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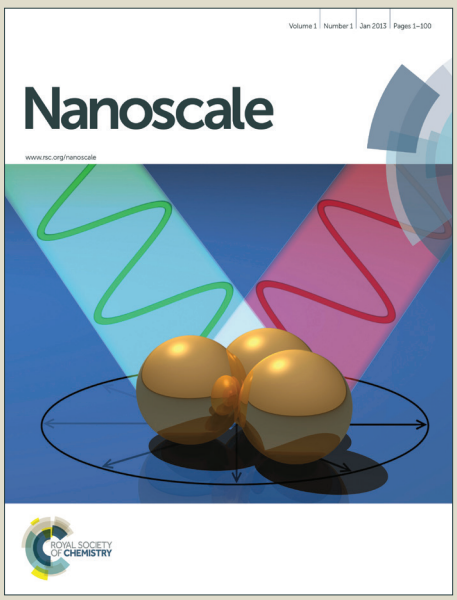

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Carbon Dioxide Conversion into Hydrocarbon Fuels on Defective Graphene-Supported Cu Nanoparticles from First Principles

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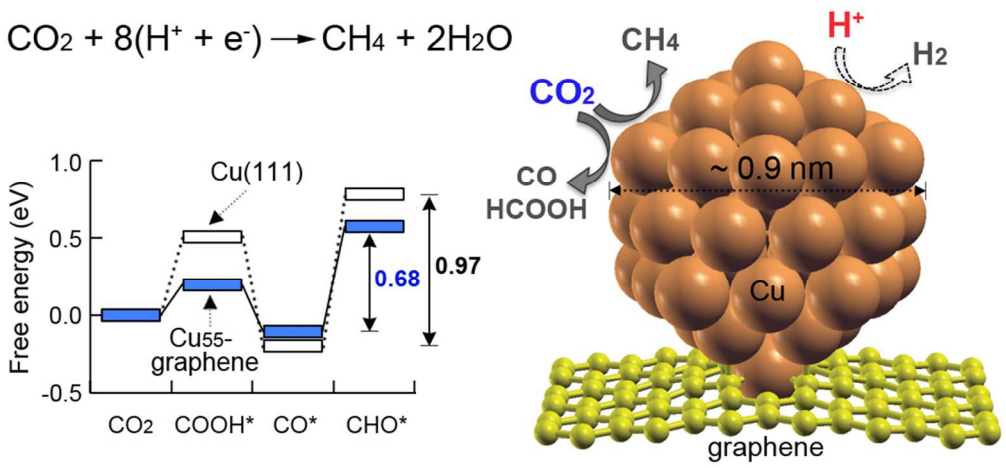
ABSTRACT

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 (CO_2) into hydrocarbon fuels (CH_4, CO, and HCOOH). We not only provide improved understanding of CO_2 conversion mechanisms on both Cu and the Cu nanoparticle system, but also explain a key factor for enhanced CO_2 conversion. A promising catalytic material for CO_2 conversion into hydrocarbon fuels may allow for geometry flexibility upon interaction with a key intermediate of CHO*.

Graphical Abstract



The electrochemical conversion of CO_2 to hydrocarbon fuels would not only assist in paving a path toward renewable energy, but also contribute to mitigating CO_2 emissions. The main challenge for advancing CO_2 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.[1] Various metal-based catalysts (i.e., copper[2-4], platinum[5,6], iron[7,8], nickel[9,10], gold[11-13]) have been used to improve energy efficiency of the electrochemical reduction of CO_2. Among them, copper has been widely accepted as a promising metal for CO_2 reduction due to its high ability to produce hydrocarbon fuels such as carbon monoxide (CO), formic acid (HCOOH), methane (CH_4), and ethane (C_2H_4)[3]; however, the quantities of produced fuels are inefficient due to the large overpotential. According to experiment[14] and density functional theory (DFT) modeling investigations[15], the production of CH_4 from CO_2 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.* [14] pointed out that the electrochemical reduction of CO_2 is primarily hindered by a high overpotential, which results from the initial electron transfer to form the intermediate species, $\bullet CO_2^-$. Also, recent DFT studies of CO_2 electrochemical reduction have used CO and CHO intermediates as activity descriptors for CO_2 reduction to methane[15-17], which is based on the fact that previous experimental studies[18-20] demonstrated that CO adsorption dominates on the electrode surface during CO_2 reduction.

