Electronic Supplementary Information (ESI) Electrochemical CO_2 reduction on Cu single atom catalyst and Cu nanoclusters: an *ab initio* approach.

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ESI1 Computational Hydrogen Electrode Approach

The computational hydrogen electrode (CHE) enables the modelling of electrochemical reactions by quantitatively incorporating insights from first-principles calculations [1–8]. The main part of this approach is a specified reaction mechanism and the evaluation of the free energy of the corresponding elementary steps, $\Delta G = \Delta H - T\Delta S$. The form of introducing electronic structure information into the model is via the free energy of each species involved on each elementary step:

$$G_i = H_i - TS_i \tag{1}$$

with the enthalpy of the i species is defined as

$$H_i = E_{el} + E_{solv} + E_{ZPE} + E_{thermal} + PV$$
⁽²⁾

where E_{el} , E_{solv} , E_{ZPE} , $E_{thermal}$ and PV correspond to the electronic energy, solvation energy, zero point vibrational energy and PV.

Here, the calculation of the electronic energy can be performed at a very high level with direct wavefunction based approaches such as post Hartree-Fock methods, however, these kind of calculations imply a large computational cost. On the other hand, density functional theory (DFT) approaches provide a cost-effective alternative, making them the main choice of combination with CHE calculations [6, 7].

In the case of electrochemistry, the solvent effects are important. These interactions are included in the term E_{solv} , and can be evaluated either by explicit models such as the inclusion of a bilayer of water or through implicit solvation models.

The term E_{ZPE} considers, from quantum mechanics, that even at temperatures close to absolute zero the oscillators have a residual motion, the sum of all those energies is defined as:

$$E_{ZPE} = \frac{1}{2} \sum_{i=1}^{3N-6} h\omega_i$$
 (3)

where N is the total number of atoms of the system, ω_i the vibrational frequencies of the system and h the plank constant.

Whereas the thermal energy $E_{thermal}$ includes translational, rotational and vibrational contributions:

$$E_{rot}^{linear} = RT \tag{4}$$

$$E_{rot} = \frac{3}{2}RT\tag{5}$$

$$E_{vib} = \sum_{i=1}^{3N-6} \left\{ \frac{h\omega_i}{k_B \left[\exp\left(\frac{h\omega_i}{k_B T}\right) - 1 \right]} \right\}$$
(6)

where k_B , h and R are the Boltzmann, Planck and gas constants. The vibrational frequencies ω_i can be efficiently calculated via DFT using the harmonic oscillator approximation by diagonalization of the mass-weighted Hessian matrix in internal coordinates.

The corresponding translational, rotational and vibrational contributions to the entropy S_i are:

$$S_{trans} = R \left\{ \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \frac{V}{N_A} \right] + \frac{5}{2} \right\}$$
(7)

$$S_{rot}^{linear} = R \left[\ln \left(\frac{8\pi^2 I k_B T}{h^2 \sigma} \right) + 1 \right]$$
(8)

$$S_{rot} = R \left\{ \ln \left[\frac{\sqrt{\pi I_A I_B I_C}}{\sigma} \left(\frac{8\pi^2 k_B T}{h^2} \right)^{\frac{3}{2}} \right] + \frac{3}{2} \right\}$$
(9)

$$S_{vib} = R \sum_{i=1}^{3N-6} \left\{ \frac{h\omega_i}{k_B T \left[\exp\left(\frac{h\omega_i}{k_B T}\right) - 1 \right]} - \ln\left[1 - \exp\left(-\frac{h\omega_i}{k_B T}\right) \right] \right\}$$
(10)

where *m* is the mass of the species, *P* is the pressure, I_x , I_y , I_z are the three principal moments of inertia for nonlinear molecule, *I* is the moment of inertia for the linear molecule and σ is the rotational symmetry number.

For the enthalpy of the gaseous molecules (H_i) , E_{solv} is neglected and PV is set to RT assuming an ideal gas. For the solvated adsorbed species, the PV term is also excluded. However, for the thermal energy and entropy terms, only the vibrational component is considered.

