Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electrochemical Reduction of CO_2 on Graphene Supported Transition Metals - Towards Single Atom Catalysts

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Table S1 Magnetic moments of the metal atom M and the three nearest C atoms for the system of single metal atoms supported at single vacancy sites of graphene.

	μ [C1] (μ_B)	μ [C2] (μ_B)	μ [C3] (μ_B)	μ [M] (μ_B)	μ [M][a] (μ_B)
Ag	0.23	0.23	0.17	0.17	-
Cu	0.20	0.20	0.20	0.33	-
Pd	0.00	0.00	0.00	0.00	-
Pt	0.00	0.00	0.00	0.00	-
Co	0.05	0.05	0.05	0.34	0.34

[a] *from reference:* Back, S.; Lim, J.; Kim, N.-Y.; Kim, Y.-H.; Jung, Y. *Chemical Science* **2017**, *8*, 1090.

Table S2 Comparison of binding energy of a metal atom on a 5×5 defective graphene (M@G), a 8×8 defective graphene (M@G128) and on a pristine graphene (M@pG). Different binding sites on the pristine graphene are investigated and the lowest adsorption energy (most favorable) is reported for each species. The energy difference between different binding sites is listed as ΔE_b [M] for the pristine graphene.

	M@G	M@G128	M@pG	
	E_b [M] (eV)	E_b [M] (eV)	E_b [M] (eV)	ΔE_b [M] (eV)
Ag	-0.32	-0.11	-2.20	0.01
Cu	0.46	0.70	-2.97	0.22
Pd	2.13	2.23	-2.26	0.29
Pt	2.26	2.32	-3.55	0.78
Co	2.96	3.02	-3.66	0.55

*Note that the binding energy is defined as $E_b[M] = E_{V_C} + \mu_M - E_{M_C}$.

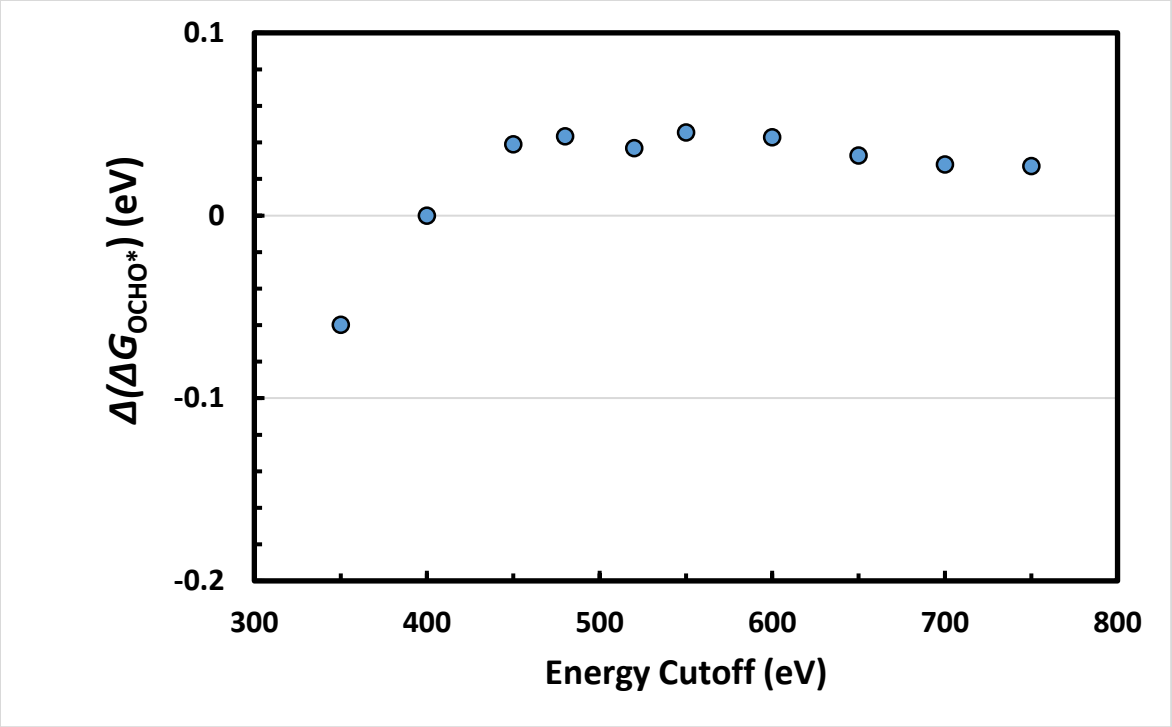

Figure S1. Variation of the formation free energy of OCHO* as a function of the energy cutoff value in the plane-wave calculations. The calculated value at a cutoff of 400 eV is set to reference zero for easy comparison.

