Electronic Supplementary Information (ESI)

PtN_3-Embedded Graphene as an Efficient Catalyst for Electrochemical Reduction of Nitrobenzene to Aniline: a Theoretical Study

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Computional Details on Dissolution Potential and Overpotential

To evaluate the stability of TMN_3/G monolayer in strong acidic media, we computed the dissolution potentials (U_{dis}, in V) of TM in TMN_3/G monolayer at pH=0, defined as: $U_{dis} = U_{TM}^{0} + \left[E_{TM,bulk} - \left(E_{TMN_3/G} - E_{N_3/G}\right)\right]/ne$, where U_{TM}^{0} is the standard dissolution potential of TM in the bulk form,[1] N_3/G is the N-doped defective graphene, and n is the coefficient for the aqueous dissolution reaction: $TM + nH^+ \leftrightarrow TM^{n+} + n/2H_2$. For example, for PtN_3/G, the U_{dis} value can be derived from: $Pt + 2H^+ \leftrightarrow Pt^{2+} + H_2$, and U_{Pt}^{0} value is 1.18 V. Thus, the U_{dis} value of Pt in PtN_3/G was computed to be about 1.24 V.

On the other hand, the overpotential (η) value was obtained according to the following equation: $\eta = U_0 - U_L$, where U_0 is the equilibrium potential of Ph-NO_2 to Ph-NH_2 ($U_0 = -(\Delta G)/n$), and U_L is the limiting potential of NBER on TMN_3/G monolayer. Since the ΔG value for NBER (Ph-NO_2 + $6H^+$ + $6e^-$ → Ph-NH_2 + $2H_2O$ in Fig. 5) was computed to be −4.42 eV, the computed U_0 is [− (−4.42)/6) = 0.75 V]. Thus, the negative overpotential (−η) of NBER on PtN_3/G is –[0.75 V – (−0.21 V)] = −0.96 V, which is much smaller than the U_{dis} value of Pt (1.24 V), suggesting that Pt within the PtN_3/G framework can survive under the realistic experimental conditions of NBER, and thus ensuring its excellent long-term stability. According to the above method, Fig. 1c in main text can be obtained.

References

1. Greeley, J.; Nørskov, J. K., *Electrochimica Acta* 2007, 52, 5829-5836.

Table S1. The computed limiting potential (U_L, V) of NBER on PtN_3/G using different supercell sizes.

supercell	U_L
5×5	–0.21
6×6	–0.22
7×7	–0.22

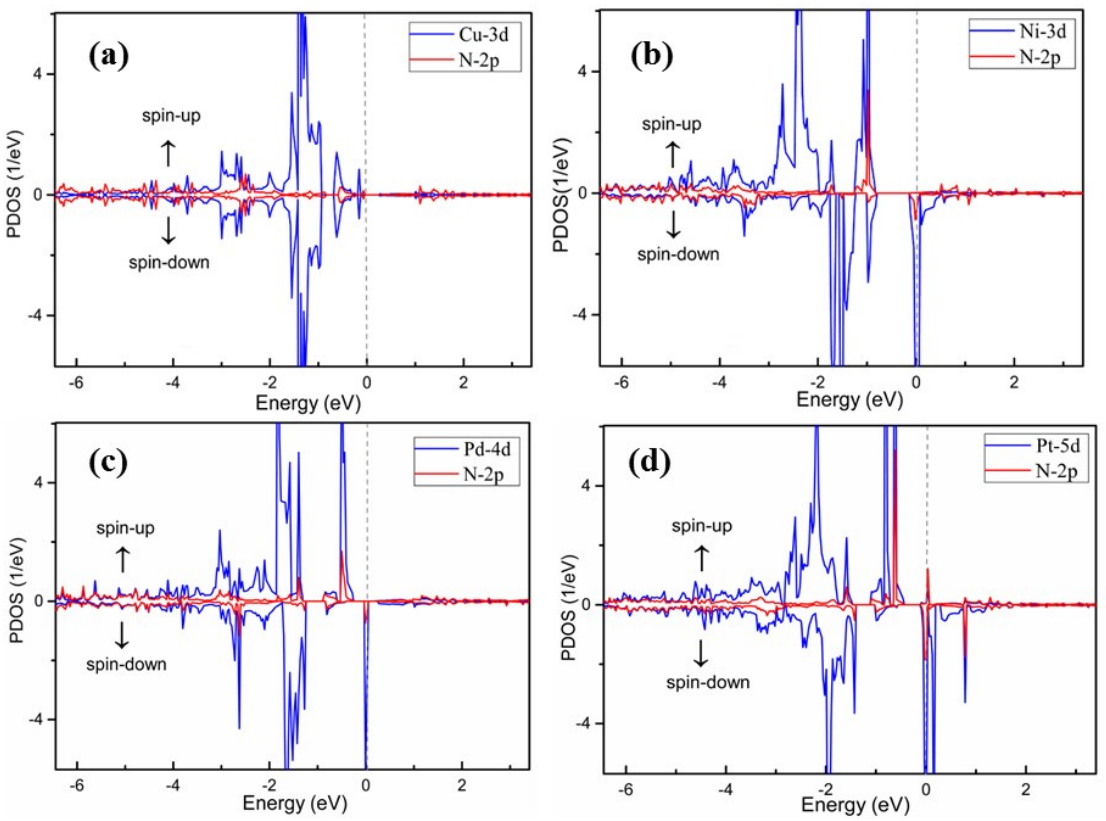

Fig. S1. The computed projected density of states (PDOSs) of (a) CuN_3/G, (b) NiN_3/G, (c) PdN_3/G, and (d) PtN_3/G. The Fermi level was set to zero.