Within the CHE approach, the general reduction scheme of the reactant A can be considered as follows:

$$A + * + H^{+} + e^{-} \longrightarrow AH*$$
(11)

where * indicates a surface site and AH* denotes that AH binds to the electrode surface.

For this reduction reaction ΔG is calculated as follows:

$$\Delta G = G_{AH*} - G_A - G_* - \mu_{\rm H^+} - \mu_{\rm e^-} \tag{12}$$

where $\mu_{\rm H^+}$ and $\mu_{\rm e^-}$ are the chemical potentials of the protons and electrons gained during the reaction, respectively. Here, the free energies of A and the adsorbed species are easily calculated with the use of standard DFT techniques. Nonetheless, the calculation of the chemical potentials of the protons and electrons with the use of standard *ab initio* techniques is far from trivial.

In order to overcome this situation we make use of the CHE model, which allows to circumvent the explicit treatment of the solvated protons [1, 6–8]. In this technique, zero voltage is defined based on the reversible hydrogen electrode (RHE), in which the reaction $H^+ + e^- \longrightarrow 1/2 H_2$ is defined to be in equilibrium at zero voltage, at any given values of pH, at all temperatures, and with H₂ at 101325 Pa pressure.

As a result, in the CHE model, the chemical potential of a proton-electron pair, $\mu_{H^+} + \mu_{e^-}$ is equal to half of the chemical potential of gaseous hydrogen (1/2 μ_{H_2}) at a potential of 0 V. In this way, the chemical potential of the proton-electron pair can be calculated simply by calculating the chemical potential of gas-phase H₂. The chemical potential of the proton-electron pair can be adjusted as a function of the applied potential by the standard relation between chemical and electrical potential, $\Delta G = -eU_{RHE}$, where *e* is the elementary positive charge and U_{RHE} is the applied bias. Since the RHE is defined to be at 0 V at all pH values, a pH correction is not needed. Hence, the total chemical potential of the proton-electron pair as a function of applied potential, at all temperature and pH values, can be calculated as:

$$\mu_{\rm H^+} + \mu_{\rm e^-} = \frac{1}{2}\mu_{\rm H_2} - eU_{RHE}$$
(13)

As described above, the reversible hydrogen electrode (RHE) potential does not depend on pH, since the RHE scale is simply normalized by the activity of the protons, however if we want to include the pH effects we can simply change the reference electrode to the standard hydrogen electrode (SHE) which is linked to the RHE scale by:

$$U_{RHE} = U_{SHE} - \frac{k_B T}{ne} log\left(\frac{a_{\rm H^+}}{\sqrt{p({\rm H}_2)}}\right) = U_{SHE} + k_B T ln(10)pH$$
(14)

where k_B is the Boltzmann constant, *T* is the temperature, *n* is the number of electrons transferred in the reaction, a_{H^+} is the proton activity, and p(H₂) is the pressure of hydrogen at 1 bar [7].

ESI2 Nanocluster design

Vacuum local minima nanocluster structures are displayed in the Figure ESI2.



Figure ESI1: Low energy structures of Cu_n nanoclusters for n = 4-13.

The binding energy of the optimized nanoclusters was calculated, showing good agreement with the experimentally determined values, Table ESI1. The binding energies (ΔE_{b_n}) of the different nanoclusters were calculated as (Eq. (15)):

$$\Delta E_{bind_n} = \frac{E_{\text{nanocluster}} - n \cdot E_{\text{single atom}}}{n} \tag{15}$$

where, $E_{\text{nanocluster}}$ and $E_{\text{single atom}}$ are the electronic energies of a single Cu atom, and a Cu_n nanocluster, whereas n is the number of total atoms of the nanocluster.

