Supporting Information

Ruthenium/graphene-like layered carbon composite as efficient hydrogen evolution reaction electrocatalyst

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Computational models and methods

In this work, Plane-wave-based DFT calculations on slab models are carried out by the exchange-correlation functional GGA-PBE.[1] The projector-augmented wave (PAW) method are employed to describe the electron−ion interaction.[2] The cutoff energy was used at 400 eV in present calculations. First-order Methfessel−Paxton smearing technique with a width of 0.1 eV was invoked. The self-consistent field iterations were considered converged when the total energy changed by $<10^{-5}$ eV. To model the Ru (001) surface and Pt (111) surface, we used a slab of five close packed layers in a 5 × 5 hexagonal supercell with a vacuum layer of 1.5nm. The optimized bulk geometry was kept except the top two layers which were relaxed for optimization. For geometry optimizations, the Brillouin zone was sampled with a Monkhorst−Pack mesh[3] of 3 × 3 × 1 k-points. All the atoms were allowed to relax until the maximum force becomes less than 2×10^{-4} eV/pm. All the calculations are performed using the program Vienna ab initio simulation package (VASP ,version 5.3.3) [4-6]. To model the Ru(001) surface and Pt(111) surface, we used a slab of five close packed layers in a 5 × 5 hexagonal supercell with a vacuum layer of 1.5nm with the H_2 coverage is 0.04ML. The optimized bulk geometry was kept except the top two layers which were relaxed for optimization. In our work, we defined the adsorption energy E_{ad} to describe the HER performance of catalyst Ru or Pt[7,8].

$\Delta E_{ad}=E_{surface-H}-(E_{surface}+E_{H2}/2)+0.24eV$

Where $E_{surface}$ is the energy of super-cell for Ru(001) and Pt(111) surfaces; $E_{surface-H}$ is the total energy of complex of hydrogen adsorption on sufaces; E_{H2} is the energy of hydrogen molecule. 0.24 eV is added to the calculated binding energies (with respect to gaseous H_2) to give adsorption free energies. [8]

