Hydrogen Adsorption-Mediated Synthesis of Pt Concave Nanocubes and Their Enhanced Electrocatalytic Activity

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Detailed description of DFT calculation

In terms of the H coverage on Pt, we calculated the H coverage according to the reaction, $H^+ + e^- \rightarrow H^*$. We found that, under the SHE condition, the equilibrium H coverage would be 1.5-1.75 ML, as illustrated in Fig. S2, since the reaction free energy is around zero. This result agrees well with the experimental observation in the literature (*ChemCatChem*, 2011, 3, 200-207) that the H coverage of 1.25-1.75 ML on Pt(100) is preferred than that on Pt(111), where the coverage only can reach 1 ML. More importantly, since the experiments is operated at a much low electrode potential (-0.56 V vs SCE, i.e., -0.32 V vs SHE), the negative potential promotes H adsorption on surface. With a correction term of eU (-0.6 eV) (*J. Phys. Chem. C*, 2004, 108, 1520), the free energy in $H^+ + e^- \rightarrow H^*$ is calculated to be below zero at the coverage of 2 ML, indicating that a H coverage of 2 ML can be thermodynamically on Pt(100). For the edge sites which are more active for H adsorption, even under the SHE condition, the free energy in H adsorption at 2 ML is already below zero. It is thus reasonable to infer that, under such a negative potential used in experiments, both Pt(100) and edge sites can reach 2 ML H coverage. It should be pointed out that, only considering the thermodynamical condition may be not accurate enough, the kinetic effects are neglected in this work because the kinetic issues is some extent beyond the current computational ability, which might cause the H coverage is a little over or less estimated comparing with the realistic value. Nevertheless, our calculations have given the theoretical evidences to support a general trend that a high H coverage can affects the position of the newly deposited Pt atoms, which will be important for understanding the deposition process in the presence of H.
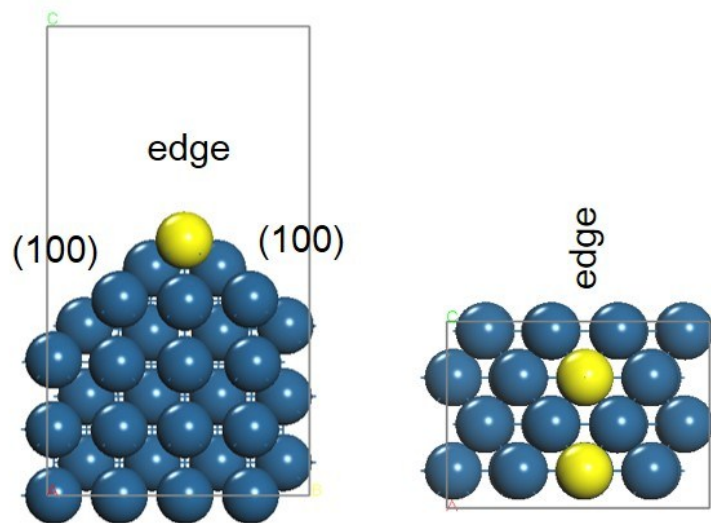
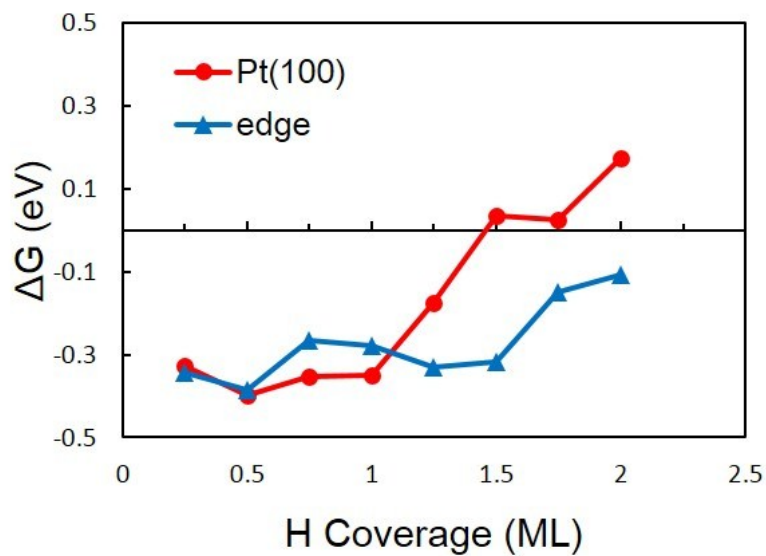**Fig. S1** Side and top views of the models of nanocube edge. Blue: Pt; yellow: Pt on edge.

