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## Supporting Information

# Computational Study on Pt, Ru Dimer Supported on Graphene for Hydrogen Evolution Reaction: New Insight into the Alkaline Mechanism

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## Models and computational details

Three noble metal dimers ($Pt_2$, $Ru_2$, and PtRu) supported on defective graphene (DG) and nitrogen-doped graphene (NG) (Fig.1a) were constructed. The configuration of metal atoms anchored to two adjacent single vacancies are based on previous experimental and computational studies.[1, 2] We firstly examine the stability of all of the six dimers on graphene by computing the formation energy for each structure. Energy reference of a single metal atom was set to be within a close-packed unit cell, and that of the substrate is the corresponding support without metal dopants. The formation energy can be calculated as follows:

$\Delta E_{formation} = E_{dimer} - (E_{metal\text{-}dopant} + E_{support})$

where $E_{dimer}$, $E_{metal\text{-}dopant}$, $E_{support}$ is the energy of catalyst with dimer structure, doping metal, and defective or nitrogen doped graphene, respectively.

Afterwards, we explored the key species i.e. hydrogen and hydroxide adsorption behaviour, on these six dimer structures. Five possible hydrogen or hydroxide adsorption sites for homogeneous $Pt_2$, $Ru_2$ dimer structures were considered as outlined in Fig. S1a. For heterogeneous PtRu dimer structures, seven possible adsorption configuration were proposed and tested to find the most thermodynamically stable adsorption site, as is shown in Fig. S1b. Beyond single reaction intermediates adsorption, the co-adsorption of hydrogen and hydroxide on dimers was also investigated for four (for homogenous dimer structures) or six (for heterogeneous dimer structures) possible configuration guesses. The transition state was also calculated to evaluate kinetic barrier of water dissociation.

All the calculations were performed by means of spin-polarized density functional theory (DFT) methods as implemented in the Vienna ab initio Simulation Package; [3-6] the projector-augmented-wave pseudopotential was utilized to treat the core electrons, while the Perdew−Burke−Ernzerhof exchange-correlation functional of the generalized gradient approximation was used for describing the electron interactions.[7] A plane-wave cutoff energy of 400 eV was adopted for all the calculations. The vacuum space in the z-direction was set as 20 Å to prevent the interaction between periodic images. The van der Waals interactions were described using the empirical correction in Grimme's scheme.[8] The reciprocal space was sampled using a 5 × 5 × 1 k-points for fully relaxed geometry optimization until the maximal residual force was < 0.02 eV/Å. For electronic structure calculations, a 10 × 10 × 1 k-points grid was used, and the Bader charge analysis was performed to reveal the charge transfer process.[9] The minimum energy path (MEP) of water dissociation on defective or nitrogen doped graphene supported metal dimers was obtained by the climbing image nudged elastic band (CI-NEB) method.[10]

The calculation of the free energy diagrams was performed by using the concept of computational hydrogen electrode (CHE).[11] In this framework, the chemical potential of the electron-proton pair ($H^+ + e^-$) can be referenced by the chemical potential of gaseous $H_2$ at equilibrium (0 V vs reversible hydrogen electrode). The change of free energy can be calculated as follows:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} + \Delta G_{sol}$$

where $\Delta E$ is the electronic energy difference directly obtained by DFT calculation. $\Delta E_{ZPE}$ is the change in zero-point energies (ZPE), T is the room temperature (T = 298.15K), and $\Delta S$ is the entropy change. ZPE and vibrational entropy of adsorbed species were obtained after frequency calculations, and entropy of gas molecules ($H_2$ and $H_2O$) were taken from standard values.[12] At different pH values, $\Delta G_{pH} = 0.059 \times pH$. $\Delta G_{sol}$ represents the correction terms for solvent effect (0 eV for H* and 0.5 eV for OH*). [1, 11]

