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

Supplementary information

Enhanced CO adsorption on α-graphyne-supported and defective graphene-supported Cu_{19} clusters and modified induction energy model

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Table S1. Bader charge (e^-) distribution for each Cu atom of Cu_{19} in Cu_{19}/αGY and Cu_{19}/G. The "–" indicates charge transfer from Cu_{19} to α-graphyne and defective graphene in Cu_{19}/αGY and Cu_{19}/G relative to the pure Cu_{19} cluster.

Atom	Charge transfer to Cu_{19}/αGY	Charge transfer of Cu_{19}/G
Cu–1	-0.012	0.013
Cu–2	0.018	0.023
Cu–3	-0.008	-0.006
Cu–4	-0.007	0.022
Cu–5	0.022	0.019
Cu–6	0.002	0.003
Cu–7	-0.010	-0.036
Cu–8	0.027	0.010
Cu–9	-0.001	0.013
Cu–10	-0.001	0.003
Cu–11	0.019	0.014
Cu–12	-0.011	-0.018
Cu–13	0.006	-0.042
Cu-14	-0.193	-0.203
Cu-15	-0.219	-0.195
Cu-16	-0.210	-0.161
Cu-17	-0.233	-0.202
Cu-18	-0.206	-0.212
Cu-19	-0.121	-0.534
Total	-1.14	-1.49

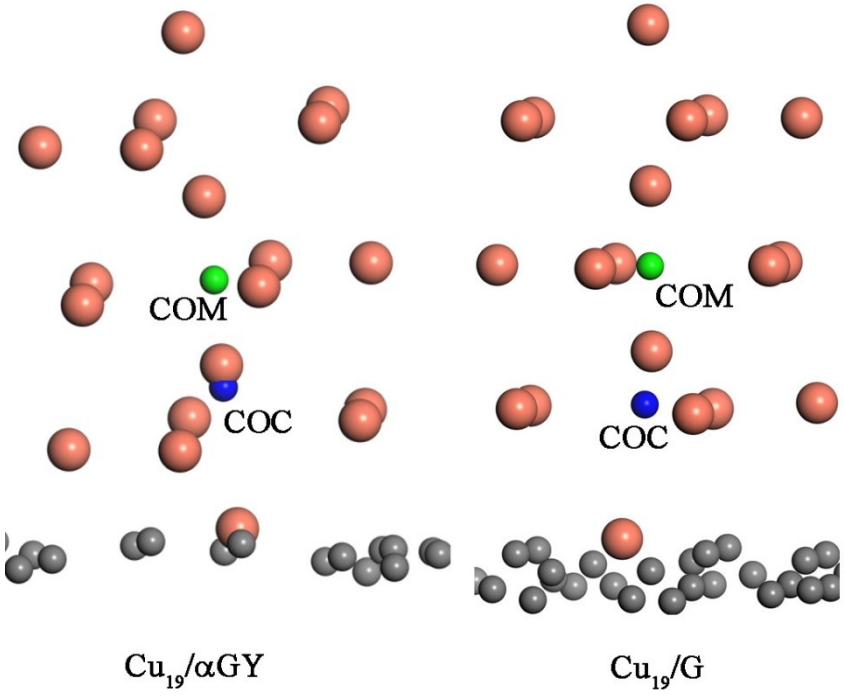

Fig. S1. The center of charge and the center of mass of Cu_{19} in Cu_{19}/αGY and Cu_{19}/G. The green point refers to the center of mass and the blue point refers to the center of charge.