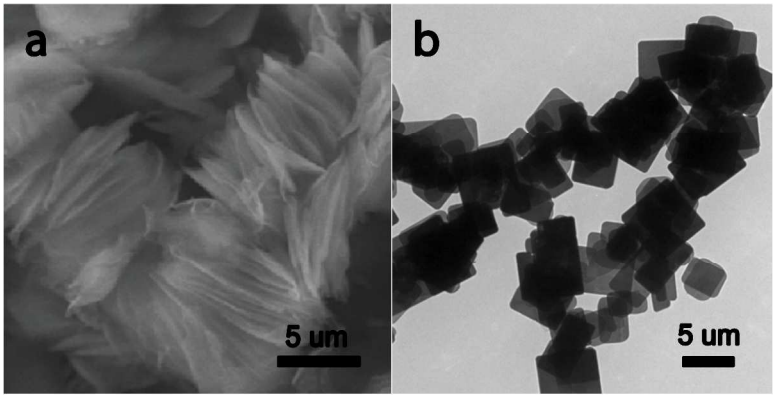

Figure S1 a) SEM and b) TEM images of RUB-15

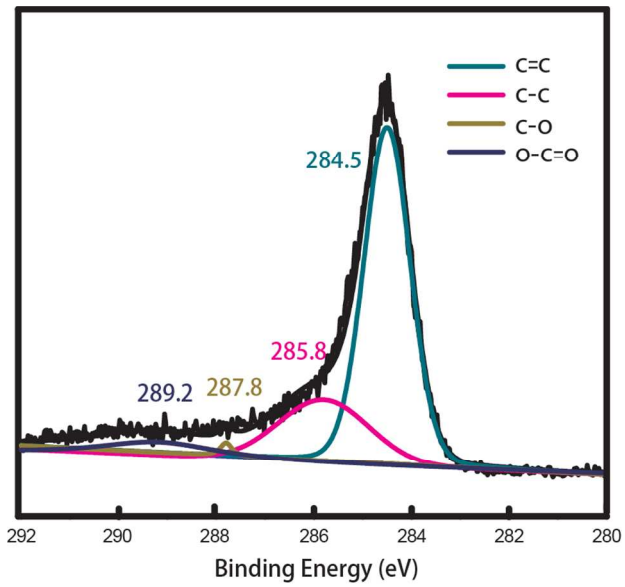

Figure S2 XPS spectra of GLC

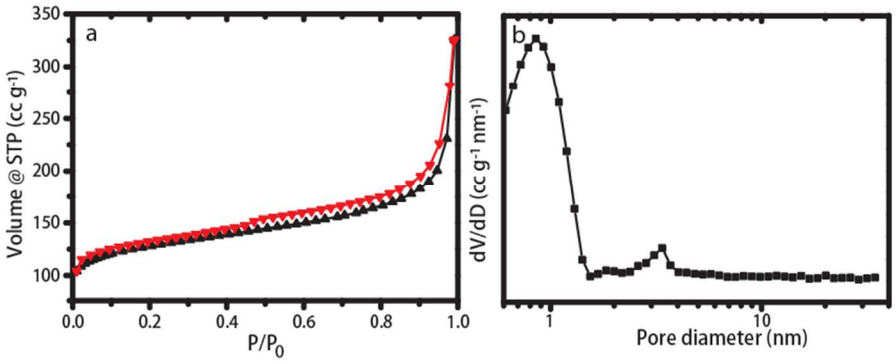

Figure S3 a) N_2 adsorption-desorption curve and b) NLDFT pore diameter distribution of GLC

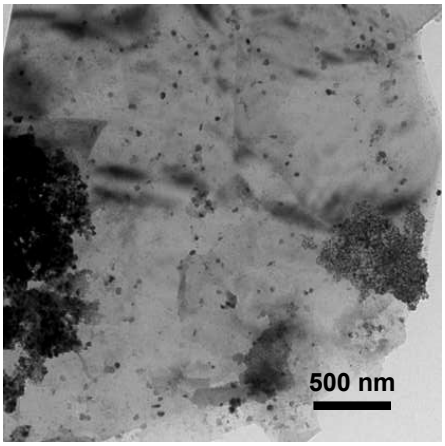

Figure S4 TEM image of Ru/commercial graphene

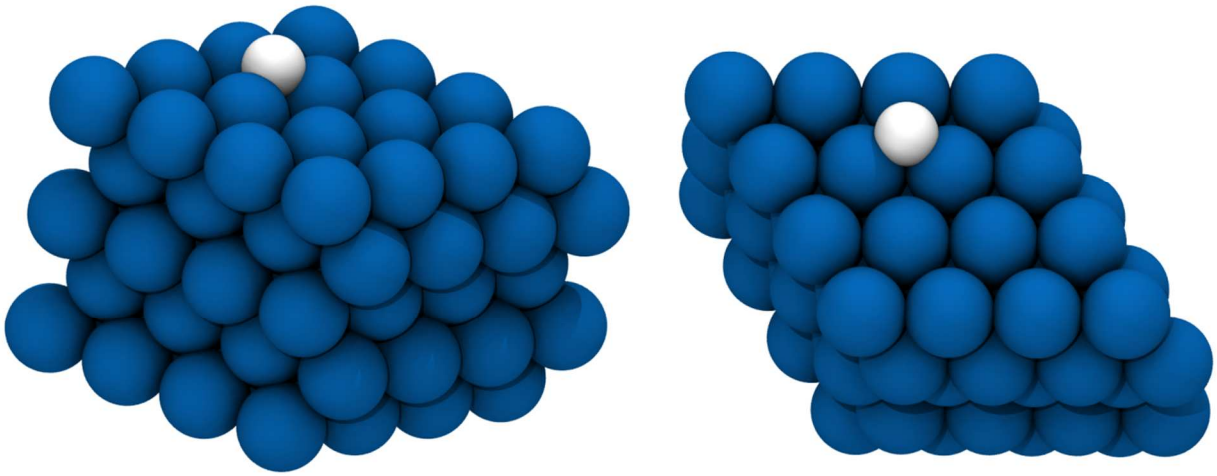

Figure S5. The super-cell structure of hydrogen adsorption on Ru(001) surface. Left: side view, right: top view. Blue ball: Ru atom, white ball: H atom.

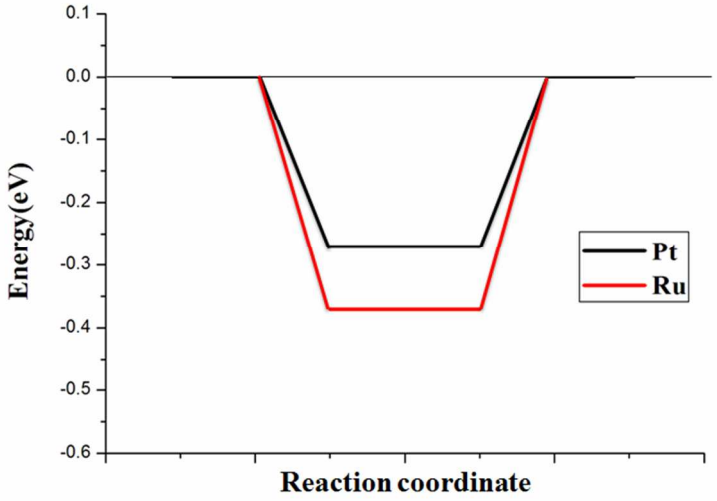

Figure S6. HER energy diagram calculated at the equilibrium potentialfor Ru and Pt metal electrocatalysts.

References

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