Table ESI1: Calculated binding energies for $Cu_n(n=4-13)$ nanoclusters

n	ΔE_b (eV	/ atom ⁻¹) Exp.[9]
4	-1.39	-1.48
5	-1.68	-1.56
6	-1.82	-1.73
7	-2.04	-1.86
8	-2.14	-2.00
9	-2.16	-
10	-2.19	-
11	-2.22	-
12	-2.25	-
13	-2.28	-

ESI3 Cu nanocluster building

Studying the formation of a Cu cluster by the aggregation of individual atoms could lead to different final structures (and possibly more stable that the Cu_{13} nano cluster used in this work). It is important to note that each time that an atom is added a large number of conformations to optimize is generated. For instance, creating a Cu_2N_4 structure from the CuN_4 surface implies at least testing 4 different initial configurations, See Figure ESI1.



(a) On top configuration.



(c) 5 fold hollow configuration.



(b) Bridge Cu-N configuration.



(d) 6 fold hollow configuration.

Figure ESI2: Schematic representation of the initial configurations of the Cu_2N_4 nanocluster and the CuN_4 surface. Colour code: black, carbon; grey, nitrogen; blue, copper, the atom in green represents the newly added Cu atom.

After optimization, the resulting structure could have lower symmetry than the CuN_4 increasing the degrees of freedom where a new Cu atom can be adsorbed. As a result, this methodology limits the possibilities for sampling all the resulting conformations, within a reasonable amount of computational time.

ESI4 Cu vacancy on the single site catalyst



(a) Geometry of the optimized Cu_{13} nanocluster.

(b) Top view, Cu vacancy

Figure ESI3: Schematic representation of the optimized geometry of the Cu_{13} nanocluster and the Cu vacancy on the N-C surface. Colour code: black, carbon; grey, nitrogen; blue, copper.

ESI5 Initial adsorption configurations for Cu₁₃ nanoclusters



(a) Single atom interaction





(c) three atom interaction

Figure ESI4: Schematic representation of the different initial configurations of the Cu_{13} nanocluster. Highlighted regions in green corresponds to those set to interact to with the catalyst surface

(b) Two atom interaction

Once that the set of initial structures were build, the systems were allowed to relax till the energy convergence and maximum force criteria were achieved. From the relaxed sites, only the configurations with a negative value for the adsorption energy were retained for further consideration. As a result, a collection of stable configurations was found for each nanocluster on the surface, but only the most stable configuration was selected for further studies.

ESI6 Cu nanoclusters on N doped carbon graphite-like systems, screening

The adsorption energies (ΔE_{ads_i}) of the different adsorbates (including the Cu₁₃ nanoclusters) were calculated as (Eq. (16)):

$$\Delta E_{ads_i} = E_{i+slab} - \left(E_{slab} + E_{i_a}\right) \tag{16}$$

in which E_{i+slab} , E_{slab} and E_{i_g} are the electronic energies of the slab-adsorbate system, the bare slab and the species *i* in gas phase, respectively.



Figure ESI5: Low energy structure of a Cu₁₃ nanocluster adsorbed. $\Delta E_{ads} = -4.94$ eV.



Figure ESI6: Low energy structure of a Cu₁₃ nanocluster adsorbed. $\Delta E_{ads} = -4.88$ eV.



Figure ESI7: Low energy structure of a Cu₁₃ nanocluster adsorbed. $\Delta E_{ads} = -4.86$ eV.



Figure ESI8: Low energy structure of a Cu₁₃ nanocluster adsorbed. $\Delta E_{ads} = -4.85$ eV.



Figure ESI9: Low energy structure of a Cu₁₃ nanocluster adsorbed. $\Delta E_{ads} = -4.82$ eV.



Figure ESI10: Low energy structure of a Cu $_{13}$ nanocluster adsorbed. $\Delta E_{ads}=-4.73$ eV.



Figure ESI11: Low energy structure of a Cu₁₃ cluster adsorbed. $\Delta E_{ads} = -4.70$ eV.



Figure ESI12: Low energy structure of a Cu $_{13}$ nanocluster adsorbed. $\Delta E_{ads}=-4.67$ eV.



Figure ESI13: Low energy structure of a Cu $_{13}$ nanocluster adsorbed. $\Delta E_{ads}=-4.63$ eV.



Figure ESI14: Low energy structure of a Cu₁₃ nanocluster adsorbed. $\Delta E_{ads} = -2.54$ eV.



