Supporting Information

Enhanced Hydrogen Evolution Reaction Catalysis via Ruthenium Single-Atom Decoration on Biphenylene: A DFT Study

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1. The derivation of the formula 2

It is well known that the Gibbs free energy change is defined as, $\Delta G = \Delta H - T\Delta S$. In surface-catalysis calculation studies, this formula is usually approximated.[1] The enthalpic term can be expressed as $\Delta H = \Delta U + P\Delta V$. For reactions occurring at solid–gas interfaces, the $P\Delta V$ contribution is negligible, and hence $\Delta H \approx \Delta U$. The internal-energy change can be decomposed as:

$$\Delta U = \Delta U_{elec} + \Delta E_{ZPE} + \Delta U_{vib} + \Delta U_{rot} + \Delta U_{trans} \quad (1)$$

U_{elec} is internal-energy from electrons in system and thus ΔU_{elec} is the change of electronic internal-energy. ΔE_{ZPE} is the change of zero-point vibrational energy due to the adsorption of H which is extracted from frequency calculations. The internal-energe change ΔU_{elec} of electrons in system does not change obviously by following the increase of temperature up to room temperature and thus $\Delta U_{\mathrm{elec}} \approx \Delta E_{\mathrm{elec}}$, where ΔE_{elec} is the energy change of electrons at zero temperature and can be calculated based on density functional theory. ΔE_{ZPE} has no obvious relation to temperature. Here, ΔE_{elec} is the adsorption energy of hydrogen ($\Delta E_{\mathrm{H}*}$). It is calculated by the formula:

$$\Delta E_{\mathrm{H}*} = E_{\mathrm{H+cat}} - E_{\mathrm{cat}} - \frac{1}{2} E_{\mathrm{H_2}} \quad (2)$$

This formula corresponds to the formula (1). The remaining vibrational, rotational and translational contributions ($\Delta U_{\mathrm{vib}} + \Delta U_{\mathrm{rot}} + \Delta U_{\mathrm{trans}}$) are related to the temperature and effectively absorbed into the entropy term $T\Delta S$, a common practice in computational heterogeneous catalysis. Thus, $\Delta U = \Delta E_{\mathrm{H}*} + \Delta E_{\mathrm{ZPE}}$. The item TΔS in the formula, $\Delta G = \Delta H - T\Delta S$ is corrected due to the contributions of vibrational, rotational and translational energy ($\Delta U_{\mathrm{vib}} + \Delta U_{\mathrm{rot}} + \Delta U_{\mathrm{trans}}$). Thus, with the formula $\Delta G = \Delta H - T\Delta S$, we obtain the formula:

$$\Delta G_{\mathrm{H}*} = \Delta E_{\mathrm{H}*} + \Delta E_{ZPE} - T\Delta S \quad (3)$$

Table 1 the detailed values from DFT calculations to obtain the $\Delta G_{\mathrm{H}*}$, including the values of $\Delta E_{\mathrm{H}*}$, ΔE_{ZPE}, $T\Delta S$ and $\Delta E_{\mathrm{ZPE}} - T\Delta S$.

site	4	46	48	468	6	68	688	8	88
ΔE_{ZPE}	0.091	0.205	0.149	0.125	0.145	0.102	0.090	0.205	0.197
$T\Delta S$	-0.148	-0.137	-0.107	-0.159	-0.136	-0.168	-0.195	-0.169	-0.090
ΔE_{ZPE} - $T\Delta S$	0.239	0.342	0.256	0.284	0.281	0.270	0.285	0.374	0.287
$\Delta E_{\mathrm{H}*}$	-0.440	-0.504	-0.474	-0.377	-0.098	-0.141	-0.099	-0.609	-0.555
$\Delta G_{\mathrm{H}*}$	-0.201	-0.162	-0.218	-0.093	0.183	0.129	0.176	-0.235	-0.268

2. The unit of exchange current density

To calculate the exchange current density, we have used the theoretical formula:

$$i_0 = -ek_0 \frac{1}{1+\exp(-\Delta G_{H^*}/kT)} \tag{4}$$

And:

$$i_0 = -ek_0 \frac{1}{1+\exp(-\Delta G_{H^*}/kT)} \exp(-\Delta G_{H^*}/kT) \tag{5}$$

From the formulas above, with the data including $k_0 = 200$ $s^{-1}site^{-1}$, $T = 300$ K and $e = -1.602 \times 10^{-19}$ C, we can get the value of exchange current density i_0 in the unit of A $site^{-1}$. In order to compare with the experimental results, the unit of site density (A $site^{-1}$) needs to be converted into (A cm^{-2}), which indicates we needs the active site density. From the reference 2, the active site density of Pt is reported as 1.5×10^{15} site per cm^2. From the reference 3, the active site density of RuO_2 is 7.2×10^{14} site per cm^2. For the Ru-BPN model proposed in our work, we have considered the single-atom catalyst with one Ru atom in a 2×2×1 supercell of BPN. Thus, the active site density is calculated to be 1.47×10^{14} sites per cm^2.

