Energy Materials

Supplementary Material

Mesostructured Pt alloy nanotubes with synergistic edge sites as bifunctional electrocatalysts for direct ethanol fuel cells

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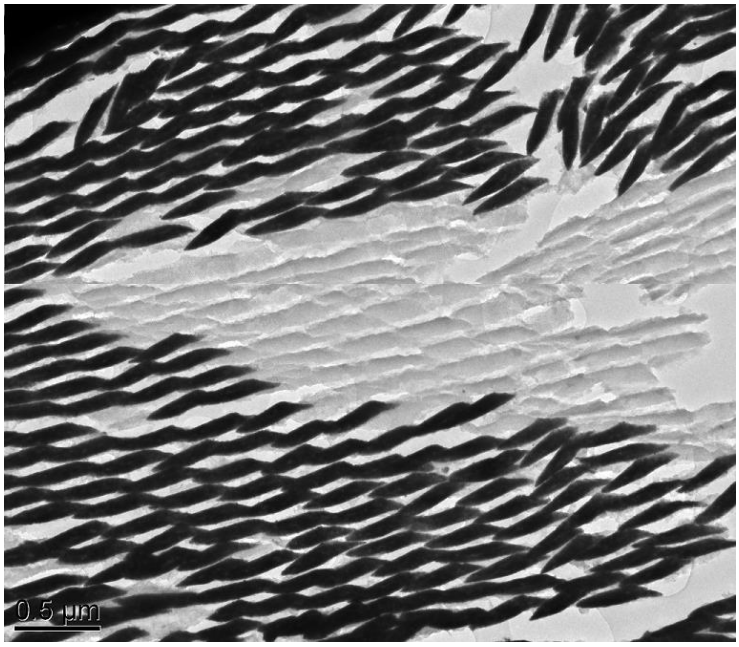

Fig. S1 TEM image of MPPNs prepared by microtome.

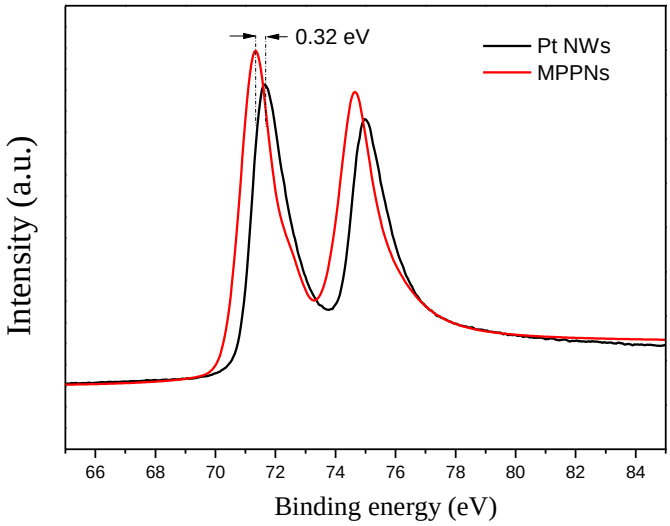

Fig. S2 XPS spectra of Pt 4f of MPPNs and Pt nanowires.