Peterson *et al.*[15,16] demonstrated by conducting DFT studies that the key step in controlling the formation of hydrocarbons in the electrochemical reduction of CO_2 is the protonation of adsorbed CO* to form the adsorbed CHO* intermediate (such that, "*", denotes the adsorbed species and will be referred to thereafter). By increasing the stability of the CHO* species relative to CO*, it is expected that the energy efficiency of the electrochemical reduction of CO_2 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 CO_2 reduction. Additionally, the unique electronic and physical properties of graphene would improve the CO_2 reduction kinetics, as it has been previously shown that graphene can enhance reaction kinetics on noble metal nanoparticles.[21-25] Also, carbon vacancies on graphene may significantly influence its physical and chemical characteristics and magnetic properties[26-30] and it 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 CO_2 reduction to hydrocarbon fuels on Cu nanoparticles anchored at carbon vacancy sites of graphene. For this, free energies of the CO_2 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.*[15,31]. Electron exchange-correlation functionals were represented with the generalized gradient approximation (GGA), and the model of Perdew, Burke and Ernzerhof (PBE)[32] was used for the nonlocal corrections. By employing the CHE model, a proton/electron ($H^+ + e^-$) 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 $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, 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. Temperature is set to 18.5 °C to compare current DFT results with the experimental data of Hori *et al.*[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 Supplementary Information Section 1.

Figure 1 depicts the Cu nanoparticle–graphene system consisting of an icosahedral Cu_{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)[33,34] of transition metal clusters providing a higher geometric or electronic stability compared to other cluster sizes. The Cu_{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_{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_{13}-defective graphene.[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 cluster with diameters of approximately 1–2.5 nm (an average diameter of 1.8 nm)[35] and on graphene quantum dots-supported platinum nanoparticle with diameters of 2.2–3.3 nm (an average diameter of 2.8 nm).[36]

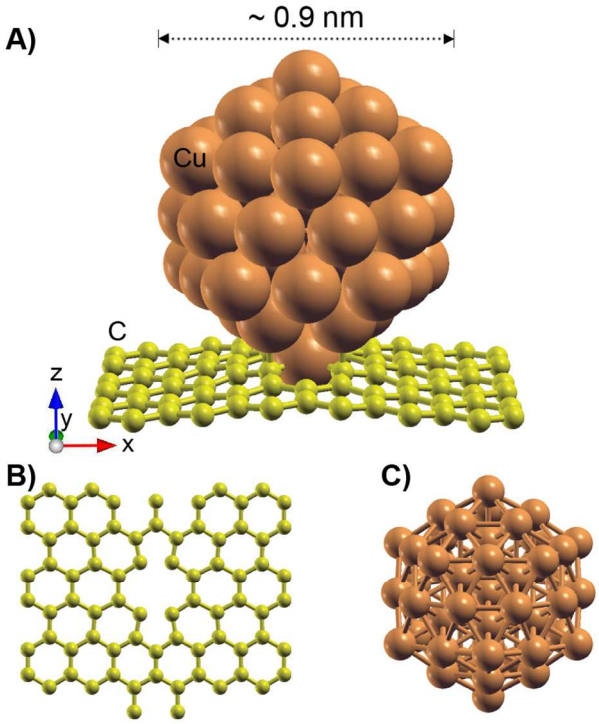


Figure 1. (A) Side view of Cu_{55} nanoparticle supported on defective graphene. (B) Top view of a 5-8-5 vacancy site of defective graphene with two missing C atoms at its center. (C) Icosahedral Cu_{55} nanoparticle. Brown and yellow colors represent Cu and C, respectively.

