## Graphene Oxide-Supported Transition Metal Catalysts for Di-Nitrogen Reduction

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## The associative and dissociative Heyrovský mechanisms and process for calculation of the free energy

In the associative Heyrovský mechanism, nitrogen molecules are protonated before the nitrogen-nitrogen bond dissociates. The individual steps are as follows (\* denotes a surface site):

$$* + N_2 \rightarrow *N_2 \tag{1a}$$

$$*N_2 + (H^+ + e^-) \rightarrow *NNH$$
(1b)

\*NNH + (H<sup>+</sup> + e<sup>-</sup>) 
$$\rightarrow$$
 \*NNH<sub>2</sub> (1c)

$$*NNH_2 + (H^+ + e^-) \rightarrow *N + NH_3$$
(1d)

$$*N + (H^+ + e^-) \rightarrow *NH$$
 (1e)

$$*NH + (H^+ + e^-) \rightarrow *NH_2$$
(1f)

$$*\mathrm{NH}_2 + (\mathrm{H}^+\!\!+\!\mathrm{e}^{-}) \to *\mathrm{NH}_3 \tag{1g}$$

$$*NH_3 \rightarrow NH_3 + * \tag{1h}$$

In the case of the dissociative Heyrovský mechanism, the nitrogen molecules dissociate on the surface, and then are subsequently protonated:

$$* + N_2 \rightarrow 2*N \tag{2a}$$

$$2*N + (H^+ + e^-) \rightarrow *NH + *N$$
(2b)

$$*N + *NH + (H^+ + e^-) \rightarrow 2*NH$$
(2c)

| $2*NH + (H^+ + e^-) \rightarrow$ | $*NH_2 + *NH$ | (2d) |
|----------------------------------|---------------|------|
|----------------------------------|---------------|------|

$$*NH_2 + *NH + (H^+ + e^-) \rightarrow 2*NH_2$$
 (2e)

$$2*\mathrm{NH}_2 + (\mathrm{H}^+ + \mathrm{e}^{-}) \rightarrow *\mathrm{NH}_3 + *\mathrm{NH}_2$$
(2f)

$$*NH_3 + *NH_2 + (H^+ + e^-) \rightarrow 2*NH_3$$
 (2g)

$$2*\mathrm{NH}_3 \rightarrow \mathrm{NH}_3 + * + *\mathrm{NH}_3 \tag{2h}$$

$$*NH_3 + NH_3 \rightarrow 2NH_3 + *$$
(2i)

We estimate the change in the free energy at zero potential by<sup>1</sup>

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \tag{3}$$

where  $\Delta E$  is the electronic energy difference before and after reaction and  $\Delta E_{ZPE}$  and  $\Delta S$ are the reaction zero point energy and entropy changes, respectively. In the above formula, the zero point energy correction and vibrational entropy of the adsorbed species can be calculated from the vibrational frequencies by applying normal mode analysis using DFT calculations.<sup>2</sup> A NIST database provides the corresponding values for gas phase molecules.<sup>3</sup>

We use the standard hydrogen electrode (SHE) as a reference potential. In this way, the chemical potential (the free energy per H) of  $(H^+ + e^-)$  is related to that of 1/2 H<sub>2</sub> (g). The free energy of each intermediate as a function of the electrode potential (U) can be given by

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S - neU \tag{4}$$

where n is the number of electrons transferred at each electrochemical step. Compared with a potential of U = 0, the free energy is shifted by -neU.

The effect of different pH values on the free energy change is shown in the following equation

$$G(pH) = kT \times pH \times \ln 10$$
(5)

In the present study, all calculations are performed at pH = 0.



Figure S1. The dependence of Ni<sub>3</sub>@GO energy on k-mesh.



**Figure S2.** Top and side views of 4 x 4 supercell of (a) graphene and (b) graphene oxide with one epoxy functional group.



**Figure S3.** Top and side views of the optimized configurations of TM@Gr (TM= Pt, Cu, Ni or Co).

Cu Cu

💽 Ni

Co

Pt

C

0



**Figure S4.** Top and side views of the optimized configurations of TM@GO (TM= Pt, Cu, Ni or Co).



Figure S5. Top and side views of the pre-optimization configurations of  $TM_3@GO$ (TM= Pt, Cu, Ni or Co).



Figure S6. Top and side views of the optimized configurations of  $TM_3@Gr$  (TM= Pt, Cu, Ni or Co).



