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Supporting Information for:

Pt-embedded monolayer g-C_3N_4 as a promising single-atom electrocatalyst for ammonia synthesis

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Free Energy Calculations

The free energies of intermediates were calculated by taking gas-phase N_2 and H_2 as reference states. The entropies and zero-point energy were calculated based on the vibrational frequencies. The entropy is calculated as

$$S(T) = \sum_{i=1}^{3N} [- Rln\left(1 - e^{-\frac{hv_i}{k_B T}}\right) + \frac{N_A hv_i \; e^{-hv_i / k_B T}}{T \; 1 - e^{-hv_i / k_B T}}],$$

in which R, h, k_B, N_A, v_i, N and T is the universal gas constant, Planck's constant, Boltzmann's constant, Avogadro's number, frequency of the normal mode, number of adsorbed atoms and temperature (298.15 K), respectively. Entropies of the gas-phase N_2 and H_2 were taken from the NIST database. The zero point energy is defined as

$$E_{ZPE} = \frac{1}{2} \sum_{i=1}^{N_{modes}} hv_i$$

where N_{modes} is the number of vibrational modes. Then, ΔE_{ZPE} and ΔS are the differences in zero point energy and entropy, respectively, between the adsorbed species and gas-phase molecules.

The operating bias U is the applied potential required to eliminate the energy barrier of the potential-limiting step and is calculated as $-\Delta G_{pls}/e$, where ΔG_{pls} is the free energy difference of the potential-limiting step. More details can be found in Ref. 17.

Table S1. Adsorption energies (E_{ad}) of N_2, N_2H, NH_2 and H on Pt/g-C_3N_4 in 2 × 2 and 3 × 3 supercells.

Size	E_{ad} of N_2 (eV)	E_{ad} of N_2H (eV)	E_{ad} of NH_2 (eV)	E_{ad} of H (eV)
2 × 2	-1.42	-2.89	-3.21	-1.06
3 × 3	-1.51	-2.95	-3.26	-1.04