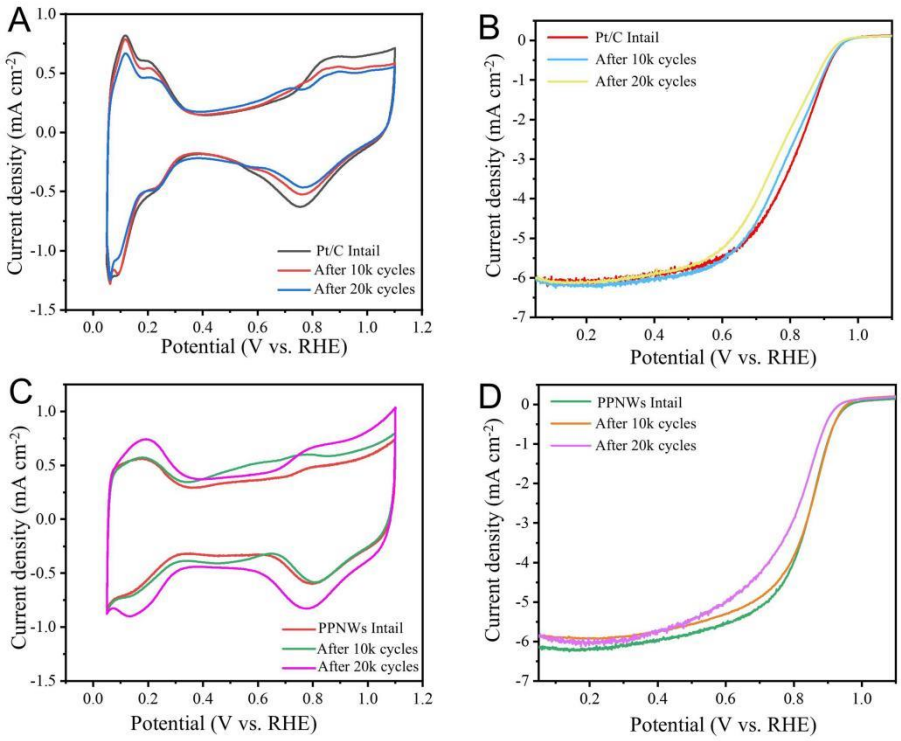

Fig. S3. (A) CV curves of commercial Pt/C. (B) The ORR polarization curves of Pt/C after the durability test. (C) CV curves of PPNWs. (D) The ORR polarization curves of PPNWs after the durability test.

Calculation methods:

According to the experiment results, it can be known that the content of Pd in PtPd nanotube alloy is about 20%. Therefore, we constructed a PtPd protocell with a Pd content of 20%, and then constructed 4-layer 2x2 PtPd (111), 6-layer Pt(111)(200) and 6-layer Pt(111)(200) models through supercell approach (Fig. S1 and S2).

For the adsorption energy of each adsorbate A, we calculate them by the following equation:

$$\Delta E_A = E_A^* - E^* - E_A$$

Where E_A^* and E^* are the energy of the totoal system and catalyst,E_A is referred to the stable molecular form of the adsorbate A in gas phase.

There are many different ethanol oxidation mechanisms in reported literatures. In this work, the most common pathways of computational hydrogen electrode model was adopted. In this model, the energy barrier at each elementary

proton-coupled-electron ($H^+ + e^-$) transfer oxidation step is often used to determine whether a reaction is easy to occur. And the energy of ($H^+ + e^-$) is equal to $\frac{1}{2}H_2$. The main barrier comes from the energy required to break chemical bonds. Therefore, we calculated the reaction energy and reaction energy barrier of possible reaction pathways, thus the energy change and possibility of the reaction pathway can be judged.

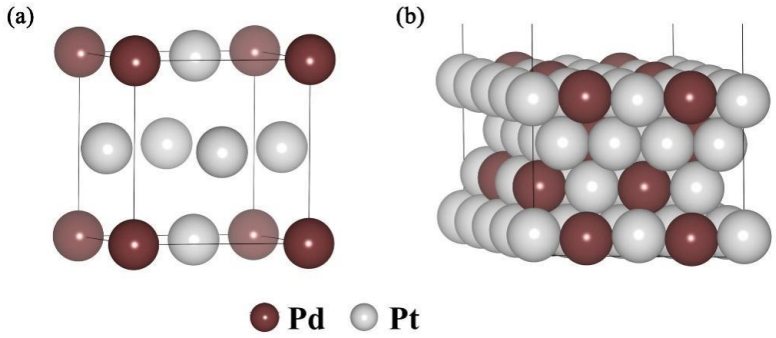

Fig. S4 (a, b) the models of PtPd protocell and PtPd(111), respectively.

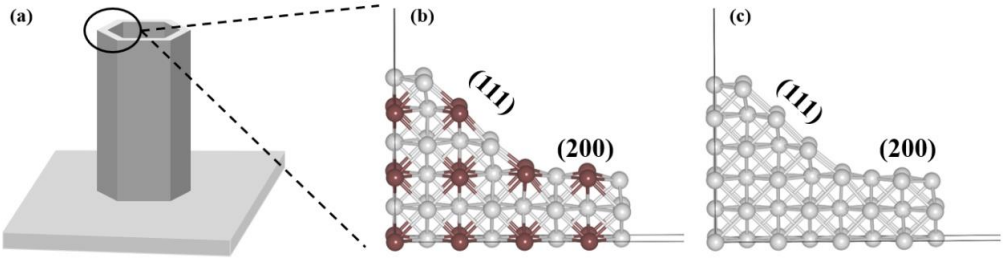

Fig. S5 (a) the Geometric structure model of PtPd mesoporous alloy. (b, c) The atomic models of PtPd(111)(200) and PtPd(111)(200) for DFT calculation.