Figure 2 shows the lowest energy pathways of CO_2 reduction on the Cu_{55}–defective graphene surface and a comparison of the CO_2 reduction mechanisms between the Cu(111) (i.e., the most stable flat Cu surface among (100), (110), and (111) faces) and the Cu_{55}–defective graphene surfaces. Peterson *et al.*[15] extensively investigated the electroreduction of CO_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 Figure 2A. By transferring ($H^+ + e^-$) from solution to an adsorbed species, a gas-phase CO_2 molecule is converted to COOH* → CO* → CHO* → CH_2O* → CH_3O* → O* → OH* → H_2O_{gas}. The reaction intermediate configurations on the Cu(111) surface are also similar to those of Figure 2A (data not shown here).

At zero electrode potential (U = 0 V) in Figure 2B, the Cu(111) surface shows the key energy barrier of 0.97 eV required for the protonation step of the CO species (CO* → CHO*: (2) → (3) in Figure 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.*[15], which is due to the fact that a step-like surface of Cu(211) is more reactive toward binding adsorbates than a flat surface. In the Cu_{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* becomes more stabilized relative to CO* on the Cu_{55}–defective graphene surface compared to on the Cu(111) surface. This implies that the Cu_{55}–defective graphene system may help enhance the energy efficiency of the electrochemical reduction of CO_2 by lowering the key energy barrier. Instead, the Cu_{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* between steps (7) and (8) (i.e., OH* → H_2O) in Figure 2B. For this step, the Cu(111) surface requires 0.39 eV, while the Cu_{55}–defective graphene system requires 0.60 eV. Considering the endothermic reaction steps of both systems in Figure 2B, the rate-limiting steps of the CO_2 reduction on the Cu(111) surface and Cu_{55}–defective graphene system lie in the CO* → CHO* step.

Figure 2C shows the CO_2 reduction mechanisms at applied electrode potentials of U = –0.97 and –0.68 V for the Cu(111) surface and the Cu_{55}–defective graphene system, respectively. The applied potentials are required voltages for eliminating the energy barriers of the rate-limiting step (CO* → CHO*), which represents that the hydrocarbon CH_4-forming reaction from CO_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 °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 Supplementary Information Section 2.