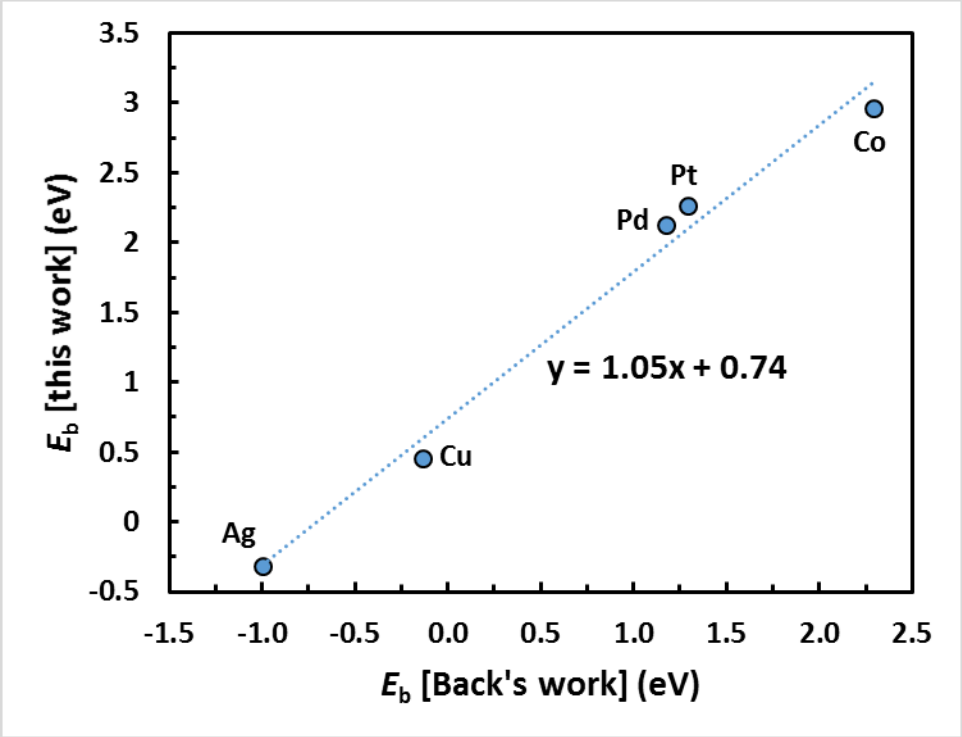

Figure S2. Comparison of the binding energies of metal atoms on single vacancy sites of graphene from our work and Back's work (ref. 16). To be consistent with the definition of the binding energy in our paper, we have reversed the signs of the values reported by Back *et al*.

