Carbon dioxide conversion into hydrocarbon fuels on defective graphene-supported Cu nanoparticles from first principles†

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Density functional theory studies demonstrate that defective graphene-supported Cu nanoparticles can modify the structural and electronic properties of copper for enhancing electrochemical reduction of carbon dioxide (CO2) into hydrocarbon fuels (CH4, CO, and HCOOH). We not only provide improved understanding of CO2 conversion mechanisms on both Cu and the Cu nanoparticle system, but also explain a key factor for enhanced CO2 conversion. A promising catalytic material for CO2 conversion into hydrocarbon fuels may allow for geometry flexibility upon interaction with a key intermediate of CHO*.

The electrochemical conversion of CO2 to hydrocarbon fuels would not only assist in paving a path toward renewable energy, but also contribute to mitigating CO2 emissions. The main challenge for advancing CO2 reduction is to improve the energy efficiency of the process. Although both reasonably high current densities and moderate efficiencies have been achieved, they have not yet been achieved together. Various metal-based catalysts (i.e., copper,platinum, iron, nickel, gold) have been used to improve energy efficiency of the electrochemical reduction of CO2. Among them, copper has been widely accepted as a promising metal for CO2 reduction due to its high ability to produce hydrocarbon fuels such as carbon monoxide (CO), formic acid (HCOOH), methane (CH4), and ethane (C2H6); however, the quantities of produced fuels are inefficient due to the large overpotential. According to experiments and density functional theory (DFT) modeling investigations, the production of CH4 from CO2 requires at least ~0.8 V vs. RHE (i.e., reversible hydrogen electrode, in which the measured potential does not change with the pH). Hori et al. pointed out that the electrochemical reduction of CO2 is primarily hindered by a high overpotential, which results from the initial electron transfer to form the intermediate species, 'CO2−'. Also, recent DFT studies of CO2 electrochemical reduction have used CO and CHO intermediates as activity descriptors for CO2 reduction to methane, which is based on the fact that previous experimental studies demonstrated that CO adsorption dominates on the electrode surface during CO2 reduction.

Peterson et al. demonstrated by conducting DFT studies that the key step in controlling the formation of hydrocarbons in the electrochemical reduction of CO2 is the protonation of adsorbed CO* to form the adsorbed CHO* intermediate (where ‘*’ denotes the adsorbed species and will be referred to as such hereafter). By increasing the stability of the CHO* species relative to CO*, it is expected that the energy efficiency of the electrochemical reduction of CO2 would increase due to a significantly lowered overpotential. This may be achieved by utilizing nanostructures of copper supported on graphene. Changes in the lattice constant, surface stress and surface energy associated with the nanoparticle size may improve the surface activity of copper for CO2 reduction. Additionally, the unique electronic and physical properties of graphene would improve the CO2 reduction kinetics, as it has been previously shown that graphene can enhance reaction kinetics on noble metal nanoparticles. Also, carbon vacancies in graphene may significantly influence its physical and chemical characteristics and magnetic properties and can be used as anchoring points for the growth of metal nanoparticles, which will increase the durability of the Cu nanoparticle-graphene system and prevent sintering of the Cu nanoparticles.

The current communication discusses improved catalysts for electrochemical CO2 reduction to hydrocarbon fuels on Cu nanoparticles anchored at carbon vacancy sites of graphene. For this, free energies of the CO2 reduction intermediates in...
electrochemical reaction pathways were calculated by using density functional theory (DFT) coupled with a computational hydrogen electrode (CHE) model suggested by Nørskov et al.\textsuperscript{15,31} Electron exchange–correlation functionals were represented with the generalized gradient approximation (GGA), and the model of Perdew, Burke and Ernzerhof (PBE)\textsuperscript{12} was used for the nonlocal corrections. By employing the CHE model, a proton/electron (H\textsuperscript+ + e\textsuperscript−) in solution can be indirectly treated and the effect of a bias can be applied by shifting ΔG by +neU, where n is the number of proton–electron pairs transferred, e is the elementary positive charge, and U is the applied potential. The free energy change (ΔG) is calculated as ΔG = ΔE + ΔZPE − TΔS, where ΔE is the total energy change directly obtained from DFT calculations, ΔZPE is the change in zero-point energies, T is temperature, and ΔS is the change in entropy. The temperature is set to 18.5 °C to compare current DFT results with the experimental data of Hori et al.\textsuperscript{3} Details of the free energy calculations including DFT total energies, ZPE, entropies, and free energies of the intermediates and the solvation energy correction are described in ESI Section 1.\textsuperscript{†}