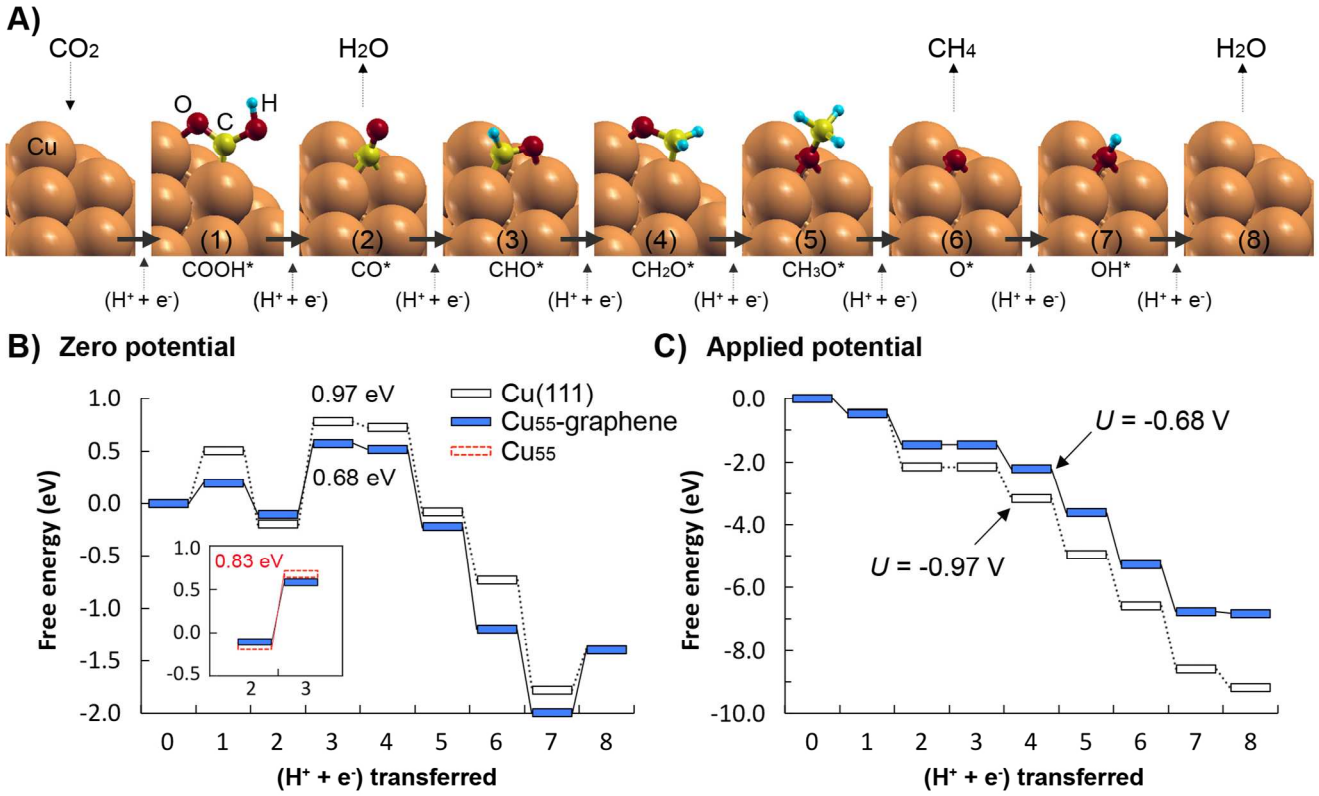


Figure 2. (A) The lowest energy pathways of CO_2 reduction on the Cu_{55}–defective graphene. (B and C) Relative free energy diagrams without (B) and with (C) applied potential for CO_2 reduction on Cu(111) (empty rectangle with dashed lines), Cu_{55}–defective graphene (filled rectangle with solid lines), and Cu_{55} cluster (empty rectangle in the inset).

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 Figure 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 Figure 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 Supplementary Information Section 3.

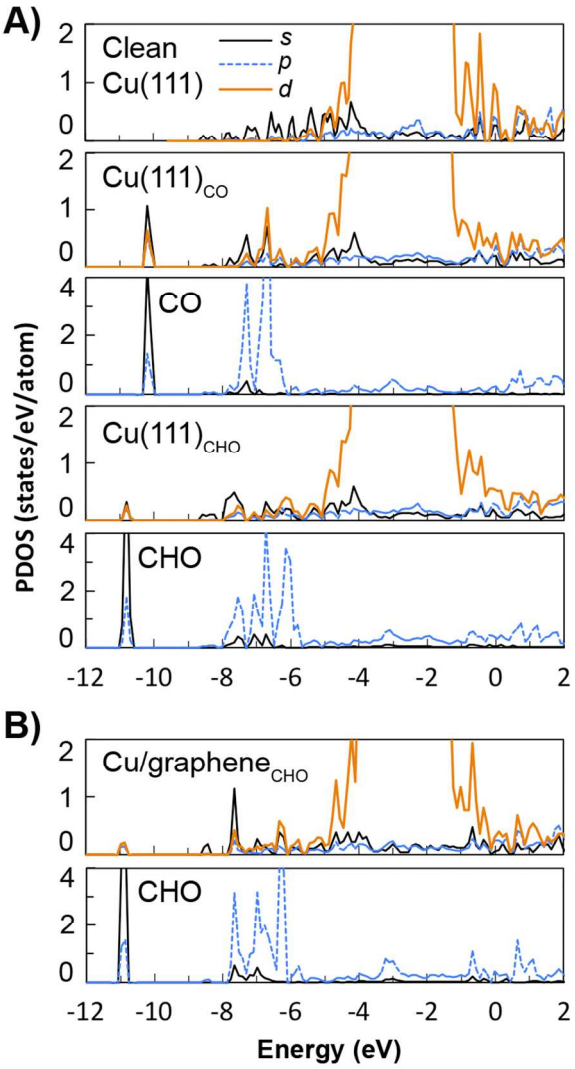


Figure 3. Projected density of states (PDOS) of the Cu(111) surface with adsorbed CO and CHO (A) and the Cu_{55}-graphene surface with CHO (B). A system title of X_Y indicates a surface (X) with adsorbed species (Y). Clean Cu, CO, and CHO represent clean Cu(111), adsorbed CO, and adsorbed CHO, respectively. The Fermi energy is referenced at 0 eV.