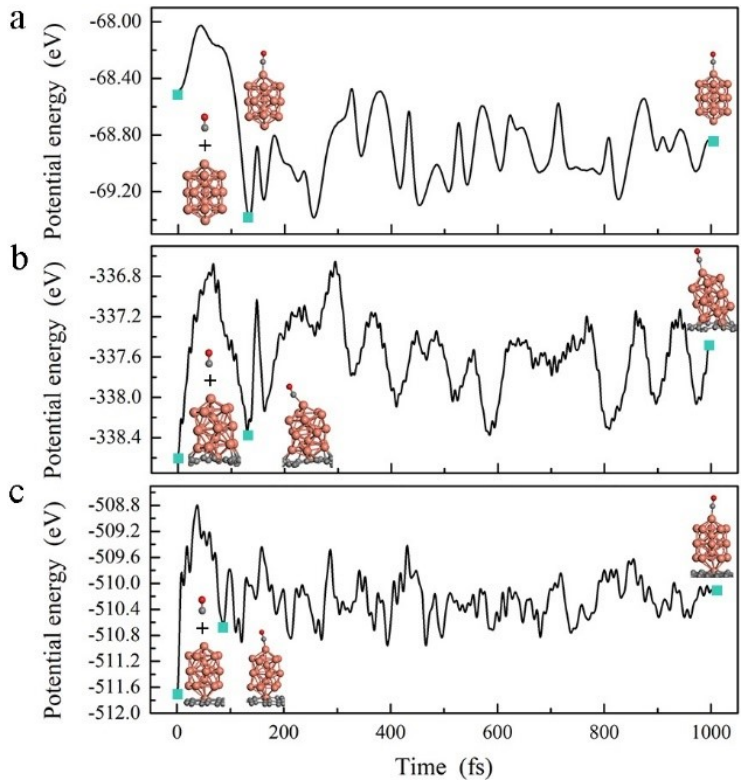

Fig. S2. Three representative AIMD trajectories of potential energy versus time for the adsorption of CO on Cu_{19}, Cu_{19}/αGY and Cu_{19}/G. (a) Cu_{19}. (b) Cu_{19}/αGY. (c) Cu_{19}/G. First, CO molecule comes in from the asymptotic region at about 7.5 Å above the substrate to attack the cluster, and is adsorbed on the adsorption site at about 100 fs. Then the AIMD trajectories show the systems evolve to stabilize at about 800 fs. The adsorption states then are obtained by optimizing the final stable structures of the entire system identified from the AIMD trajectories.

Table S2. ICOHP values and adsorption energies (in eV) for all adsorption sites of CO adsorption on Cu_{19}, Cu_{19}/αGY and Cu_{19}/G.

Adsorption sites		ICOHP	E^{ad}
Top	T1	-2.04	-1.35
	T2	-1.74	-1.17
	T3	-1.59	-1.01
	T1/αGY	-2.42	-1.34
	T2-1/αGY	-2.29	-1.32
	T2-2/αGY	-2.24	-1.41
	T3/αGY	-2.11	-1.28
	T1/G	-2.75	-1.54
	T2-1/G	-2.53	-1.34
	T2-2/G	-2.56	-1.40
	T3/G	-2.36	-1.40
Bridge	B1	-2.75	-0.96
	B2	-2.69	-0.97
	B1/αGY	-3.65	-1.16
	B1-1/G	-3.91	-1.37
	B1-2/G	-4.15	-1.40
Hollow	H1	-3.50	-0.89
	H1/αGY	-4.86	-1.25
	H1/G	-5.38	-1.43

Table S3. The values (Å) of R_{cont}, R_{co} and r_{core} and the induction energy $V_{ind}(R_{eff})$ (eV) on Cu_{19}/αGY and Cu_{19}/G for the modified induction energy model.

