Electronic Supplementary Information

Embedding the Tetrahedral 3*d* Transition Metal TM_4 Clusters into the Cavity of Two-Dimensional Graphdiyne to Construct Highly Efficient and Nonprecious Electrocatalysts for Hydrogen Evolution Reaction

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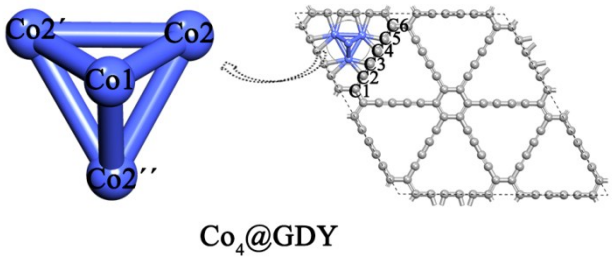
(I) The computational test on the effect of TM_4-concentration on the calculated free energy of H* (ΔG_{H^*})

We have performed a computational test to explore the effect of TM_4-concentration on the computed ΔG_{H^*} value by sampling Co_4@GDY system, where the supercell size of GDY is enlarged from the original 1×1 into 2×2, as illustrated Figure S1. Based on the enlarged structural models with the lower metal loading, we have computed the ΔG_{H^*} values by considering all the possible adsorption sites. Table S1 collects the correlative computed results. It can be found that all the computed ΔG_{H^*} values based on 2×2 supercell model with lower metal loading can be very close to the corresponding those from the original 1×1 supercell size, with a negligible change in the range of 0.005~0.077 eV, reflecting that the obtained ΔG_{H^*} results based on 1×1 supercell size can be reasonable and reliable, and 1×1 supercell model can be used to simulate the realistic situation with the lower metal loading.



Co_4@GDY

Figure S1. The top view of structural model for Co_4@GDY system with 2×2 supercell size of GDY.

Table S1. The comparison between the computed ΔG_{H^*} values on Co_4@GDY by using 1×1 and 2×2 supercell size of GDY.

Adsorption sites	ΔG_{H^*} (eV)	
	1×1	2×2
T_{C1}	1.081	1.057
T_{C2}	-0.286	-0.281
T_{C3}	0.055	0.011
T_{C4}	-0.400	-0.448
T_{C5}	-0.360	-0.283
T_{C6}	0.943	0.994
T_{Co1}	-0.016	0.014
$B_{Co1\text{-}Co2}$	0.027	0.018
$H_{Co2\text{-}Co2'\text{-}Co2''}$	-0.112	-0.096

(II) Diffusion barrier of TM1 atom into the neighboring C ring for Fe_4@GDY and Co_4@GDY systems

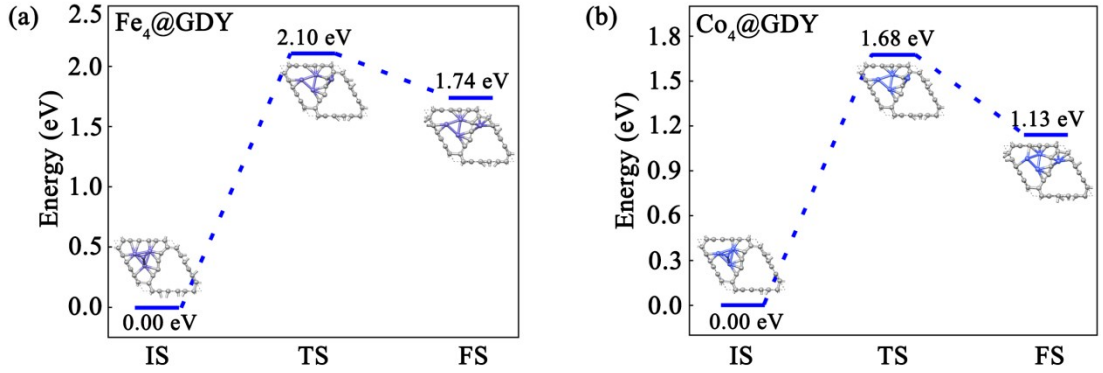


Figure S2. Atomic configurations for the diffusion of TM1 atom into the neighboring C ring for the representative TM_4@GDY system for TM = Fe (a) and Co (b), respectively, including the initial state (IS), transition state (TS) and final state (FS). The energy is given with respect to IS.