Electronic Supplementary Information

for

A Mechanistic Study of B₃₆-Supported Atomic Au Promoted CO₂ Electroreduction to Formic Acid

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Computational details:

All calculations were performed with the Grimme's D3-dispersion corrected M06-2X functional in conjunction with the basis sets of 6-311G(d, p) (for B, C, O, and H) and Lanl2dz (for Au, Ag, and Cu) using the Gaussian 16 program.^{S1} In the present study we employed the Lanl2dz ECP which is a commonly used method for Au atom/nanoparticle calculations.^{S2,S3} The relativistic effect (mass-velocity contractions and Darwin corrections) has been taken into account.^{S3} Vibrational frequency analyses were carried out at the same level of theory and the zero-point energy (ZPE) and thermal free-energy corrections were taken into account to evaluate the binding energies and reaction free energies. In addition, the solvent effect using the SMD model (solvent = water) was corrected for all relevant structures along the CRR pathways (Fig. 2 and Fig. 3).

Considering the CRR process contains proton-coupled electron transfer steps, the computational hydrogen electrode (CHE) model proposed by and the Nørskov et al. was applied to evaluate the electrochemical free energies.^{S4} The CHE model provides a readily strategy to treat the solvated protons and has been widely accepted in electrochemical calculations, no matter in periodic or cluster systems. The free energy of the proton-electron pair (H⁺ + e⁻) was estimated as the energy of half gaseous H₂ at standard condition.^{S4} For example, the reaction * + CO₂ + (H⁺ + e⁻) \rightarrow *OCHO is treated as a hydrogenation reaction * + CO₂ + 1/2 H₂ \rightarrow *OCHO. Note that in general the ΔG is a function of the applied electrical potential $\Delta G(U) = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} + \Delta G_U$, where ΔG_U was defined as *-neU* to describe the electrical potential

with respect to standard hydrogen electrode (SHE), here U = 0 was considered. Moreover, the mechanism we proposed is in acid medium (pH = 0) and the term ΔG_{pH} is set to 0.

As reported previously,^{S5} DFT calculations on the enthalpies of OCO-containing gas-phase molecules (e.g. CO₂, HCOOH) are remarkably inconsistent with experiments. Here to check the inaccuracy and to quantify an optimal correction value, enthalpy corrections were carried out by using the approach proposed by Nørskov and co-workers.^{S6} As listed in Table S1, a set of 21 reactions (14 reactions affected by the OCO-containing molecules and 7 bystander reactions) were taken into account. For the 14 affected reactions, we compared the calculated (M06-2X-D3/6-311G(d,p)) and experimental (taken from NIST^{S7}) reaction enthalpies to find an optimal correction with the lowest mean absolute value (and with the lowest standard deviation if the mean absolute values are same). For the 7 unaffected reactions, we also calculated the absolute error between theoretical and experimental data for each reaction, to ensure the current computational level is reliable with a small enough error (0.20 eV was used as the criterion in ref S4). For the 7 bystander reactions, the mean absolute errors of reaction enthalpies is 0.17 eV, suggesting the current method is reliable to describe the free energies of species. For the 14 affected reactions, we found the optimal correction is +0.35 eV (Table S2), which gives rise to a remarkable reduction of the mean absolute error from the original 0.27 to 0.08 eV. Therefore the correction of +0.35 eV was applied to CO₂ and HCOOH in the present work.

Reaction	Stoichiometry
1	$CO_2 + H_2 \rightarrow CO + H_2O$
2	$4 \text{ H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2 \text{ H}_2\text{O}$
3	$CO_2 + H_2 \rightarrow HCOOH$
4	$CO + H_2O \rightarrow HCOOH$
5	$3 \text{ H}_2 + \text{CO}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$
6	$3 H_2 + CO_2 \rightarrow 1/2 CH_3 CH_2 OH + 3/2 H_2 O$
7	$10/3 \text{ H}_2 + \text{CO}_2 \rightarrow 1/3 \text{ C}_3\text{H}_8 + 2 \text{ H}_2\text{O}$
8	$7/2 H_2 + CO_2 \rightarrow 1/2 C_2H_6 + 2 H_2O$
9	$3 H_2 + CO_2 \rightarrow 1/2 C_2H_4 + 2 H_2O$
10	$11/4 \text{ H}_2 + \text{CO}_2 \rightarrow 1/4 \text{ CH}_2 = \text{CHCH} = \text{CH}_2 + 2 \text{ H}_2\text{O}$
11	$2 \text{ H}_2 + \text{CO}_2 \rightarrow 1/2 \text{ CH}_3 \text{COOH} + \text{H}_2 \text{O}$
12	$CO + H_2 \rightarrow 1/2 CH_3COOH$
13	$2 \text{ H}_2 + \text{CO}_2 \rightarrow 1/2 \text{ HCOOCH}_3 + \text{H}_2\text{O}$
14	$CO + H_2 \rightarrow 1/2 HCOOCH_3$
15	$3 \text{ H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$
16	$2 H_2 + CO \rightarrow CH_3OH$
17	$2 \text{ H}_2 + \text{CO} \rightarrow 1/2 \text{ CH}_3\text{CH}_2\text{OH} + 1/2 \text{ H}_2\text{O}$
18	$7/3 \text{ H}_2 + \text{CO} \rightarrow 1/3 \text{ C}_3\text{H}_8 + \text{H}_2\text{O}$
19	$5/2 \text{ H}_2 + \text{CO} \rightarrow 1/2 \text{ C}_2\text{H}_6 + \text{H}_2\text{O}$
20	$2 \text{ H}_2 + \text{CO} \rightarrow 1/2 \text{ C}_2\text{H}_4 + \text{H}_2\text{O}$
21	$7/4 H_2 + CO \rightarrow 1/4 CH_2 = CHCH = CH_2 + H_2O$