Table. S2 The Gibbs free energy (ΔG_{H^*}), the exchange current density i_0 with the unit (A cm^{-2}), the active site density, the exchange current density i_0 with the unit (A cm^{-2}), and the $\lg(i_0/(\text{A cm}^{-2}))$ for Ru468, Pt and RuO_2, and the experimental value of Pt's $\lg(i_0/(\text{A cm}^{-2}))$, which is -2.63 from the reference 7.

catalyst	Ru468 (this work)	Pt	RuO_2
ΔG_{H^*}(eV)	-0.093	-0.08 (Ref.4)	0.240 (Ref.5, 6)
i_0 (A $site^{-1}$)	8.71×10^{-19}	1.41×10^{-18}	3.14×10^{-21}
active site density(site cm^{-2})	1.47×10^{14}	1.50×10^{15} (Ref. 2)	7.20×10^{14} (Ref. 3)
i_0 (A cm^{-2})	1.29×10^{-4}	2.12×10^{-3}	2.26×10^{-6}
$\lg(i_0)$ with i_0 in A cm^{-2}	-3.89	-2.67，-2.63 (Ref.7)	-5.64

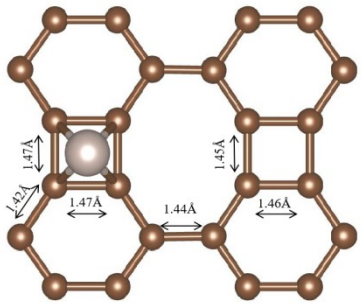

Fig. S1 The Ru468 structure after the Ru atom's adsorption and some of its relative coordinates.

The atomic coordinates of the BPN slab in Ru468 are listed below.
Three base vectors are,
a = (9.02, 0.0, 0.0); b= (0.0, 7.52, 0.0); c= (0.0, 0.0, 20.0)
The fractional coordinates of the BPN slab and Ru atom in Ru468 are,

C	0.166000	0.400000	0.501000
C	0.327000	0.092500	0.498000
C	0.328000	0.400000	0.501000
C	0.166000	0.092500	0.499000
C	0.077000	0.245000	0.500000
C	0.417000	0.245000	0.500000
C	0.665000	0.398000	0.507000
C	0.828000	0.093100	0.497000
C	0.828000	0.398000	0.507000
C	0.666000	0.093000	0.496000
C	0.576000	0.243000	0.500000
C	0.918000	0.243000	0.501000
C	0.166000	0.900000	0.498000
C	0.328000	0.592000	0.501000
C	0.327000	0.900000	0.498000
C	0.166000	0.592000	0.501000
C	0.077000	0.747000	0.500000
C	0.417000	0.747000	0.499000
C	0.666000	0.899000	0.496000
C	0.828000	0.594000	0.507000
C	0.828000	0.899000	0.497000
C	0.665000	0.594000	0.507000
C	0.576000	0.750000	0.500000
C	0.918000	0.750000	0.501000
Ru	0.745000	0.496000	0.593000

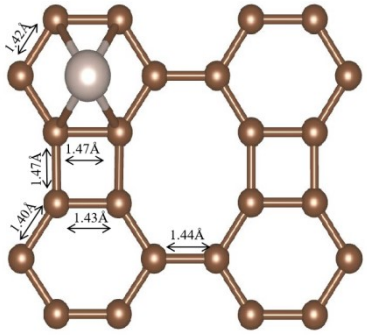

Fig. S2 The Ru6 structure after the Ru atom's adsorption and some of its relative coordinates.