Fig. S4a is the geometric structure model of PtPd mesoporous alloy, which has hexagonal pore observed experimentally. According to the structural characteristics of the catalyst, we construct atomic model composed of PtPd(111) and PtPd(200) to simulate the inner side of the pore (Fig. S4b). In order to explore the effect of introducing Pd on the electrooxidation of ethanol, Pt(111)(200) is also constructed (Fig. S4c).

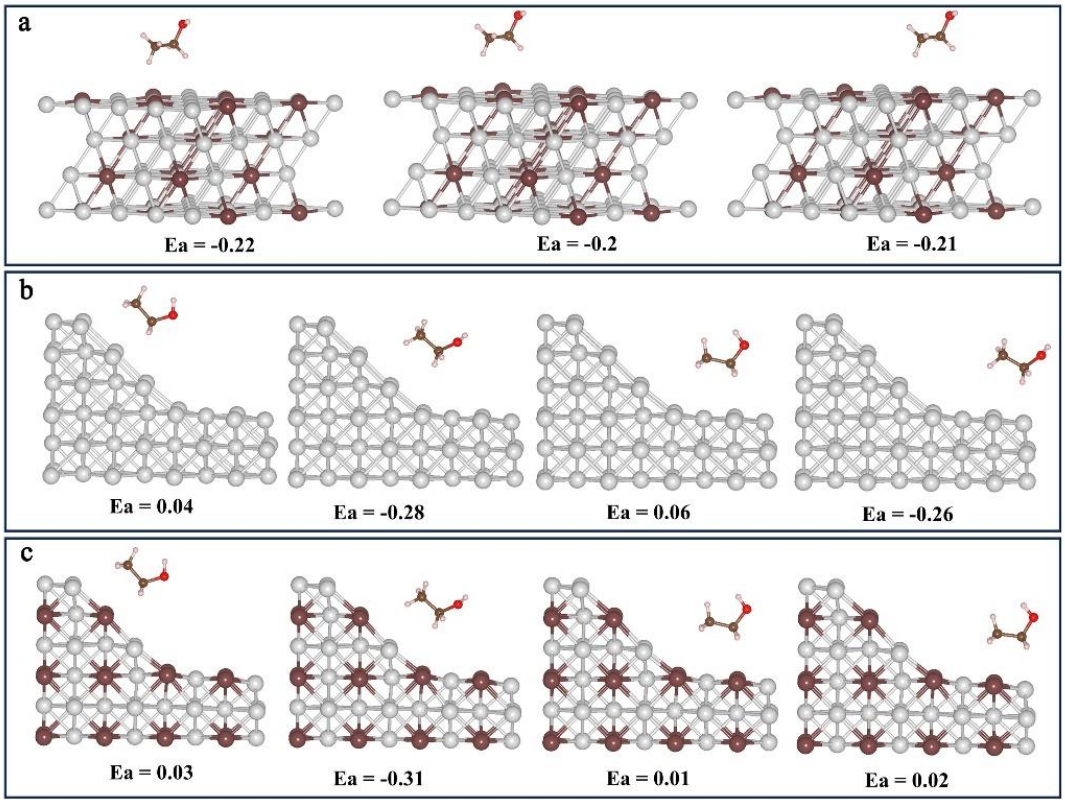

Fig. S6 (a, b) The optimized ethanol adsorption models and adsorption energy of PtPd (111), Pt(111)/(200) and PtPd(111)/(200) at different sites, respectively.