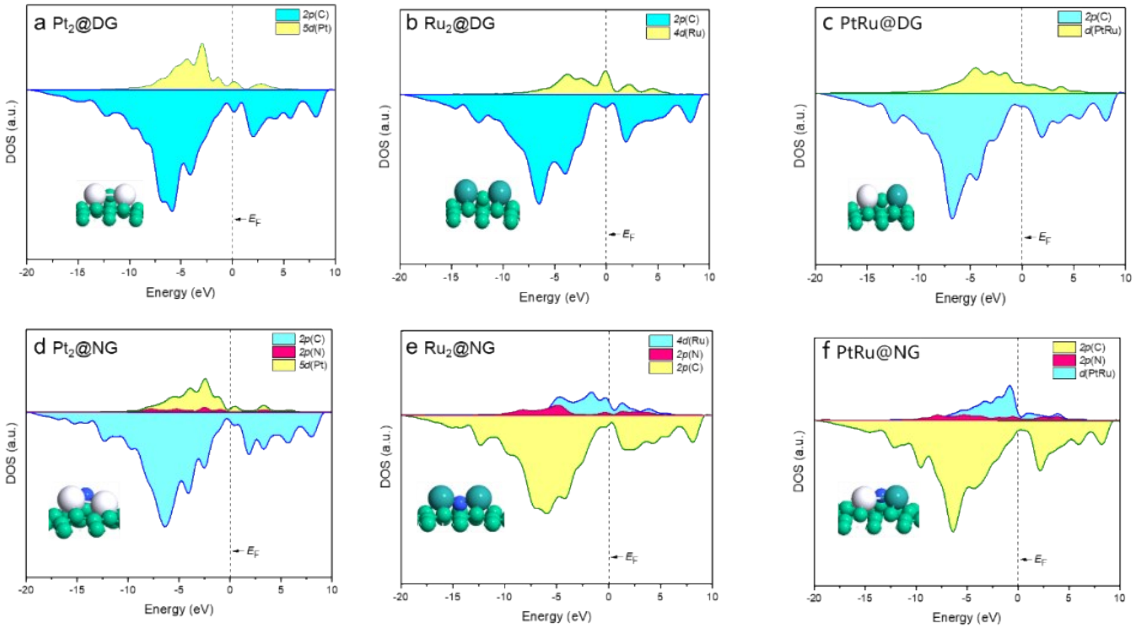


**Figure S1.** Projected density of states illustrating the 2p orbital of carbon or nitrogen, the d orbital of Pt and Ru, for (a) Pt$_2$@DG; (b) Ru$_2$@DG; (c) PtRu@DG; (d) Pt$_2$@NG; (e) Ru$_2$@NG; (f) Pt$_2$@NG.

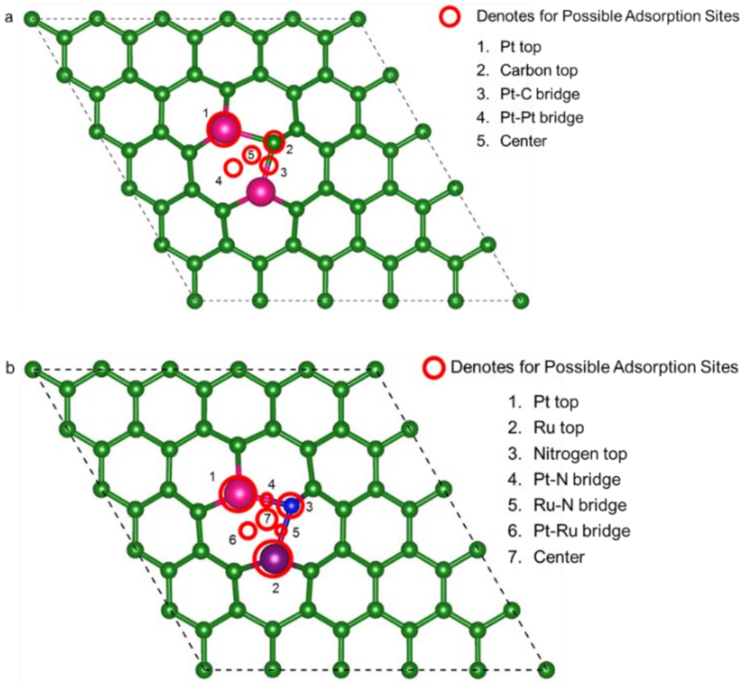


**Figure S2.** Illustration of possible adsorption sites on dimer including top, bridge and centre sites: (a) five possible sites on Pt$_2$@DG, (b) seven possible sites on PtRu@NG.