Figure ESI15: Low energy structure of a Cu₁₃ nanocluster adsorbed. $\Delta E_{ads} = -2.80$ eV.



Figure ESI16: Low energy structure of a Cu₁₃ nanocluster adsorbed. $\Delta E_{ads} = -4.97$ eV.

ESI7 Optimized structures of the intermediate species involved on the 2 proton 2 electron reduction of CO₂

The structures of adsorbed CO_2^- on the CuN_4 and the $Cu_{13}N_4$ surfaces were obtained by removing an H atom from the previously optimized *COOH and *HCOO species, and performing a single point calculation, see Figures ESI19 and ESI20. This methodology has shown its capabilities to reproduce experimental observations. [10]. This methodology is applied to overcome the lack of stability of CO_2^- species which desorbs upon relaxation, which under reductive potentials (actual reaction conditions) would be stabilized on the surface. A Bader charge analysis was performed and it was found that the adsorbate (CO_2) gains between 0.63 and 0.74 electrons from the surface (in all the cases)

ESI7.1 CO_2^- adsorption



Figure ESI17: Optimized structures of CO_2^- adsorbed (CO formation path) on the CuN_4 and on the $Cu_{13}N_4$ surfaces. Colour code: black, carbon; gray, nitrogen; blue, copper and red, oxygen.



Figure ESI18: Optimized structures of CO_2^- adsorbed (HCOOH formation path) on the CuN_4 and the $Cu_{13}N_4$ surfaces. Colour code: black, carbon; grey, nitrogen; blue, copper and red, oxygen.

ESI7.2 COOH, HCOO and CO adsorption



Figure ESI19: Optimized structures of COOH adsorbed on the CuN_4 and $Cu_{13}N_4$ surfaces. Colour code: black, carbon; grey, nitrogen; blue, copper, red, oxygen and white, hydrogen.



Figure ESI20: Optimized structures of HCOO adsorbed on the CuN_4 and $Cu_{13}N_4$ surfaces. Colour code: black, carbon; grey, nitrogen; blue, copper, red, oxygen and white, hydrogen.



Figure ESI21: Optimized structures of CO adsorbed on the CuN_4 and $Cu_{13}N_4$ surfaces. Colour code: black, carbon; grey, nitrogen; blue, copper and red, oxygen.

ESI8 Optimized structures of selected intermediate species involved on the reduction of CO to C₂ species



Figure ESI22: Optimized structure of 2 CO coadsorbed species on the $Cu_{13}N_4$ surface. Colour code: black, carbon; grey, nitrogen; blue, copper and red, oxygen.

Analogous calculations to those performed to obtain the CO_2^- species were used in the calculation of the COCO⁻ adsorbed species, by removing an H atom to the COCOH adsorbed species.



Figure ESI23: Optimized structure of COCO⁻ adsorbed on the Cu₁₃N₄ surface. Colour code: black, carbon; grey, nitrogen; blue, copper and red, oxygen.



Figure ESI24: Optimized structure of COCOH adsorbed on the $Cu_{13}N_4$ surface. Colour code: black, carbon; grey, nitrogen; blue, copper; red, oxygen and white, hydrogen.

ESI9 Cu(111) reaction profile



Figure ESI25: Calculated free energy profiles at -1.20 V vs RHE for CO_2 reduction to HCOOH and CO on Cu(111). Energy levels are reported in eV and were calculated with $CO_{2(g)}$ and the respective surface (*) as reference.

ESI10 HER reaction profile

The Gibbs free energy of reaction has been calculated for the HER on each of the studied surfaces. It has been found that the $Cu_{13}N_4$ cluster has the lowest thermodynamic barrier towards the adsorption of H⁺ on the

surface, which can be associated with the lowest coordination Cu sites available on the surface. Nevertheless, this high affinity for *H can avoid the interaction between 2 adsorbed H atoms and hence, the formation of H_2 can be avoided.



Figure ESI26: Calculated free energy profiles at -1.20 V vs RHE for hydrogen evolution reaction (HER) on the CuN_4 , $Cu_{13}N_4$ and Cu(111) surfaces. Energy levels are reported in eV and were calculated with $H_2O_{(aq)}$ and the respective surface (*) as reference.