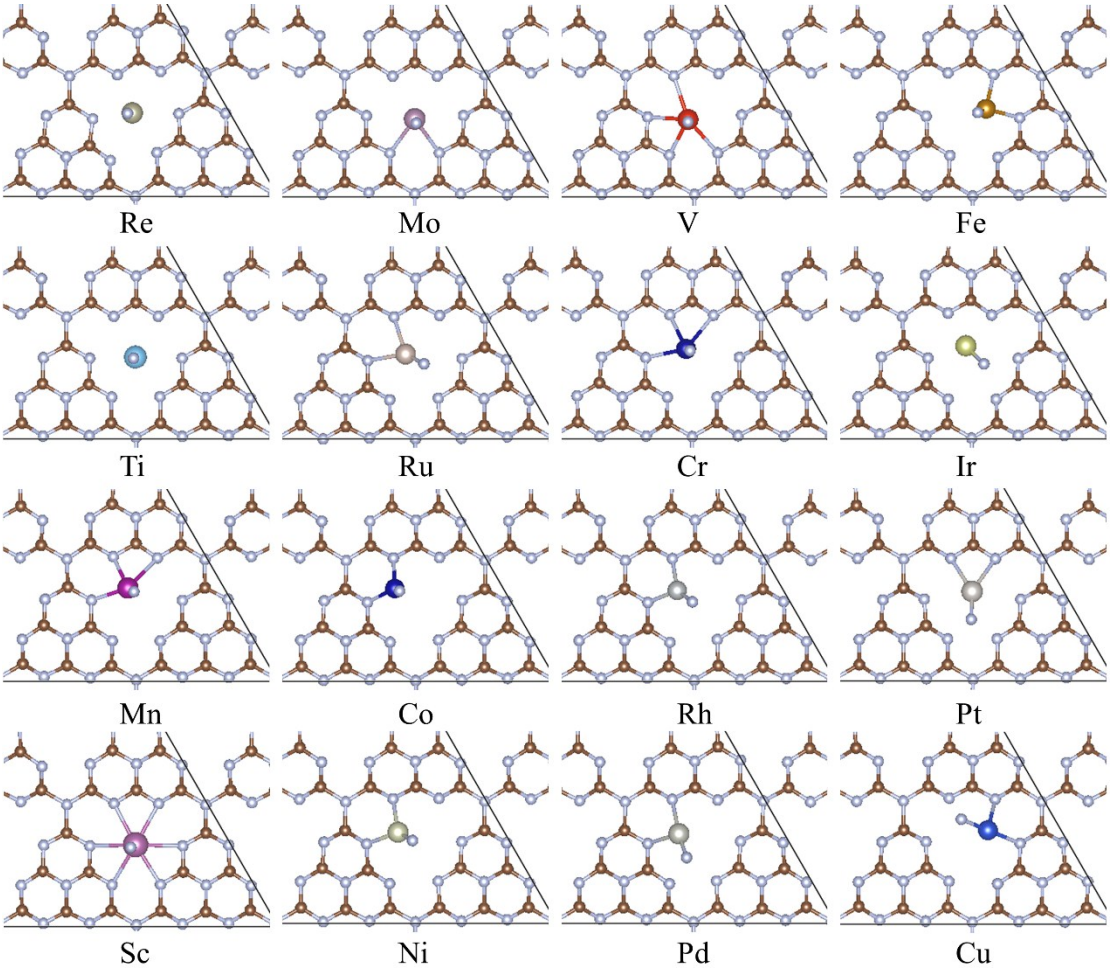

Figure S1. The adsorption configurations of N atom on TM/g-C_3N_4 (TM = Re, Mo, V, Fe, Ti, Ru, Cr, Ir, Mn, Co, Rh, Pt, Sc, Ni, Pd and Cu).