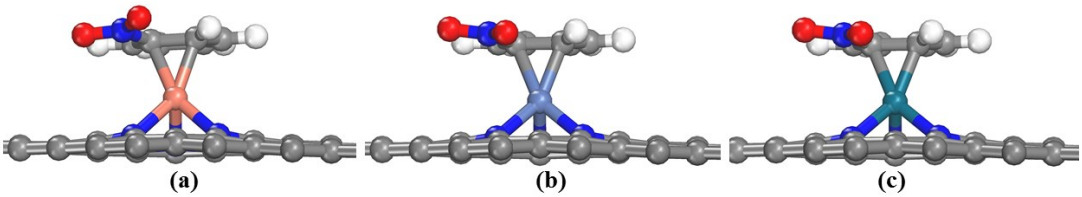

Fig. S2. The obtained most stable adsorption configurations of Ph-NO_2 molecule on the surfaces of (a) CuN_3/G, (b) NiN_3/G, and (c) PdN_3/G.

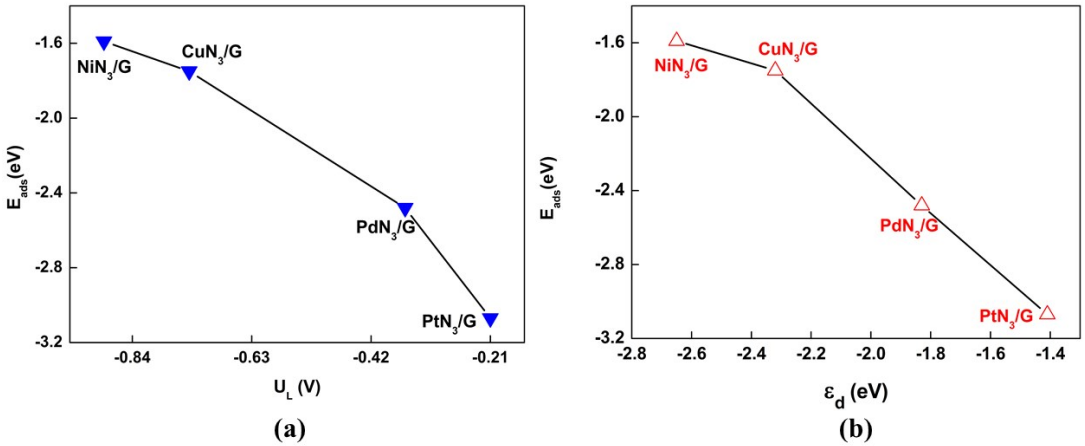

Fig. S3. Calculated adsorption energy (E_{ads}) plotted versus (a) limiting potential (U_L) and (b) d-band center (ε_d).

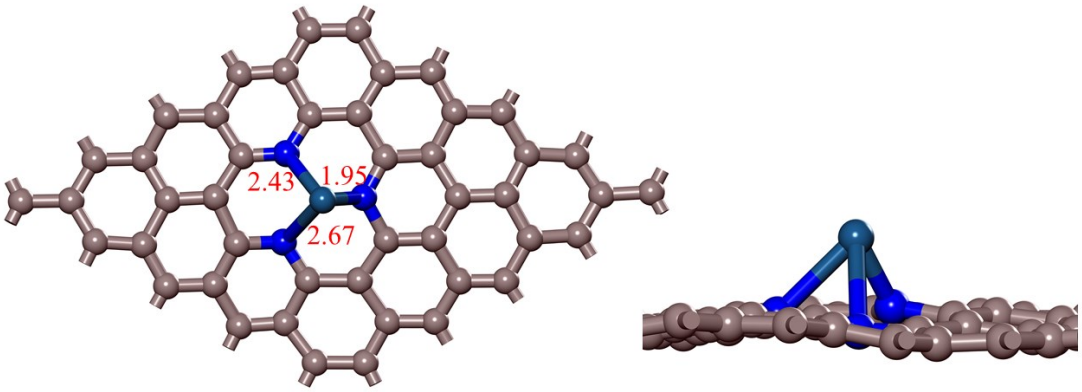

Fig. S4. Snapshots of PtN_3/G equilibrium structure at 500 K after 10 ps MD simulations.

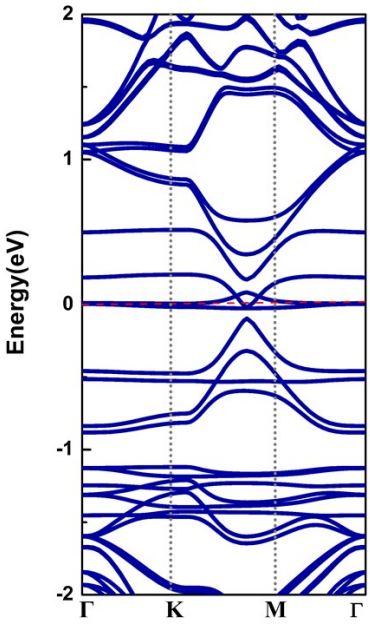

Fig. S5. The computed band structure of PtN_3/G. The Fermi level is set to zero in red dashed line.