 Table S1. Selected reactions for enthalpy correction

Table S2. Uncorrected (ΔH (expt.) and ΔH (calc.)) and corrected (ΔH (cor.), with +0.35 eV for CO₂, HCOOH, CH₃COOH, and HCOOCH₃) reaction enthalpies (units in eV) of the reactions listed in Table S1. Reaction ΔH (expt.) ΔH (calc.) error ΔH (cor.) error 1 0.43 0.66 0.23 0.31 0.12 2 -1.71 -1.27 0.44 -1.62 0.09 3 0.15 0.18 0.03 0.18 0.03 4 -0.27 -0.48 -0.13 0.14 0.21

-0.24

-0.57

-0.88

-0.95

-0.20

-0.19

-0.45

-1.11

-0.09

-0.76

-1.93

-0.90

-1.23

-1.54

-1.61

-0.86

-0.85

0.31

0.32

0.42

0.42

0.46

0.46

0.22

0.01

0.08

0.16

0.21

0.08

0.09

0.18

0.19

0.23

0.23

-0.59

-0.92

-1.23

-1.30

-0.55

-0.54

-0.62

-0.94

-0.27

-0.58

-1.93

-0.90

-1.23

-1.54

-1.61

-0.86

-0.85

0.04

0.03

0.07

0.07

0.11

0.11

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0.10

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Reference

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-0.55

-0.89

-1.30

-1.37

-0.66

-0.65

-0.67

-1.10

-0.17

-0.6

-2.14

-0.98

-1.32

-1.72

-1.80

-1.09

-1.08

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Figure S1. Calculated NPA charge distribution of (a) B₃₆ and (b) B₃₆Au.



Figure S2. Structures, relative energies, and conformational population based on Boltzmann distribution of $B_{36}Au$ configurations in which the gold atom resides in the (a) corner, (b) edge, (c) central vacancy, and (d) concave center.



Figure S3. Structures and relative energies of (a-c) $B_{36}Au_2$ and (d-e) $B_{36}Au_3$ configurations.



Figure S4. Structures and relative energies of $B_{36}Au_6$ configurations.



Figure S5. Per-Au binding energies $(E_b/Au = [E(B_{36}Au_n) - E(B_{36}) - nE(Au)]/n)$ of all $B_{36}Au_n$ structures (a-f: n = 1-6).



Figure S6. Per-Ag binding energies $(E_b/Ag = [E(B_{36}Ag_n) - E(B_{36}) - nE(Ag)]/n)$ of $B_{36}Ag_n$ (n = 1,2) structures.



Figure S7. Per-Cu binding energies $(E_b/Cu = [E(B_{36}Cu_n) - E(B_{36}) - nE(Cu)]/n)$ of $B_{36}Cu_n$ (n = 1,2) structures.



Figure S8. Structures and reaction free energies of (a) $B_{36}Au-CO_2$, (b) $B_{36}Au-H_2O$, (c) $B_{36}-CO_2$, and (d) $B_{36}-H_2O$.



Figure S9. Calculated NPA charge distribution of (a) $B_{36}Au$ -CO₂, (b) $B_{36}Au$ -OCHO, and (c) $B_{36}Au$ -COOH.



Figure S10. (a) Structure and (b) NPA charge distribution of $Au@C_{22}H_{12}$.



Figure S11. SOMO diagrams of (a) B₃₆Au and (b) Au@C₂₂H₁₂



Figure S12. Migration of the Au from corner to edge site.

Motif –	NPA charge (e)		
	B ₃₆ -Au-CO ₂	B ₃₆ -Au-OCHO	B ₃₆ -Au-COOH
B ₃₆	-0.44	-0.14	-0.09
Au	+0.40	+0.80	+0.50
others	+0.04	-0.66	-0.41

Table S3. Fragmental NPA charge of $B_{36}Au$ -CO₂, $B_{36}Au$ -OCHO, and $B_{36}Au$ -COOH

Table S4. Calculated vertical electron affinities (EA) and ionic potentials (IP) of COOH and OCHO radicals

	СООН	ОСНО
Vertical EA (eV)	0.10	2.51
Vertical IP (eV)	10.22	13.69