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 Figure 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 0.78 to 0.63 eV by modifying the electron properties of the anchored Cu_{55}. 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 Cu_{55} cluster and the Cu_{55}–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 Cu_{55}–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 Cu_{55}–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 Cu_{55}–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 Supplementary Information 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 in that 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 Gross[38] 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 Supplementary Information Section 3.

Furthermore, the reaction pathways toward the production of formic acid (HCOOH) and carbon monoxide (CO) gases are shown in Figure 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 Figure 4A and 4B, 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 experiments[14] in addition to previous DFT studies[15,16] in that the formation of HCOOH and CO gases requires about –0.4 ~ –0.5 V (*vs.* RHE). The COOH* species is more stable on the Cu_{55}–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 Cu_{55}–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 CO_2 reduction, the hydrogen evolution reaction (HER) significantly affects the electrochemical reduction of CO_2 since HER is competitive against CO_2 reduction. Effective CO_2 reduction catalysts should show poor activity for the competitive HER.[15-17] In terms of the selectivity of H_2 gas production, the Cu_{55}–defective graphene system shows a slightly poor activity for HER compared to the Cu(111) system as shown in Figure 4C, indicating limiting potentials of –0.22 and –0.24 V on the Cu(111) and Cu_{55}–defective graphene surfaces, respectively. In both cases, the potential limiting barriers for HER are present in the H_2 gas desorption step ($H^* + H \rightarrow H_{2(gas)}$), 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 Cu_{55}–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) surface[17] 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 surface,[15,17] but the magnitude is different due to the stronger hydrogen adsorption at the fcc hollow sites of the Cu(111) surface. Note that the potential limiting step for HER may vary slightly depending on the DFT functional; for example, Peterson et al.'s work using the revised PBE (RPBE) functional suggests a limiting potential of –0.03 V due to an endothermic adsorption of atomic hydrogen on the Cu(211) step site.[15] Nevertheless, we may conclude from Figure 4 that the Cu_{55}–defective graphene system promotes CO_2 reduction into hydrocarbon fuels by lowering the rate-limiting energy barriers and relatively slightly inhibiting HER, at least showing similar selectivity of H_2 compared to the Cu(111) surface.