The atomic coordinates of the BPN slab in Ru6 are listed below.
Three base vectors are,
a = (9.02, 0.0, 0.0); b= (0.0, 7.52, 0.0); c= (0.0, 0.0, 20.0)
The fractional coordinates of the BPN slab and Ru atom in Ru6 are,

C	0.169000	0.404000	0.499000
C	0.331000	0.095700	0.499000
C	0.331000	0.404000	0.499000
C	0.169000	0.095700	0.499000
C	0.081600	0.250000	0.499000
C	0.418000	0.250000	0.499000
C	0.669000	0.404000	0.504000
C	0.831000	0.096400	0.504000
C	0.831000	0.404000	0.504000
C	0.669000	0.096400	0.504000
C	0.578000	0.250000	0.500000
C	0.922000	0.250000	0.500000
C	0.169000	0.904000	0.500000
C	0.331000	0.596000	0.500000
C	0.331000	0.904000	0.500000
C	0.169000	0.596000	0.500000
C	0.079800	0.750000	0.501000
C	0.420000	0.750000	0.501000
C	0.671000	0.901000	0.503000
C	0.829000	0.599000	0.503000
C	0.829000	0.901000	0.503000
C	0.671000	0.599000	0.503000
C	0.580000	0.750000	0.503000
C	0.920000	0.750000	0.503000
Ru	0.750000	0.250000	0.589000

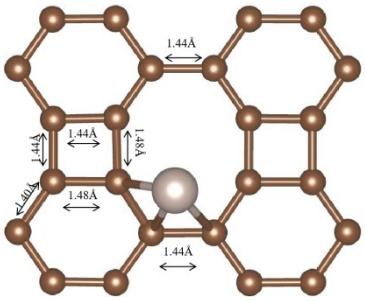

Fig. S3 The Ru88 structure after the Ru atom's adsorption and some of its relative coordinates.

The atomic coordinates of the BPN slab in Ru88 are listed below.
Three base vectors are,
a = (9.02, 0.0, 0.0); b= (0.0, 7.52, 0.0); c= (0.0, 0.0, 20.0)
The fractional coordinates of the BPN slab and Ru atom in Ru88 are,

C	0.172000	0.404000	0.513000
C	0.328000	0.096300	0.490000
C	0.337000	0.401000	0.507000
C	0.167000	0.096500	0.500000
C	0.080500	0.252000	0.509000
C	0.420000	0.245000	0.490000
C	0.663000	0.401000	0.507000
C	0.833000	0.096500	0.500000
C	0.828000	0.404000	0.513000
C	0.672000	0.096300	0.490000
C	0.580000	0.245000	0.490000
C	0.920000	0.252000	0.509000
C	0.167000	0.903000	0.500000
C	0.337000	0.599000	0.507000
C	0.328000	0.904000	0.490000
C	0.172000	0.596000	0.513000
C	0.080500	0.748000	0.509000
C	0.420000	0.755000	0.490000
C	0.672000	0.904000	0.490000
C	0.828000	0.596000	0.513000
C	0.833000	0.903000	0.500000
C	0.663000	0.599000	0.507000
C	0.580000	0.755000	0.490000
C	0.920000	0.748000	0.509000
Ru	0.480000	0.360000	0.584000

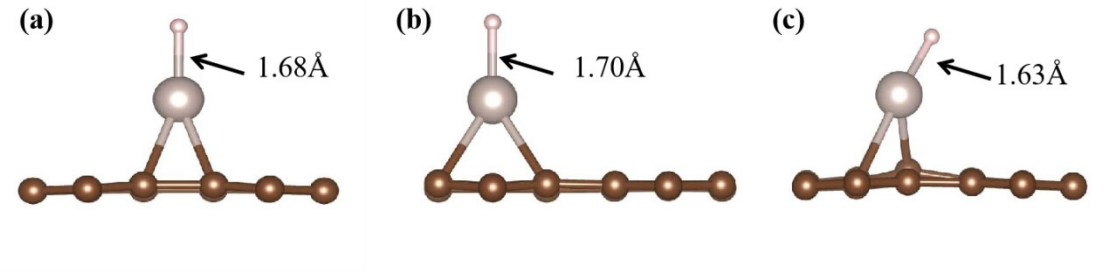

Fig. S4 The (a)Ru468, (b)Ru6, (c)Ru88's H adsorption structure and their Ru-H bond.