Fig. 1 depicts the Cu nanoparticle–graphene system consisting of an icosahedral Cu\textsubscript{55} nanoparticle (diameter of ~0.9 nm) adsorbed onto a 5-8-5 vacancy site of graphene (70 carbon atoms), which is motivated by the magic numbers (13, 55, 147, etc.)\textsuperscript{33,34} of transition metal clusters providing a higher geometric or electronic stability compared to other cluster sizes. The Cu\textsubscript{55} nanoparticle shows a strong DFT adsorption energy of −4.26 eV, in which Cu is interacting with the dangling bonds of the neighboring carbons near the 5-8-5 vacancy site, which implies that the strong interaction may help to prevent sintering of the Cu nanoparticles. The size of the Cu nanoparticle used in the DFT calculations is smaller than those conventionally synthesized experimentally; however, considering the limitation of DFT calculations in terms of the system size that can be efficiently treated, Cu\textsubscript{55} is adequately large thereby minimizing the strong binding effect associated with highly undercoordinated Cu atoms that cause unrealistically high reactivity, thereby leading to an overestimation of overpotentials as was previously discussed in the work by Lim and Wilcox on the oxygen reduction reaction on Pt\textsubscript{13}-defective graphene.\textsuperscript{29,30} In addition, the Cu nanoparticle size (−0.9 nm) may be plausible in electrochemical experiments as demonstrated in oxygen reduction reactions on graphene supported-gold clusters with diameters of approximately 1–2.5 nm (an average diameter of 1.8 nm)\textsuperscript{30} and on graphene quantum dots-supported platinum nanoparticles with diameters of 2.2–3.3 nm (an average diameter of 2.8 nm).\textsuperscript{36}

Fig. 2 shows the lowest energy pathways of CO\textsubscript{2} reduction on the Cu\textsubscript{55}-defective graphene surface and a comparison of the CO\textsubscript{2} reduction mechanisms between the Cu(111) (i.e., the most stable flat Cu surface among (100), (110), and (111) faces) and the Cu\textsubscript{55}-defective graphene surfaces. Peterson et al.\textsuperscript{35} extensively investigated the electroreduction of CO\textsubscript{2} on a Cu(211) surface and determined the lowest energy intermediates. Based on this, we have examined three possible adsorption configurations for each intermediate and determined the lowest energy pathways as shown in Fig. 2A. By transferring (H\textsuperscript+ + e\textsuperscript−) from solution to an adsorbed species, a gas-phase CO\textsubscript{2} molecule is converted to COOH\textsuperscript* → CO\textsuperscript* → CHO\textsuperscript* → CH\textsubscript2}OH\textsuperscript* → O\textsuperscript* → OH\textsuperscript* → H\textsubscript2}O\textsubscript{gas}. The reaction intermediate configurations on the Cu(111) surface are also similar to those of Fig. 2A (data not shown here).

At zero electrode potential (U = 0 V) in Fig. 2B, the Cu(111) surface shows a key energy barrier of 0.97 eV required for the protonation step of the CO species (CO\textsuperscript* → CHO\textsuperscript*; (2) → (3)) in Fig. 2B. This agrees reasonably well with the protonation step barrier of 0.74 eV on the Cu(211) step surface conducted by Peterson et al.,\textsuperscript{35} which is due to the fact that a step-like surface of Cu(211) is more reactive toward binding adsorbrates than a flat surface. In the Cu\textsubscript{55}-defective graphene system, reaction across the uncoordinated site significantly lowers the energy barrier of the key potential-limiting step to 0.68 eV; in other words, CHO\textsuperscript* becomes more stabilized relative to CO\textsuperscript* on the Cu\textsubscript{55}-defective graphene surface compared to on the Cu(111) surface. This implies that the Cu\textsubscript{55}-defective graphene system may help enhance the energy efficiency of the electrochemical reduction of CO\textsubscript{2} by lowering the key energy barrier. Instead, the Cu\textsubscript{55}-defective graphene system may hinder further reaction steps toward oxygen reduction due to an increased energy barrier associated with the proton/electron-transfer step of OH\textsuperscript* between steps (7) and (8) (i.e., OH\textsuperscript* → H\textsubscript2}O\textsubscript{gas}) in Fig. 2B. For this step, the Cu(111) surface requires 0.39 eV, while the Cu\textsubscript{55}-defective graphene system requires 0.60 eV. Considering the endothermic reaction steps of both systems in Fig. 2B, the rate-limiting steps of the CO\textsubscript{2} reduction on the Cu(111) surface and Cu\textsubscript{55}-defective graphene system lie in the CO\textsuperscript* → CHO\textsuperscript* step.