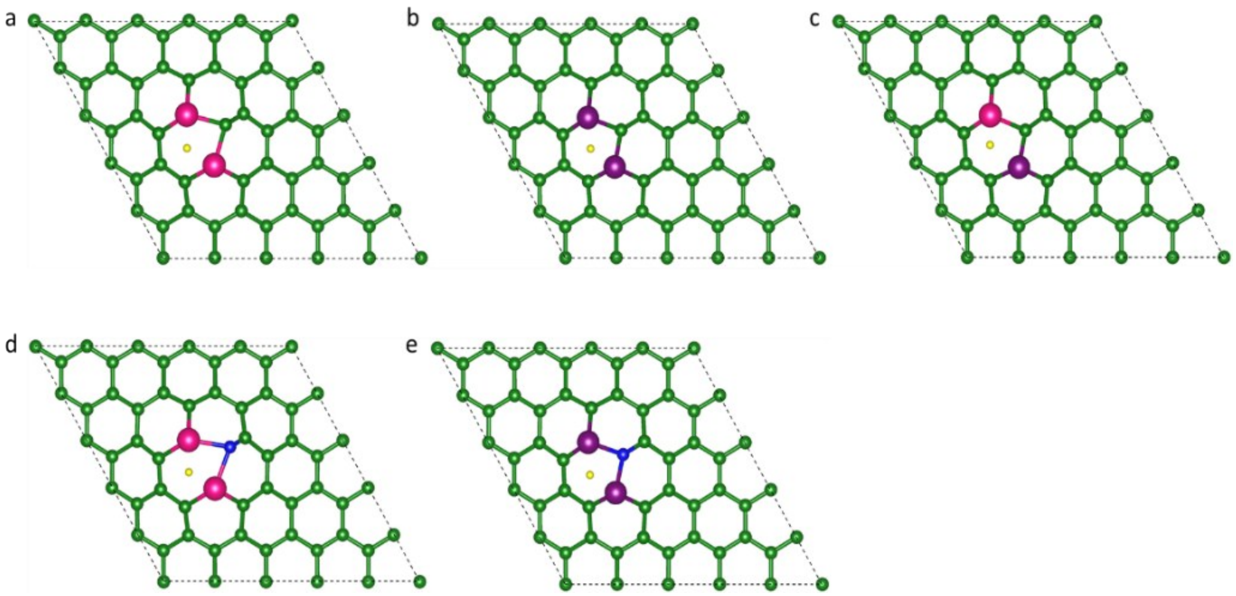


**Figure S3.** Illustration of hydrogen adsorption pattern on (a) $Pt_2$@DG, (b) $Ru_2$@DG, (c) PtRu@DG, (d) $Pt_2$@NG, (e) $Ru_2$@NG.

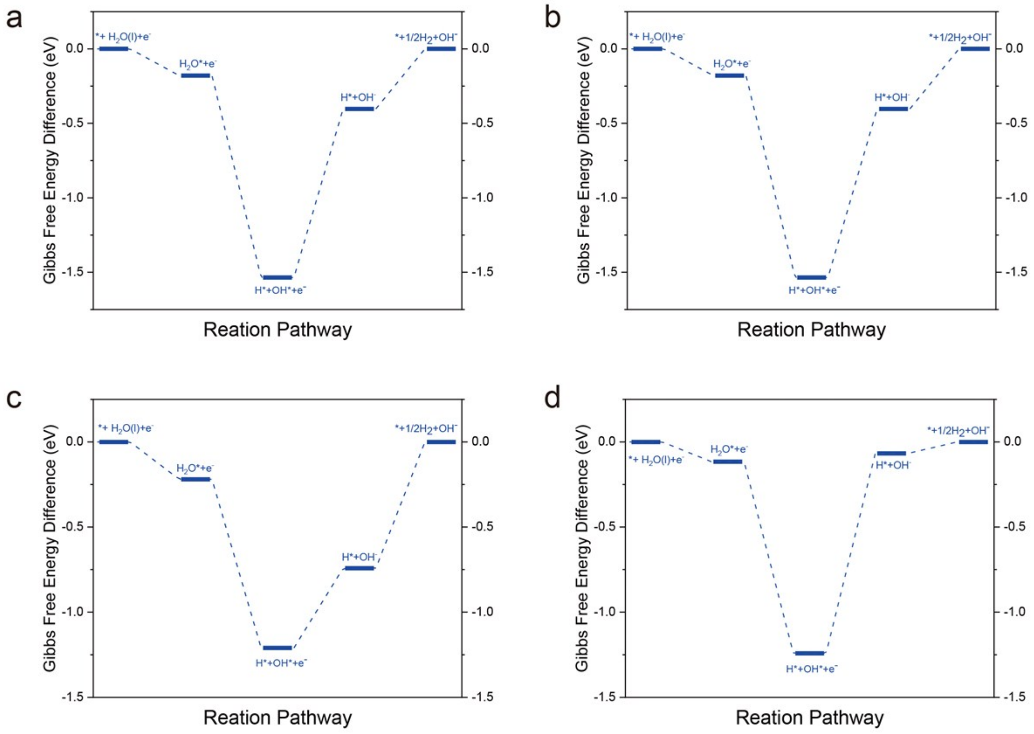


**Figure S4.** Gibbs free energy diagram of alkaline hydrogen evolution reaction on (a) $Ru_2$@DG; (b) PtRu@DG; (c) $Pt_2$@NG; (d) PtRu@NG.

