catal.* **2018**, *8*, 3116–3122.
- (56) Cheng, Q.; Mao, K.; Ma, L.; Yang, L.; Zou, L.; Zou, Z.; Hu, Z.; Yang, H. Encapsulation of Iron Nitride by Fe–N–C Shell Enabling Highly Efficient Electroreduction of CO₂ to CO. *ACS Energy Lett.* **2018**, *3*, 1205–1211.

TOC

Figure 1. (a) conceptual synthesis of the grafiN6 heterostructure from C_2N and C_3N . (b) Top view and side view of bimetallic FeFe-grafiN6 heterojunction. (c) The Gibbs free energy changes for the first step of CO₂RR: $^*CO_2 \rightarrow ^*COOH$ or *HCOO compared with the hydrogen evolution reaction (ΔG^*H)

239x140mm (119 x 119 DPI)

Figure 2. The Gibbs free energy changes for CO₂ reduction to CH₃OH (blue) and CH₄ (red) for (a) FeFe-grafin6 and (b) FeCu-grafin6. The red line is the best overall reaction path for generating CH₄, and the blue line is the best overall reaction path for generating CH₃OH. (The specific values of each step of the reaction are shown in Table S4.)

Figure 4. (a) Free energy for CO₂ reduction to CH₃CH₂OH and CH₂CH₂ on the FeFe-grafin6 catalyst. (The specific values of each step of the reaction are shown in Table S6.) (b) The IS, TS, and FS structure diagrams and energy changes involved in the reaction process *CO + *COH → *COCO for FeFe-grafin6.

Figure 5. (a) Free energy for CO_2 reduction to $\text{CH}_3\text{CH}_2\text{OH}$ and CH_2CH_2 for the FeCu-grafin6 catalyst. (The specific values of each step of the reaction are shown in Table S7.) (b) The IS, TS, and FS structure diagrams and energy changes involved in the reaction process $^*\text{CO} + ^*\text{CH}_2 \rightarrow ^*\text{COCH}_2$ for FeCu-grafin6. The top views are shown below the side view.