Fig. 2C shows the CO\textsubscript{2} reduction mechanisms at applied electrode potentials of U = −0.97 and −0.68 V for the Cu(111) surface and the Cu\textsubscript{55}-defective graphene system, respectively. The applied potentials are required voltages for eliminating the energy barriers of the rate-limiting step (CO\textsuperscript* → CHO\textsuperscript*), which shows that the hydrocarbon CH\textsubscript2}O-forming reaction from CO\textsubscript{2}...
may occur at $-0.97$ and $-0.68$ V (vs. RHE) on the Cu(111) surface and the Cu$_{55}$–defective graphene system, respectively. The DFT potential of $-0.97$ V on the Cu(111) surface agrees fairly well with experimental measurements, in which the formation of CH$_4$ from CO$_2$ on copper is initiated at about $-0.8$ V and is maximized at about $-1.0$ V at $18.5^\circ$C. $^{3,15}$ An interesting finding is that the Cu$_{55}$–defective graphene system requires approximately 30% less potential compared to the planar Cu(111) surface. Details of the CO$_2$ reduction reactions and free energy data are shown in ESI Section 2. $^{†}$

To understand in greater detail the reason for the smaller potential required for CH$_4$ formation on the Cu$_{55}$–defective graphene system, the projected density of states (PDOS) of CO$^*$, CHO$^*$, and surface Cu atoms neighboring the adsorbates were analyzed by decomposing the electron density and wave function into the atomic orbital contributions. In Fig. 3A, the Cu(111) surfaces with CO$^*$ and CHO$^*$ show hybridized s-, p-, and d-orbitals of Cu with s- and p-orbitals of the adsorbates between $-6$ and $-12$ eV. This phenomenon is also similarly shown in the case of the Cu$_{55}$–defective graphene systems as indicated in Fig. 3B. Both surface systems show strongly hybridized orbitals when CO is adsorbed; however, when CHO is adsorbed, the Cu(111) surface with the CHO$^*$ intermediate species indicates relatively weaker hybridization while the Cu$_{55}$–defective graphene system with CHO$^*$ shows stronger hybridization between $-8$ and $-6$ eV and near the edge of the valence zone. This greater CHO-Cu overlap population on the Cu nanoparticle represents a relatively stronger stabilization of the CHO species on the Cu$_{55}$–defective graphene system compared to the Cu(111) surface. Full details of each PDOS are shown in ESI Section 3. $^{†}$

The stronger orbital hybridization between Cu and CHO on the Cu$_{55}$–defective graphene system may be attributed to the advantage associated with graphene’s unique electronic and physical properties as previously discussed. To confirm this, the key potential limiting step of CO$^*$ → CHO$^*$ was examined on a Cu$_{55}$ cluster without graphene as shown in the inset of Fig. 2B. Without the graphene support, the energy barrier of the key step is 0.78 eV, demonstrating that the graphene support contributes to lowering the energy barrier of the key step from 0.83 to

Fig. 2 (A) The lowest energy pathways of CO$_2$ reduction on the Cu$_{55}$–defective graphene. (B and C) Relative free energy diagrams without (B) and with (C) applied potential for CO$_2$ reduction on Cu(111) (empty rectangle with dashed lines), Cu$_{55}$–defective graphene (filled rectangle with solid lines), and Cu$_{55}$ cluster (empty rectangle in the inset).

Fig. 3 Projected density of states (PDOS) of the Cu(111) surface with adsorbed CO and CHO (A) and the Cu$_{55}$–graphene surface with CHO (B). A system title of XY indicates a surface (X) with adsorbed species (Y). Clean Cu, CO, and CHO represent clean Cu(111), adsorbed CO, and adsorbed CHO, respectively. The Fermi energy is referenced at 0 eV.
0.68 eV by modifying the electron properties of the anchored Cu55. To better understand this, the d-band centers of Cu atoms were calculated. The d-band centers of all Cu atoms (or two Cu atoms where CHO* is adsorbed) of the Cu55 cluster and the Cu55-defective graphene are −2.24 (or −2.10) and −2.17 (or −2.07) eV, respectively. The higher shift of the d-band centers of the Cu55-defective graphene toward the Fermi level indicates the higher reactivity of Cu atoms resulting in an increase in the stability of adsorbates, which is attributed to the fact that an upshift of the d-band center causes the antibonding orbitals to shift higher, potentially making them more difficult to fill.