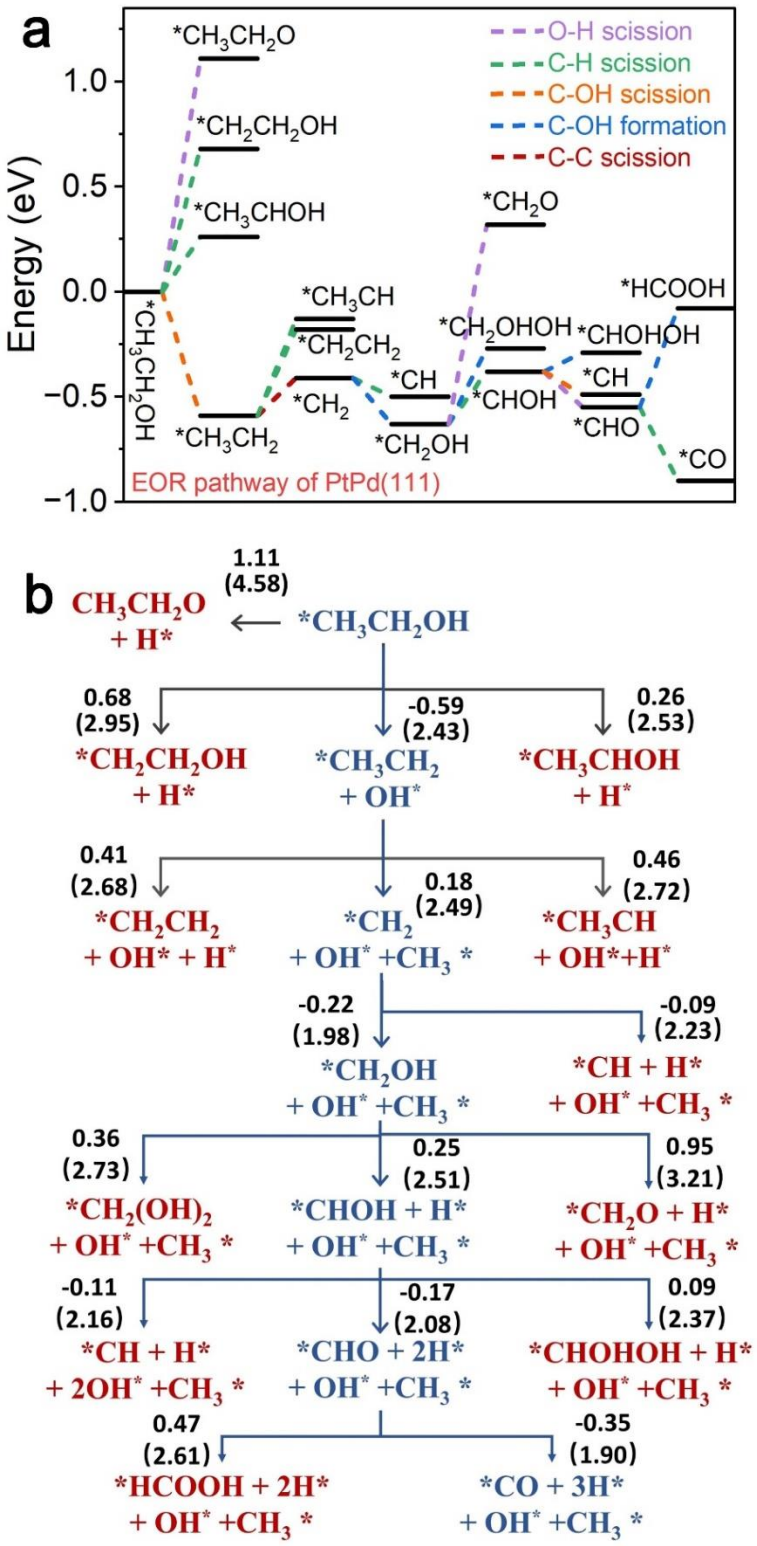

Fig. S7 (a) The possible pathways for ethanol decomposition on the surface of PtPd(111). (b) The specific energy change and energy barrier (values in brackets) for of each reaction step.