Figure S7. Top and side views of the optimized configurations of TM@Gr (TM= Pt, Cu,

Ni or Co) in the supercell size of 6  $\times$  6.



Figure S8. Top and side views of the optimized configurations of TM@GO (TM= Pt, Cu, Ni or Co) in the supercell size of  $6 \times 6$ .



Figure S9. Top and side views of the optimized configurations of TM<sub>3</sub>@Gr (TM= Pt, Cu, Ni or Co) in the supercell size of  $6 \times 6$ .



Figure S10. Top and side views of the optimized configurations of TM<sub>3</sub>@GO (TM= Pt, Cu, Ni or Co) in the supercell size of  $6 \times 6$ .

**Table S1**. The computed binding energies  $(E_b)$  of  $TM_n$  (n = 1 or 3) and polarization positive charges of TM taken from the Gr or GO support in TM@Gr ,TM@GO,  $TM_3@Gr$  , and  $TM_3@GO$ , respectively. The supercell size is 6  $\times$  6.

| Т | $E_{\rm b}({\rm eV})$ |      |        | TM charge (e <sup>+</sup> ) |      |      |        |                    |
|---|-----------------------|------|--------|-----------------------------|------|------|--------|--------------------|
| Μ | TM@G                  | TM@G | $TM_3$ | TM <sub>3</sub> @G          | TM@G | TM@G | $TM_3$ | TM <sub>3</sub> @G |
|   | r                     | 0    | Gr     | 0                           | r    | 0    | Gr     | 0                  |

| Pt | 2.23 | 3.75 | 4.82 | 6.09 | 0.01 | 0.29 | 0.02 | 0.73 |
|----|------|------|------|------|------|------|------|------|
| Cu | 0.55 | 1.76 | 1.58 | 4.35 | 0.28 | 0.62 | 0.55 | 1.38 |
| Ni | 1.95 | 3.34 | 2.54 | 5.78 | 0.36 | 0.59 | 0.56 | 1.51 |
| Co | 2.10 | 5.32 | 1.85 | 6.91 | 0.53 | 0.75 | 0.64 | 1.64 |



**Figure S11.** From left to right: the optimized geometries of initial state (IS), transition state (TS), final state (FS), and the potential energy profile TM<sub>3</sub> diffusion on GO.



Figure S12. Top and side views of the optimized configurations of TM<sub>3</sub>@GO-OH (TM=

Pt, Cu, Ni or Co).

**Table S2**. The computed binding energies ( $E_b$ ) of TM<sub>3</sub> and polarization positive charges of TM taken from the Gr or GO support in TM<sub>3</sub>@Gr , TM<sub>3</sub>@GO, and TM<sub>3</sub>@GO-OH, respectively.

| TM |                     | $E_{\rm b}({\rm eV})$ |                        | TM charge (e <sup>+</sup> ) |                     |                        |  |
|----|---------------------|-----------------------|------------------------|-----------------------------|---------------------|------------------------|--|
|    | TM <sub>3</sub> @Gr | TM <sub>3</sub> @GO   | TM <sub>3</sub> @GO-OH | TM <sub>3</sub> @Gr         | TM <sub>3</sub> @GO | TM <sub>3</sub> @GO-OH |  |
| Pt | 5.16                | 6.38                  | 5.28                   | 0.03                        | 0.81                | 0.55                   |  |
| Cu | 1.52                | 4.34                  | 4.03                   | 0.50                        | 1.57                | 0.74                   |  |
| Ni | 2.63                | 6.06                  | 5.17                   | 0.57                        | 1.53                | 1.26                   |  |
| Co | 1.98                | 6.92                  | 4.91                   | 0.74                        | 1.64                | 1.37                   |  |



Figure S13. The optimized structures of various intermediates for  $N_2$  conversion to  $NH_3$  on  $Ni_3$ @GO via the Heyrovský associative mechanism.



Figure S14. Free energy profiles for the associative mechanism of nitrogen reduction on  $Ni_3@GO$  at two applied potentials vs SHE.



Reaction coordinate

Figure S15. Calculated ORR free-energy diagram for TM<sub>3</sub>@GO (TM= Pt, Cu, Ni or Co).



Reaction coordinate

Figure S16. Calculated HER free-energy diagram for TM<sub>3</sub>@GO (TM= Pt, Cu, Ni or Co).

## REFERENCES

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