ESI11 C-C coupling paths

As described on the main text there are several combinations in which the C-C coupling can take place. In this regard, the free energies of reaction for each of these elementary steps have been calculated, Figure ESI27.



Figure ESI27: Proposed reaction network for C-C coupling reactions on the $Cu_{13}N_4$ catalyst at 1.20 V vs vs RHE. The numbers in bold corresponds to the calculated free energies of reaction in eV.

The first competitive reaction corresponds to the proton coupled electron transfer (PCET) of *CO *vs* the coadsorption of CO. For this reaction the calculated free energies of reaction at 1.20 eV *vs* amount to -1.15 and -0.37 eV for the PCET of *CO and the coadsorption of CO, respectively. Making the first reaction more favourable. However, in this path the coupling steps are endergonic and independent of the applied potential, making this path thermodynamically unfavourable. On the other hand, the coupling between 2 coadsorbed CO species has a lower free energy of reaction and it can be enhanced at more negative potentials. Furthermore, several initial configurations for the adsorption of *COH and *CO were tested resulting on the formation of *COCOH upon relaxation, hence this path was discarded. As a result, in the main text only this path has been reported.

ESI12 Free energy corrections for molecules and adsorbed species involved on the CO_2RR

species	E_{ZPE} (eV)	$\int C_v dT$ (eV)	-TS (eV)
H _{2(g)}	0.28	0.11	-0.53
$H_2O_{(aq)}$	0.56	0.08	-0.58
$CO_{2(g)}$	0.31	0.11	-0.75
CO _(g)	0.15	0.10	-0.69
HCOOH _(aq)	0.90	0.15	-0.89
$C_2H_4O_{2(aq)}$	0.96	0.12	-0.85
$C_2H_5OH_{(aq)}$	2.11	0.12	-0.82
$C_2H_4O_{(aq)}$	1.46	0.11	-0.79
C ₂ H _{4(g)}	1.35	0.08	-0.70

Table ESI2: Free energy corrections for molecules at T = 298.15

Table ESI3: Free energy corrections for adsorbed species on ${\rm CuN_4}$ at T=298.15

species	E_{ZPE} (eV)	$\int C_v dT$ (eV)	-TS (eV)
*	0.00	0.00	0.00
$*CO_2^-$	0.26	0.11	-0.23
*COOH	0.59	0.12	-0.26
*OCOH	0.58	0.12	-0.27
*CO	0.20	0.07	-0.15

Table ESI4: Free energy corrections for adsorbed species on $\rm Cu_{13}N_4$ at T=298.15

species	E_{ZPE} (eV)	$\int C_v dT$ (eV)	-TS (eV)
*	0.00	0.00	0.00
$*CO_2^-$	0.27	0.09	-0.18
*COOH	0.62	0.10	-0.20
*OCOH	0.61	0.10	-0.19
*CO	0.27	0.09	-0.18
*CO, CO	0.62	0.10	-0.20
*CO-CO ⁻	0.62	0.10	-0.20
*CO-CO-H	0.71	0.13	-0.24
*H-CO-CO-H	1.05	0.13	-0.24
*C-C-OH	0.60	0.11	-0.19
*H-C-C-OH	0.96	0.21	-0.41
*H-C-C	0.47	0.07	-0.13
*H ₂ C-С	0.78	0.07	-0.13
*H ₂ C-CH	1.08	0.09	-0.19
*C-C-O	0.34	0.09	-0.18
*CH-C-O	0.61	0.10	-0.21
*CH ₂ -CH-O	1.21	0.11	-0.22
*CH ₃ -CH-O	1.50	0.14	-0.32
$*CH_3-CH_2-O$	1.85	0.13	-0.27
$*CH_2-CH_2$	1.48	0.11	-0.23
*0	0.08	0.02	-0.04
*О-Н	0.33	0.06	-0.12
*9b	1.53	0.13	-0.27
*10b	1.84	0.13	-0.26

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