Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Synergizing Cu Dimer and N atoms in Graphene Towards an Active Catalyst for Hydrogen Evolution Reaction

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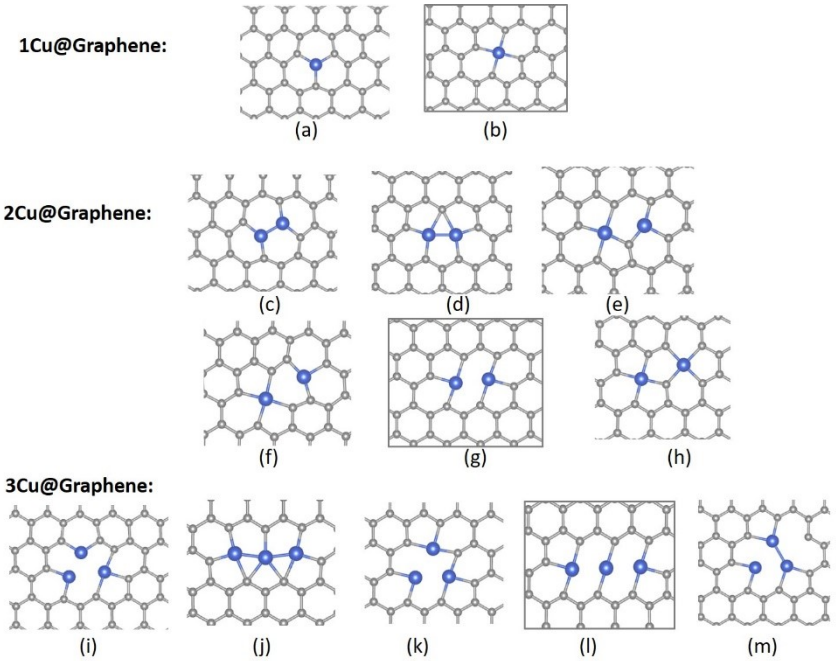

Figure S1. All possible geometries for Cu monomer, dimer and trimer @Graphene. The one with a black box is adopted as the final model on the basis of its highest formation energy. The grey and blue spheres correspond to carbon and copper atoms, respectively.

Table S1 Formation energy (E_{form}) for each possible geometry of the Cu mer catalyst (in eV). The structure for each possible geometry can be found in Figure S1.

	Geometry	Label	E_{form} /Cu (eV)
1Cu@Graphene	1C missing	a	-1.71
	2C missing	b	-5.20
2Cu@Graphene	2C missing	c	0.33
	3C missing	d	-3.86
		e	-2.55
		f	-4.30
	4C missing	g	-5.89
3Cu@Graphene	5C missing	i	-4.13
		j	-5.16
	6C missing	k	-5.69
		l	-6.16
	7C missing	m	-5.38

Table S2. The calculated ΔG_{H*} (in eV) for each possible geometry of Cu_2N_x@Graphene with x = 0 to 6. The related geometries can be found in Figure 3.

geometries	ΔG_{H*}	geometries	ΔG_{H*}
0N-a	-1.89	3N-l	-0.63
1N-b	-0.90	4N-m	-0.30
1N-c	-1.05	4N-n	-0.64
2N-d	-0.57	4N-o	-0.51
2N-e	-0.94	4N-p	-0.09
2N-f	-0.63	4N-q	-0.28
2N-g	-0.48	4N-r	-0.65
2N-h	-0.63	5N-s	-0.32
2N-i	-0.84	5N-t	-0.80
3N-j	-0.65	5N-u	-0.49
3N-k	-0.61	6N-v	0.42

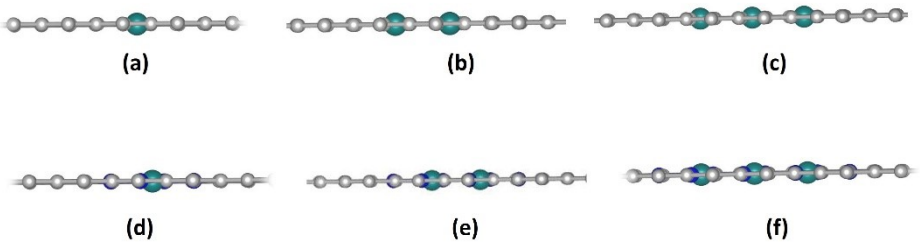

Figure S2. Sideview of structures a: Cu_1N_0@Graphene, b: Cu_2N_0@Graphene, c: Cu_3N_0@Graphene, d: Cu_1N_4@Graphene, e: Cu_2N_6@Graphene and f: Cu_3N_8@Graphene. Grey, navy and green spheres represent C, N and Cu atoms, respectively.

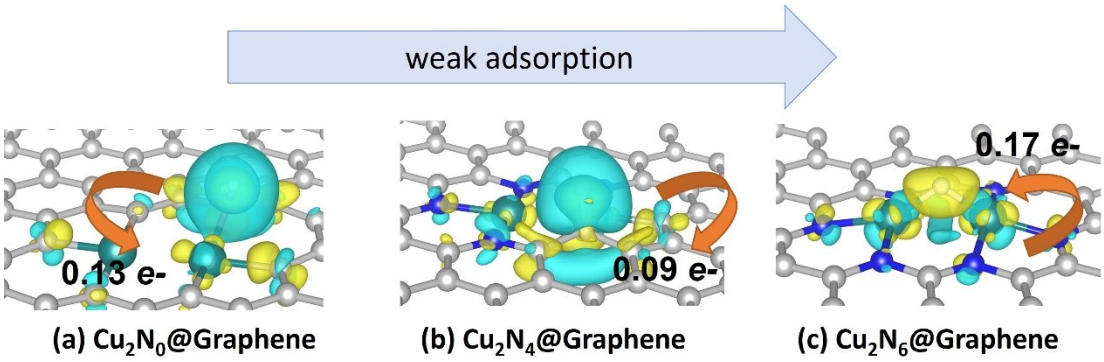

Figure S3: The isosurface of charge density difference of (a) Cu_2N_0@Graphene, (b) Cu_2N_4@Graphene and (c) Cu_2N_6@Graphene systems. Yellow and blue correspond to electron density accumulation and depletion region, respectively. The arrow shows the charge transfer direction and the charge transfer amount quantified by Bader charger is shown in the figures. The isosurface is taken as 0.0025 e/Å^{-3}