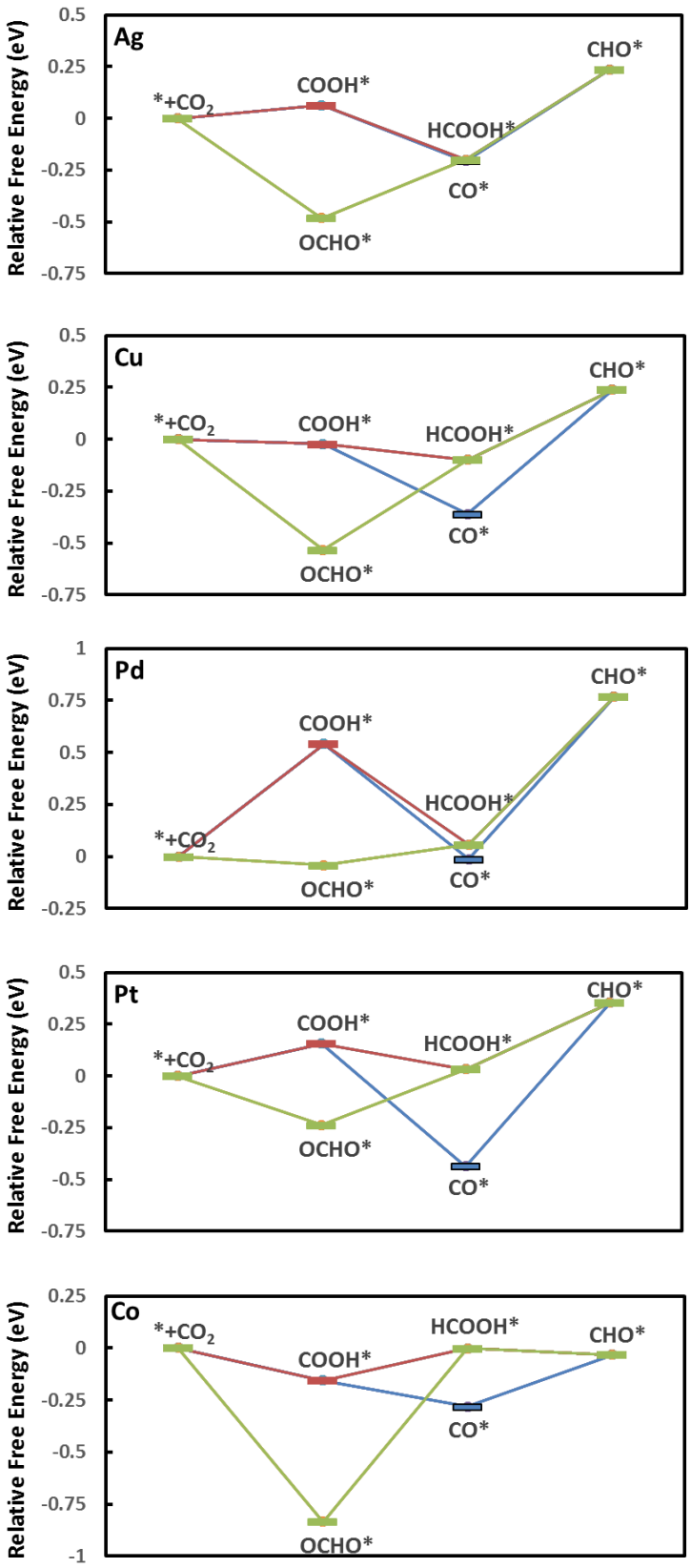

Figure S3 Three pathways to generate CHO* for single metal atom supported on graphene.

Blue: COOH*→CO*→CHO*;

Red: COOH*→HCOOH*→CHO*;

Green: OCHO*→HCOOH*→CHO*.

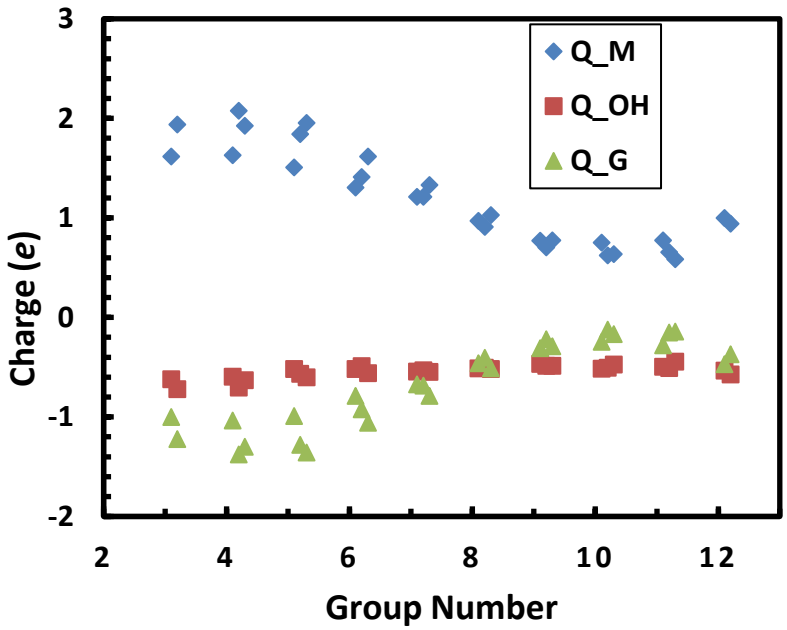

Figure S4 Variation of charges on the metal dopant (Q_M), on the OH group (Q_OH) and on the defective graphene (Q_G) as a function of the group number of elements. Note that the elements in the same group are slightly shifted in accordance with their period number for clarity.