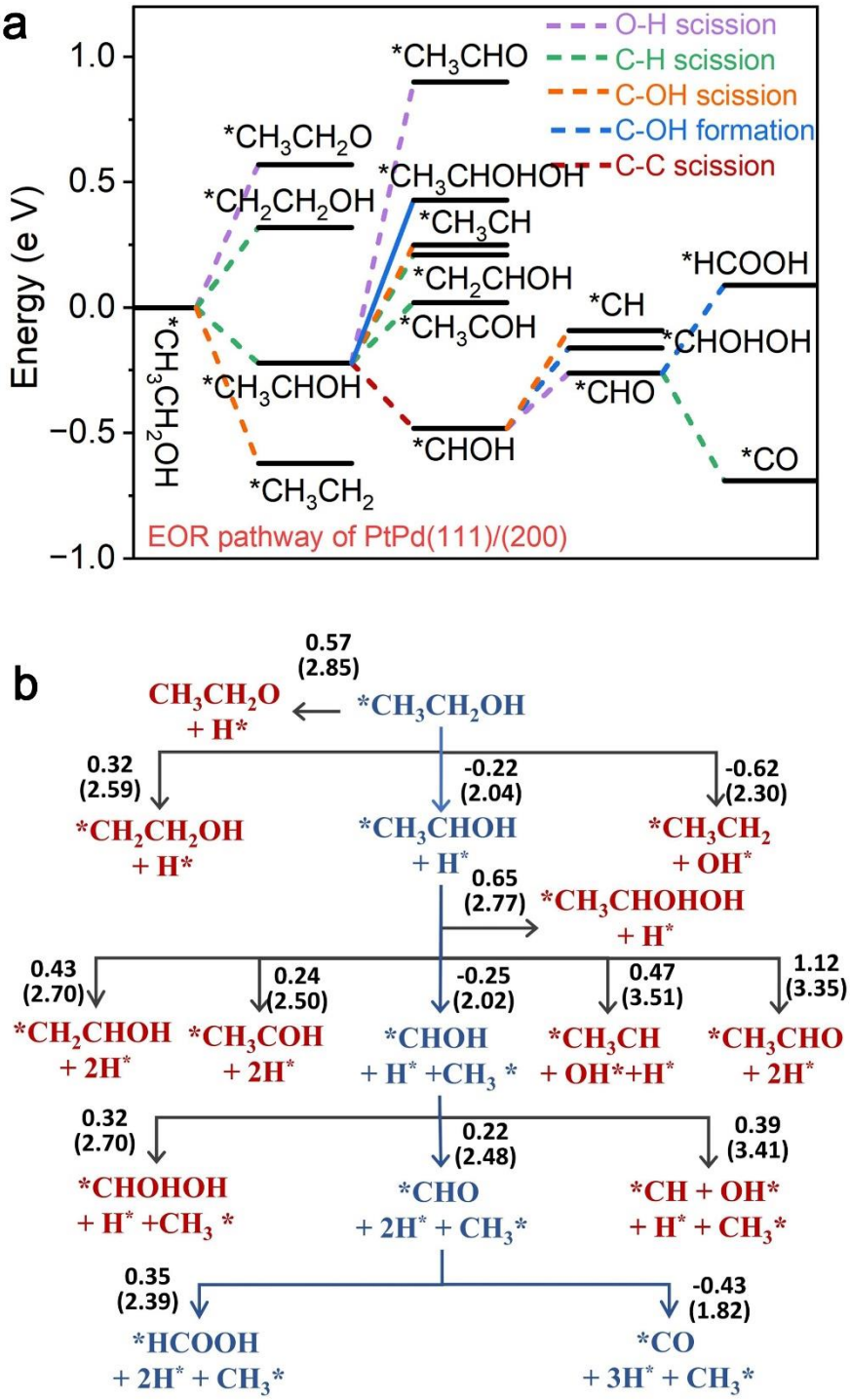

Fig. S8 (a) The possible pathways for ethanol decomposition on the surface of PtPd(111)/(200). (b) The specific energy change and energy barrier (values in brackets) of each reaction step.