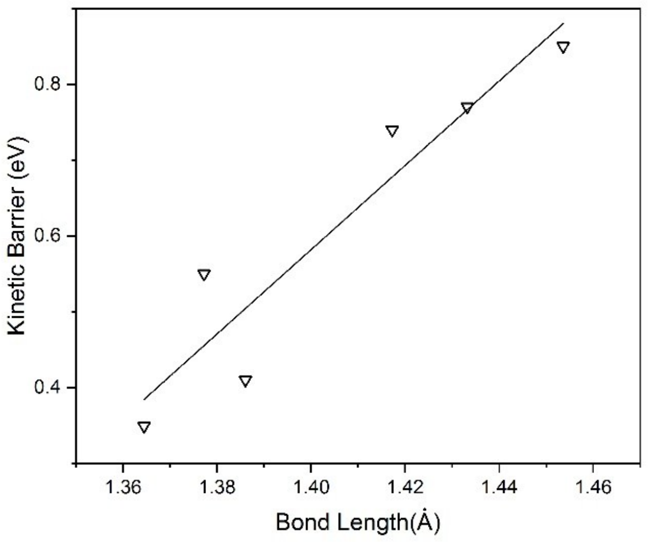


**Figure S5.** The linear correlation between the bond length of stretched O-H and kinetic barrier ($E_a$).

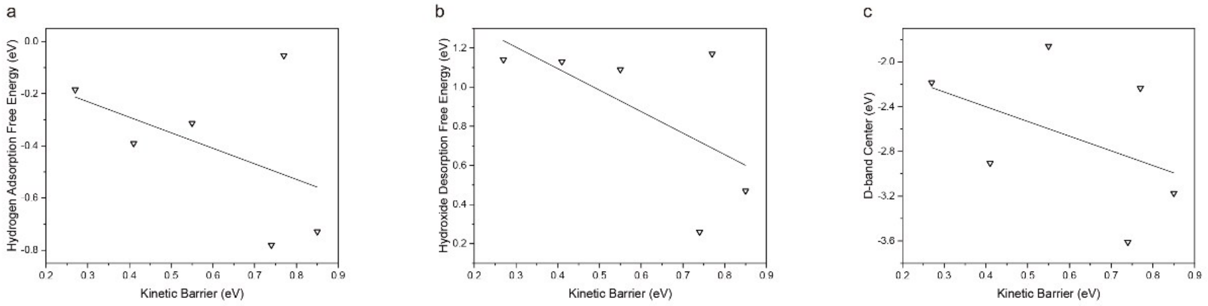
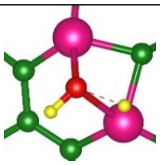
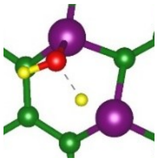
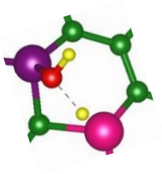
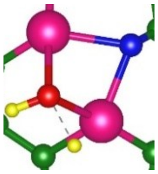
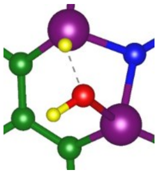
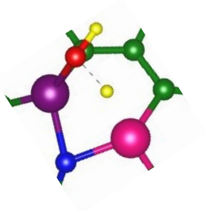


**Figure S6.** Correlation between kinetic barriers ($E_a$) with (a) hydrogen adsorption free energy; (b) hydroxide desorption free energy; (c) d-band centre.

**Table S1.** Summary of kinetic barrier of water dissociation on dimer structure, relevant transition states (TS) models and the bond length of stretched O-H of TS.

| Dimer Name | Dimer Structure | Kinetic Barrier (eV) | O-H Bond length (Å) |
|---|---|---|---|
| $Pt_2$@DG |  | 0.74 | 1.42 |
| $Ru_2$@DG |  | 0.55 | 1.38 |
| PtRu@DG |  | 0.41 | 1.39 |
| $Pt_2$@NG |  | 0.85 | 1.45 |
| $Ru_2$@NG |  | 0.35 | 1.36 |
| PtRu@NG |  | 0.77 | 1.43 |

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