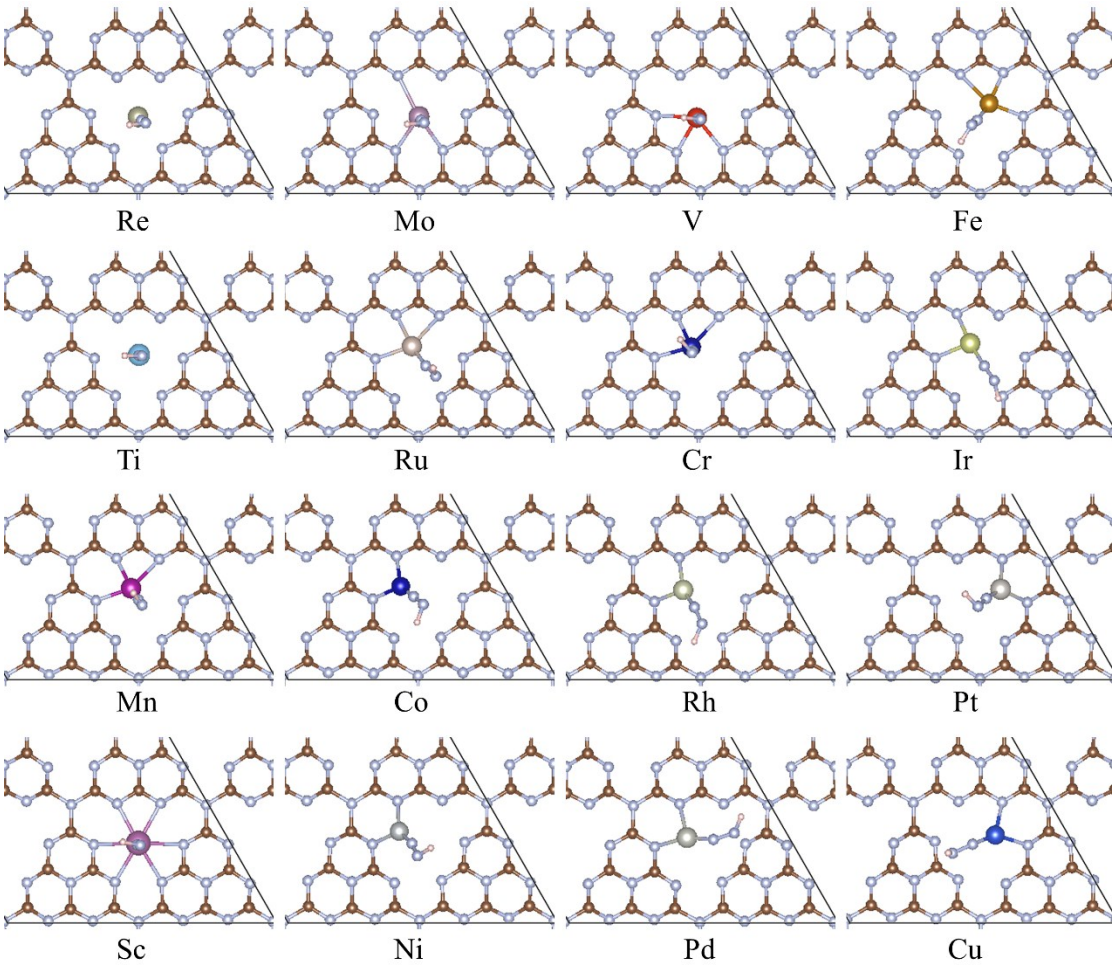

Figure S2. The adsorption configurations of N_2H on TM/g-C_3N_4 (TM = Re, Mo, V, Fe, Ti, Ru, Cr, Ir, Mn, Co, Rh, Pt, Sc, Ni, Pd and Cu).