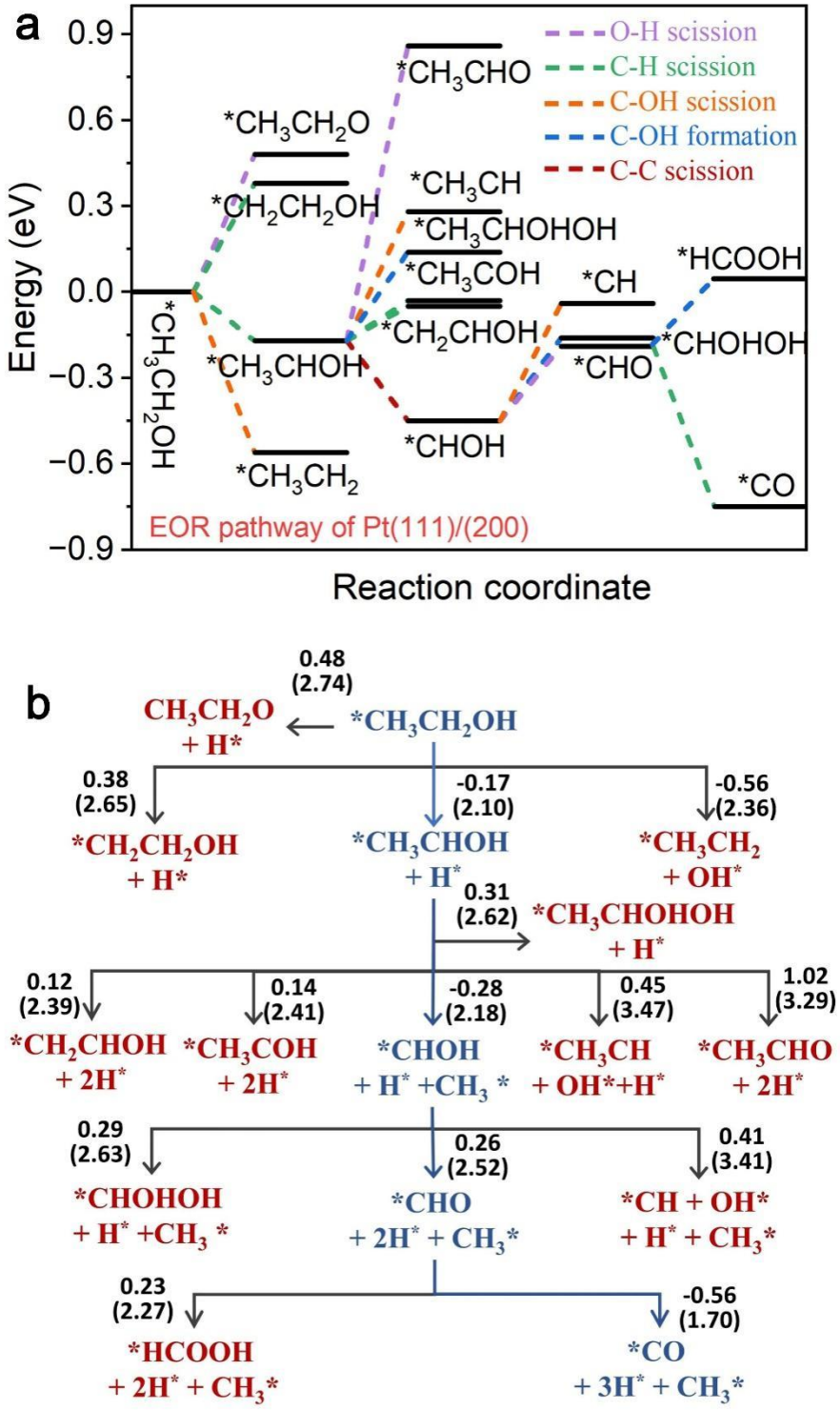

Fig. S9 (a) The possible pathways for ethanol decomposition on the surface of Pt(111)/(200). (b) The specific energy change and energy barrier (values in brackets) of each reaction step.

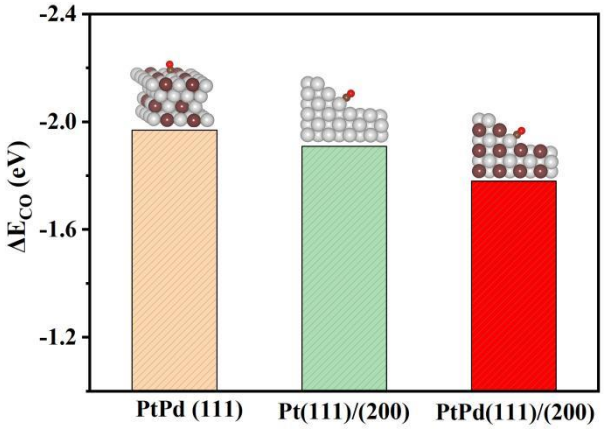

Fig. S10 The comparison of binding energy between CO and catalyst surface.

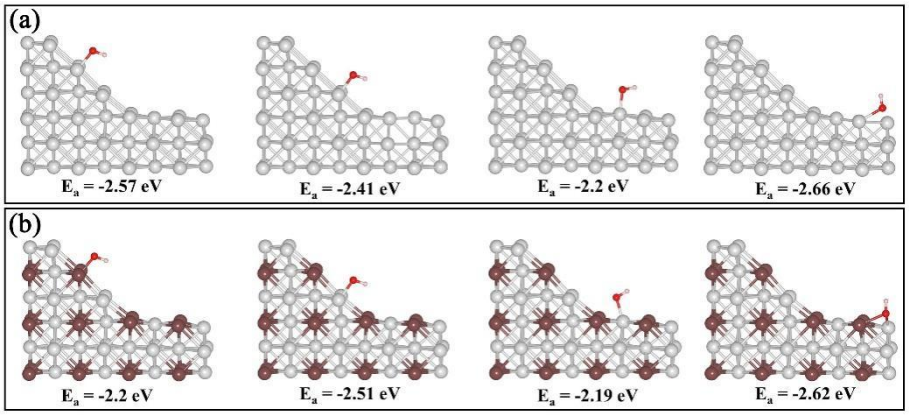

Fig. S11 The optimized OH adsorption models and adsorption energy at different sites. (a) Pt(111)(200). (b) PtPd(111)(200).