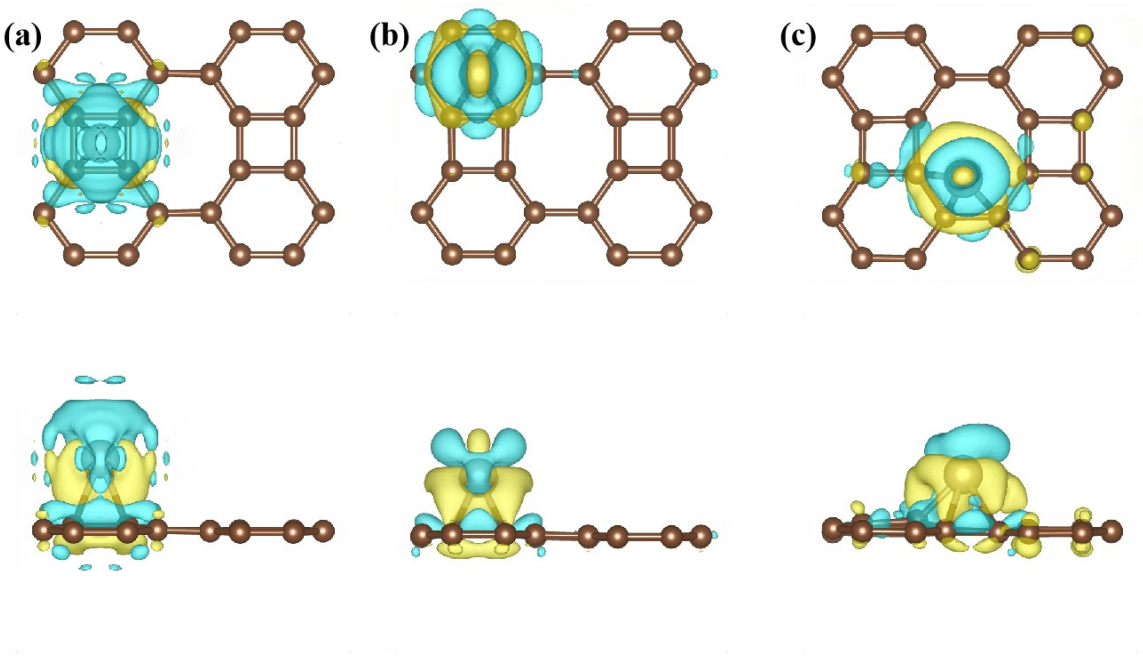

Fig. S5 The distributions of differential charge density between (a) Ru above C_4 ring in BPN and BPN (Ru468 model), and (b) Ru above C_6 ring in BPN and BPN (Ru6 model), and (c) Ru above C_8 ring in BPN and BPN (Ru88 model).

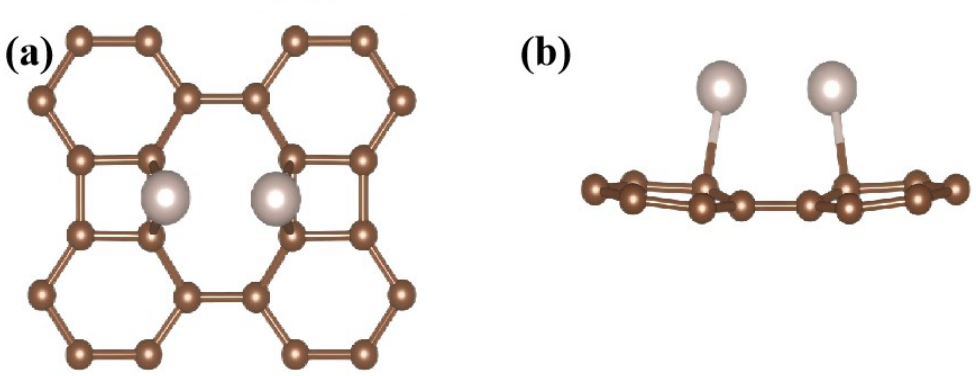

Fig. S6 (a) The top view (a) and (b) side view (b) of two Ru atoms adsorbed on biphenylene.