Also, another important factor for the stronger orbital hybridization between Cu and CHO on the Cu55-defective graphene system may be the geometry flexibility of the Cu nanoparticle. The geometry of the Cu nanoparticle is more flexible than that of the Cu(111) surface, which promotes CHO binding on the Cu nanoparticle by increasing the Cu–Cu distance when the CHO* species is formed on the Cu nanoparticle surface. This is supported by the Cu–Cu distance measured at the CHO adsorbed site across both systems. The Cu–Cu distance of the Cu55-defective graphene system increases from 2.584 to 2.895 Å (12.1% increase), while that of the Cu(111) surface is expanded from 2.571 to 2.683 Å (4.4% increase) (see ESI Section 4†). In other words, the geometry flexibility of the Cu nanoparticle has locally caused an expansive lattice strain effect, which in turn strengthens the Cu interaction with CHO species. This kind of strain effect is well known in metals or metal alloys, where an expansion in the lattice parameter can induce a shift in the d-band interaction toward the Fermi energy, resulting in strengthening the adsorbate interaction on catalytic surfaces.37 Sakong and Gross38 reported that the lattice expansive strain of copper surfaces (Cu(100), Cu(110), and Cu(111)) causes an upshift in the d-band centers. On the other hand, electronic ligand effects induced by the modification of electronic properties may have a minimal effect on the stability of the CHO* intermediate species on both systems. This is because the PDOS of both clean systems are not significantly different, as shown in ESI Section 3.†

Furthermore, the reaction pathways toward the production of formic acid (HCOOH) and carbon monoxide (CO) gases are shown in Fig. 4. HCOOH and CO gases are produced when the second proton and electron (i.e., H+ + e−) are transferred at steps 2(a) and 2(b) in Fig. 4A and B, respectively. On the Cu(111) surface, the formation of both HCOOH and CO requires a potential of −0.51 V, by which the potential-limiting energy barriers at the first H+ + e− step are eliminated. This is in agreement with previous experiments14 in addition to previous DFT studies15,16 where the formation of HCOOH and CO gases requires about −0.4 to −0.5 V (vs. RHE). The COOH* species is more stable on the Cu55-defective graphene system compared to the Cu(111) surface for a similar reason as discussed previously with regard to the flexibility of the Cu nanoparticle geometry, resulting in limiting potentials of −0.19 and −0.39 V for the production of HCOOH and CO gases, respectively. This lower overpotential on the Cu55-defective graphene system may lead to the higher selectivity of HCOOH and CO compared to that on the Cu(111) surface.

In addition to the key rate-limiting steps of the protonation of adsorbed CO (CO* → CHO*) in CO2 reduction, the hydrogen evolution reaction (HER) significantly affects the electrochemical reduction of CO2 since HER is competitive against CO2 reduction. Effective CO2 reduction catalysts should show poor activity for the competitive HER.15–17 In terms of the selectivity of H2 gas production, the Cu55-defective graphene system shows a slightly poor activity for HER compared to the Cu(111) system as shown in Fig. 4C, indicating limiting potentials of −0.22 and −0.24 V on the Cu(111) and Cu55-defective graphene surfaces, respectively. In both cases, the potential limiting barriers for HER are present in the H2 gas desorption step (H* + H → H2(gas)), which is attributed to the fact that atomic hydrogen adsorption is exothermic and its desorption is endothermic. The adsorption free energies of atomic hydrogen on the Cu(111) surface and Cu55-defective graphene surfaces are −0.30 and −0.32 eV, respectively, which are comparative to the atomic hydrogen adsorption energy of −0.18 eV on the Cu(111) surface37 calculated using the GGA-PW91 functional. The predicted potential limiting step for HER in the current work agrees with previous DFT studies using a PBE functional and showing a potential of −0.1 V on the Cu(211) step.
The current work provides theoretical evidence for improved CO₂ conversion into hydrocarbon fuels by using defective graphene-supported Cu nanoparticles. The results imply that an alternative catalytic material that allows for geometry flexibility upon interaction with adsorbates, especially with CHO*, may improve CO₂ conversion into hydrocarbon fuels. A promising material may be Cu nanoparticles supported on defective graphene as demonstrated here. In addition to the benefits of Cu nanoparticles, the defective graphene support may not only promote electron transport to the key potential limiting step species of CHO*, but also help prevent sintering of Cu nanoparticles due to the strong anchoring nature of its defect sites. An improved understanding of CO₂ conversion mechanisms and the key factor regarding the geometry flexibility for the enhanced CO₂ conversion may help design promising materials for CO₂ conversion into hydrocarbon fuels. Also, future studies may need to focus on improving our understanding of solvation energies of COOH* species showing the influence on HCOOH and CO gas production and its selectivity.

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Notes and references