Adsorption state		R_{cont}	R_{co}	r_{core}	$V_{ind}(R_{eff})$
Cu_{19}/αGY	T1(T1/G)	5.06	7.54	4.34	-0.18
	T2(T2-1/αGY)	4.20	6.29	2.79	-0.12
	T2(T2-2/αGY)	2.67	5.13	2.32	-0.29
	T3(T3/αGY)	2.69	5.03	2.26	-0.31
	B1(B1/αGY)	2.82	5.18	2.44	-0.33
	H1(H1/αGY)	2.74	5.24	2.42	-0.29
Cu_{19}/G	T1(T1/G)	5.39	7.85	4.63	-0.30
	T2(T2-1/G)	4.66	6.53	3.22	-0.26
	T2(T2-2/G)	2.77	5.19	2.34	-0.48
	T3(T3/G)	2.93	5.01	2.23	-0.55
	B1(B1-1/G)	3.09	5.40	2.40	-0.39
	B1(B1-2/G)	2.21	4.28	0.82	-0.20
	H1(H1/G)	2.86	5.39	2.48	-0.44

Table S4. The predicted adsorption energy E_{supp}^{pred} of Cu_{19} supported by α-graphyne and

defective graphene calculated using our original induction energy model. $E_{Cu_{19}}^{ad}$ is the adsorption energy of Cu_{19}, and E_{supp}^{ad} is the adsorption energy on Cu_{19}/αGY or Cu_{19}/G. The parameters of R_{cont}, R_{cc} and r_{core} to calculate $V_{ind}(R_{eff})$ are presented in Table S5. The units of adsorption energies are in eV.

Adsorption state		$E_{Cu_{19}}^{ad}$	$V_{ind}(R_{eff})$	E_{supp}^{pred}	E_{supp}^{ad}	Error
Cu_{19}/αGY	T1(T1/αGY)	-1.35	-0.26	-1.61	-1.34	-0.27
	T2(T2-1/αGY)	-1.17	-0.28	-1.45	-1.32	-0.13
	T2(T2-2/αGY)	-1.17	-0.24	-1.41	-1.41	0.00
	T3(T3/αGY)	-1.01	-0.19	-1.2	-1.28	0.08
	B1(B1/αGY)	-0.97	-0.18	-1.15	-1.16	-0.01
	H1(H1/αGY)	-0.89	-0.19	-1.08	-1.25	0.17
	MSE					-0.03
	MUE					0.11
Cu_{19}/G	T1(T1/G)	-1.35	-0.46	-1.81	-1.54	-0.27
	T2(T2-1/G)	-1.17	-0.49	-1.66	-1.34	-0.32
	T2(T2-2/G)	-1.17	-0.60	-1.77	-1.40	-0.37
	T3(T3/G)	-1.01	-0.30	-1.31	-1.40	0.09
	B1(B1-1/G)	-0.97	-0.50	-1.47	-1.37	-0.10
	B1(B1-2/G)	-0.97	-0.49	-1.46	-1.40	-0.06
	H1(H1/G)	-0.89	-0.49	-1.38	-1.43	0.05
	MSE					-0.14
	MUE					0.18

Table S5. The values (Å) of R_{cont}, R_{cc} and r_{core} and the induction energy $V_{ind}(R_{eff})$

(eV) on Cu_{19}/αGY and Cu_{19}/G for the original induction energy model.

Adsorption state		R_{cont}	R_{cc}	r_{core}	$V_{ind}(R_{eff})$
Cu_{19}/αGY	T1(T1/αGY)	3.61	6.08	3.19	-0.26
	T2(T2-1/αGY)	3.04	5.37	2.50	-0.28
	T2(T2-2/αGY)	2.91	5.29	2.34	-0.24
	T3(T3/αGY)	2.29	4.76	1.54	-0.19
	B1(B1/αGY)	2.13	4.46	1.25	-0.18
	H1(H1/αGY)	2.19	4.34	1.23	-0.19
Cu_{19}/G	T1(T1/G)	3.41	5.86	2.99	-0.46
	T2(T2-1/G)	2.83	5.24	2.39	-0.49
	T2(T2-2/G)	3.20	5.55	2.86	-0.60
	T3(T3/G)	2.20	4.66	1.40	-0.30
	B1(B1-1/G)	2.57	4.76	1.93	-0.50
	B1(B1-2/G)	1.90	4.09	1.25	-0.49
	H1(H1/G)	1.96	4.15	1.32	-0.49