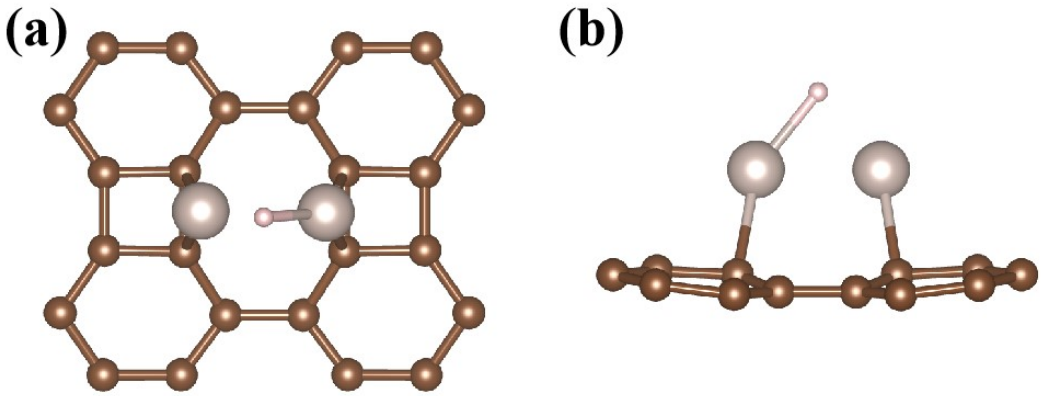

Fig. S7 The top view (a) and (b) side view (b) of 1 H atom adsorbed on the 2Ru-BPN.

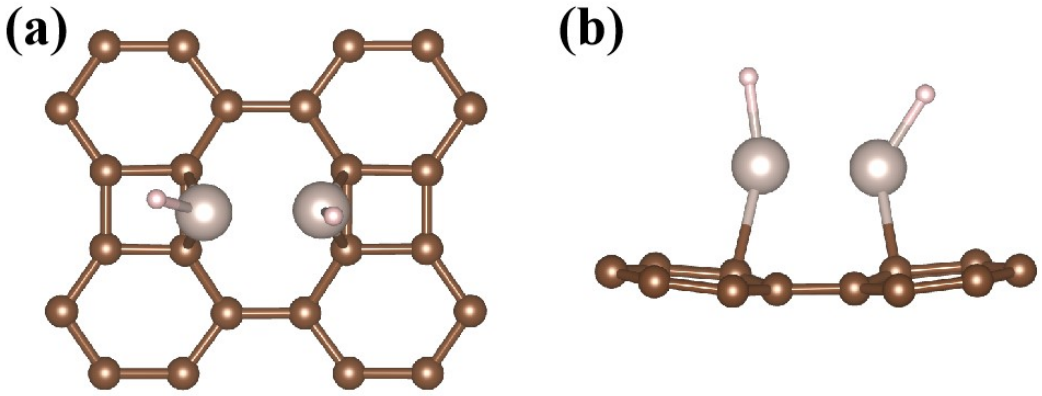

Fig. S8 The top view (a) and (b) side view (b) of 2 H atoms adsorbed on the 2Ru-BPN.

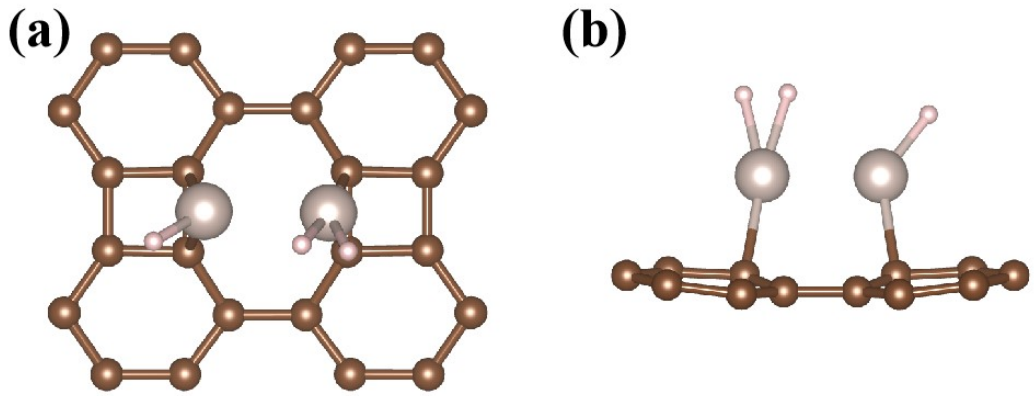

Fig. S9 The top view (a) and (b) side view (b) of 3 H atoms adsorbed on the 2Ru-BPN.