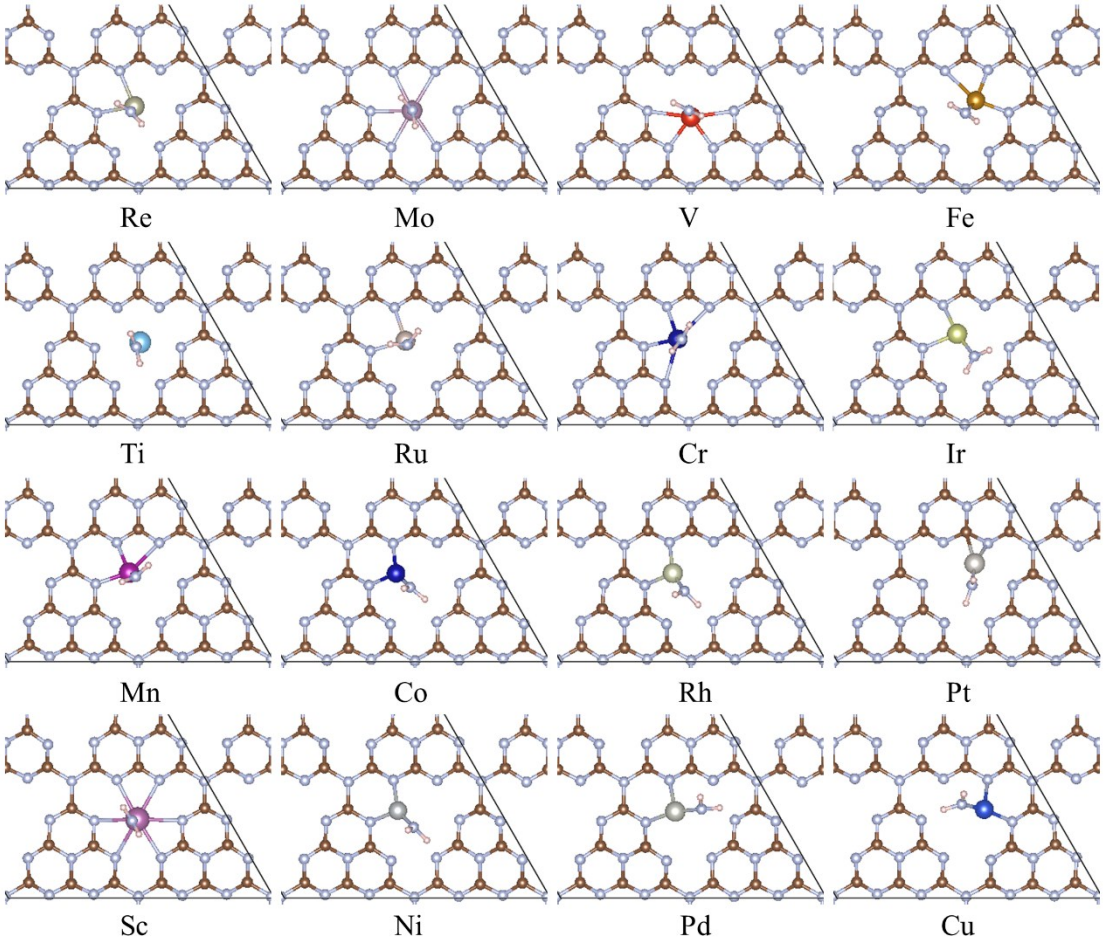

Figure S3. The adsorption configurations of NH_2 atom on TM/g-C_3N_4 (TM = Re, Mo, V, Fe, Ti, Ru, Cr, Ir, Mn, Co, Rh, Pt, Sc, Ni, Pd and Cu).

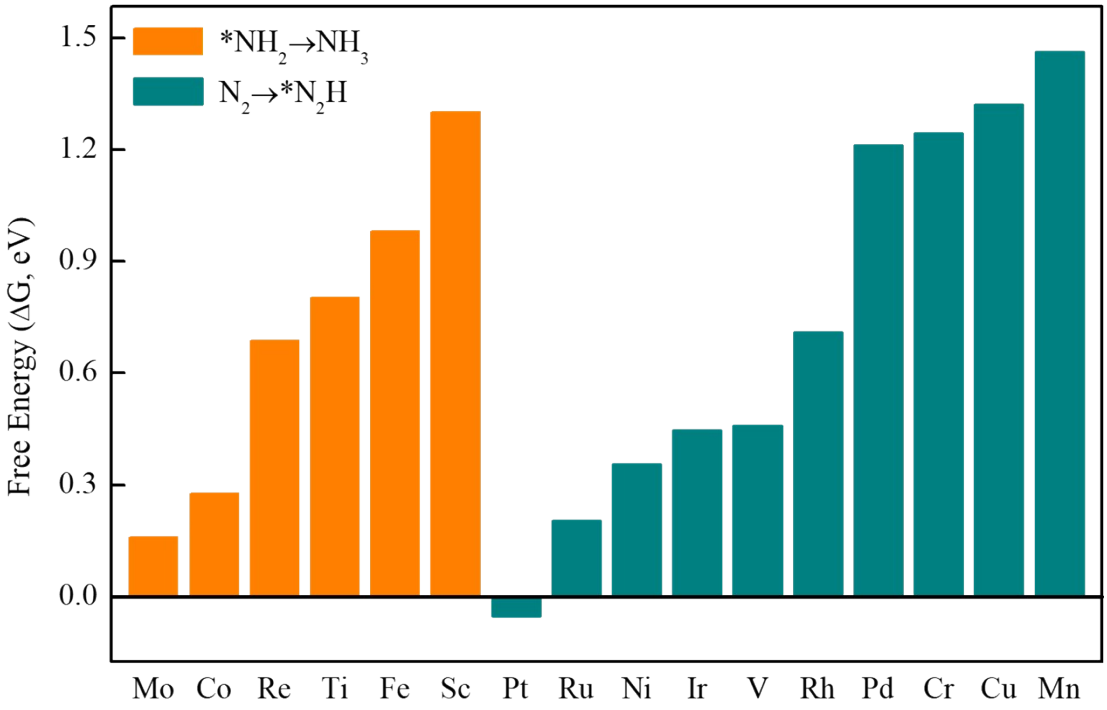

Figure S4. Calculated free energy ($\Delta G = \max[\Delta G_{(*NH_2 \rightarrow NH_3)}, \Delta G_{(N_2 \rightarrow *N_2H)}]$) for the reduction adsorption of $*N_2H$ and reduction desorption of $*NH_2$ on TM/g-C_3N_4.