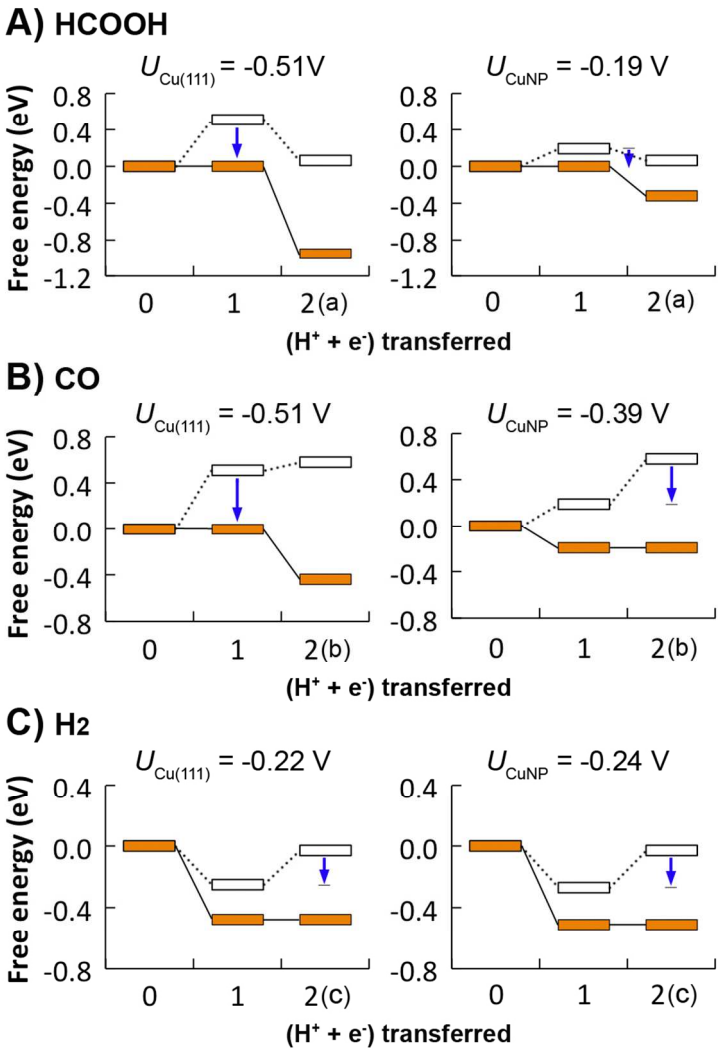


Figure 4. Relative free energy diagrams for HCOOH (A), CO (B), and H_2 (C) gas production on Cu(111) (left) and Cu_{55}–defective graphene (right). Empty rectangles (with dashed lines) and filled rectangles (with solid lines) represent reactions without and with applied potentials. (H^+ + e^-) transferred steps of 0 and 1 are the same steps as shown in Figure 2. The steps of 2(a), 2(b), and 2(c) represent $HCOOH_{(gas)}$ + surface, $CO_{(gas)}$ + $H_2O_{(gas)}$ + surface, and $H_{2(gas)}$ + surface, respectively. $U_{Cu(111)}$ and U_{CuNP} indicate necessary potentials to produce the gases on Cu(111) and Cu_{55}–defective graphene, respectively. Arrows show the potential-liming energy barriers that should be overcome for the gas production.

Lastly, it is worth noting the solvation effect in DFT modeling. Since an explicit treatment of a number of water molecules is still difficult to carry out using DFT, indirect methods may provide insight into better understanding the solvation effect. According to Peterson *et al.*'s solvation energy approximation on flat metal surfaces[15,31,39], OH*, R-OH*, CO*, and CHO* gas-phase adsorbates may be stabilized in liquid water by approximately 0.5, 0.25, 0.1, and 0.1 eV, respectively. The current work employs this simple approximation for the adsorbed species and uses chemical potentials of the gas-phase molecules calculated in the work of Peterson *et al.*[15] where standard ideal-gas methods[40] were used to convert electronic energies of gas-phase molecules into chemical potentials at 18.5 °C (e.g., the free energy of liquid water was calculated as an ideal gas and adjusted to a fugacity of 3,534 Pa, which is the vapor pressure of water) (see Supplementary Information Section 1). If the solvation correction is not considered, the energy barrier of the first $H^+ + e^-$ transfer step (i.e., $CO_2 \rightarrow$ COOH*) is overestimated resulting in the required potential of –0.76 V for the HCOOH and CO formation on the Cu(111) surface, which does not agree with the experimental observation (between –0.4 ~ –0.5 V).[3] Overall, the solvation energy correction lowers the reaction energy states and the reaction energy barriers become smaller; however, the relatively large solvation energy of OH* causes an increase in the energy barrier for H_2O desorption. In other words, the desorption energy of H_2O from catalytic surfaces may be underestimated if the solvation effect is not taken into account. A detailed comparison between with and without solvation is provided in Supplementary Information Section 5.

Conclusions

The current work provides theoretical evidence for improved CO_2 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 CO_2 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 CO_2 conversion mechanisms and the key factor regarding the geometry flexibility for the enhanced CO_2 conversion may help design promising materials for CO_2 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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Supplementary Information Available

Details of DFT calculation methods, CO_2 reduction pathways, PDOS, and solvation effect diagrams are available via the Internet at http://pubs.rsc.org.

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