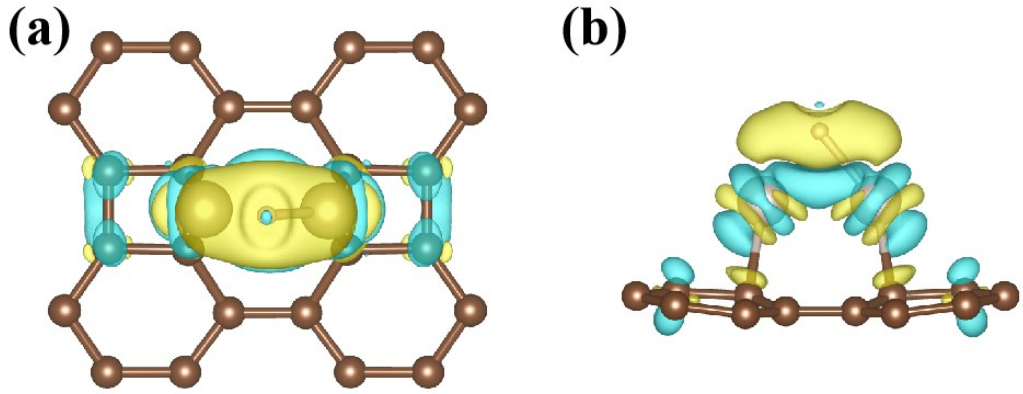

Fig. S10 The top view and side view of charge difference of 1 H atom adsorbed on 2Ru-BPN.

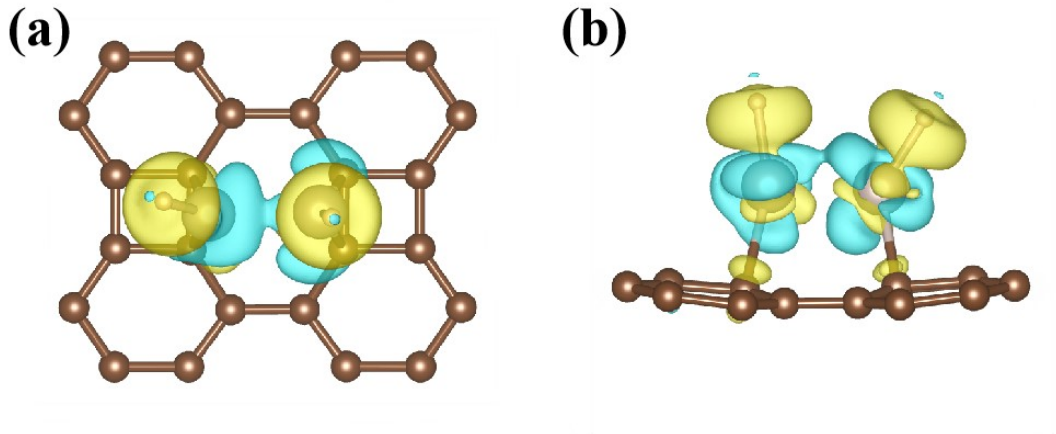

Fig. S11 The top view and side view of charge difference of 2 H atom adsorbed on 2Ru-BPN.

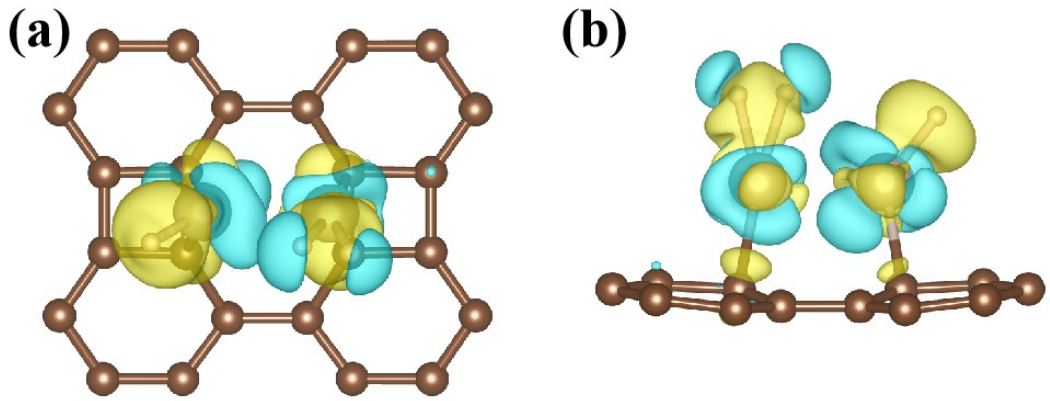

Fig. S12 The top view and side view of charge difference of 3 H atom adsorbed on 2Ru-BPN.

References

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