Fig. S2 Differential free energy (ΔG, in eV) of H adsorption against the increase of H coverage.
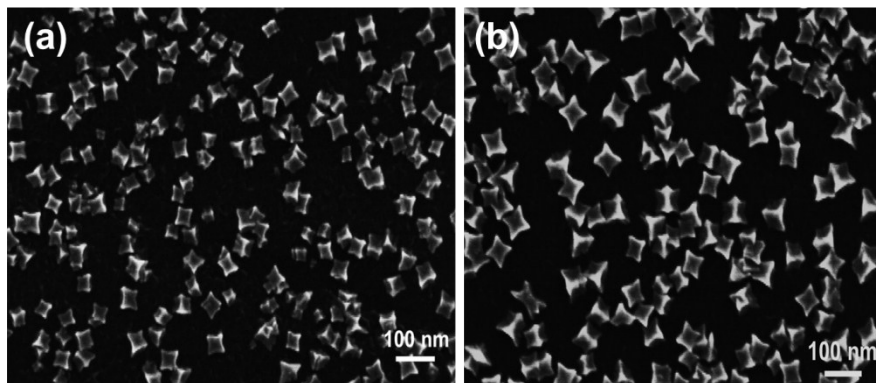
Fig. S3 Pt concave nanocubes obtained at different E_N. (a) -0.80 V, (b) -0.40 V.
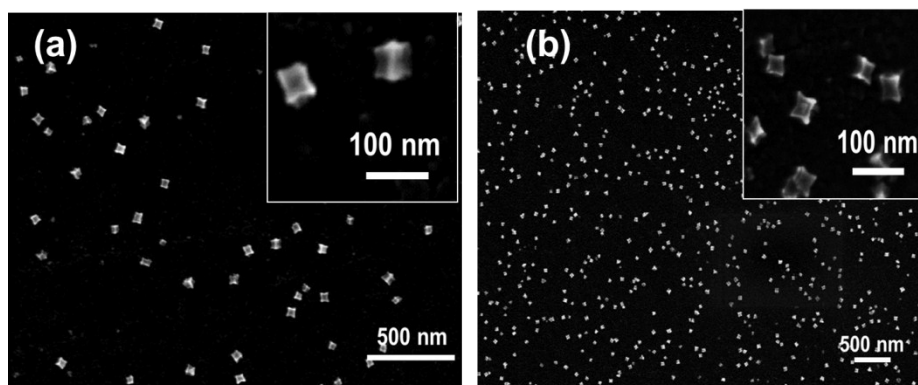

Fig. S4 Pt concave nanocubes obtained in different concentration of H_2PtCl_6. (a) 0.1 mM, (b) 0.5 mM.

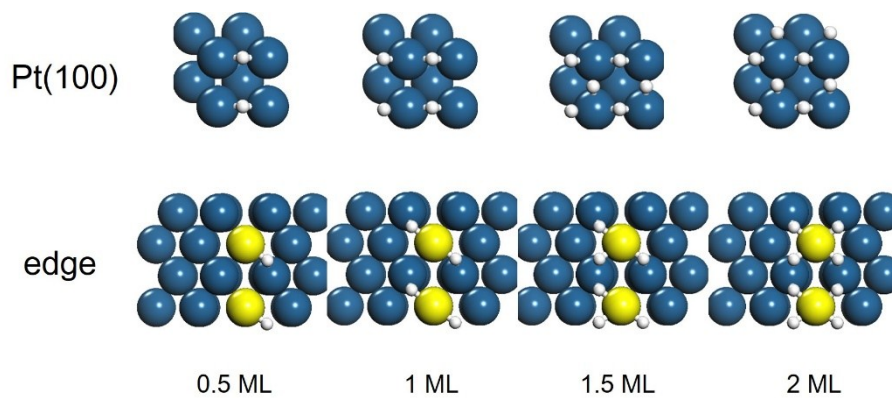
Pt(100)

edge

0.5 ML   1 ML   1.5 ML   2 ML

Fig. S5 Models of H adsorption on Pt(100) and edge sites with a coverage from 0.5 ML to 2 ML.
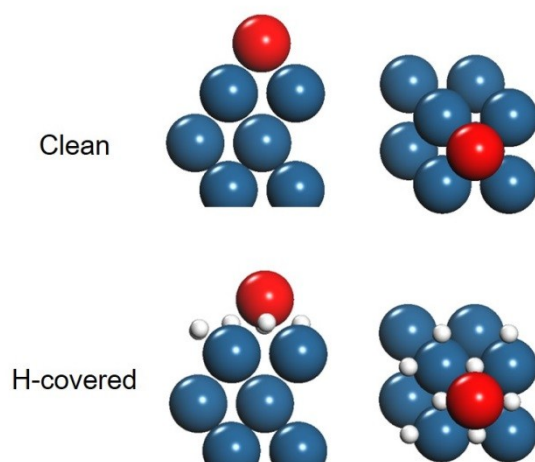
Fig. S6 Side and top views of the newly deposited Pt atom on the clean and H-covered **Pt(100) surfaces**. Red: newly deposited Pt atom.
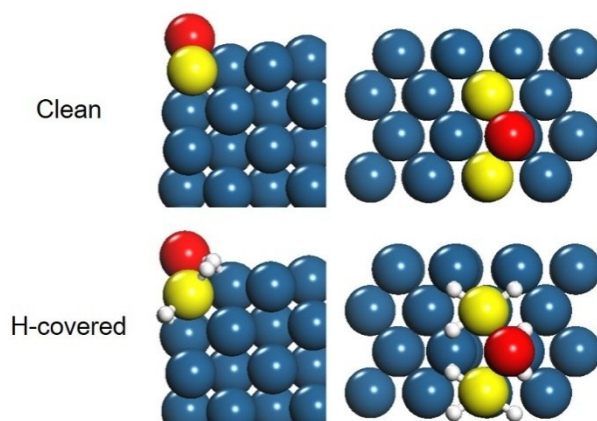

Fig. S7 Side and top views of the newly deposited Pt atom at the clean and H-covered **edge sites**. Red: newly deposited Pt atom.
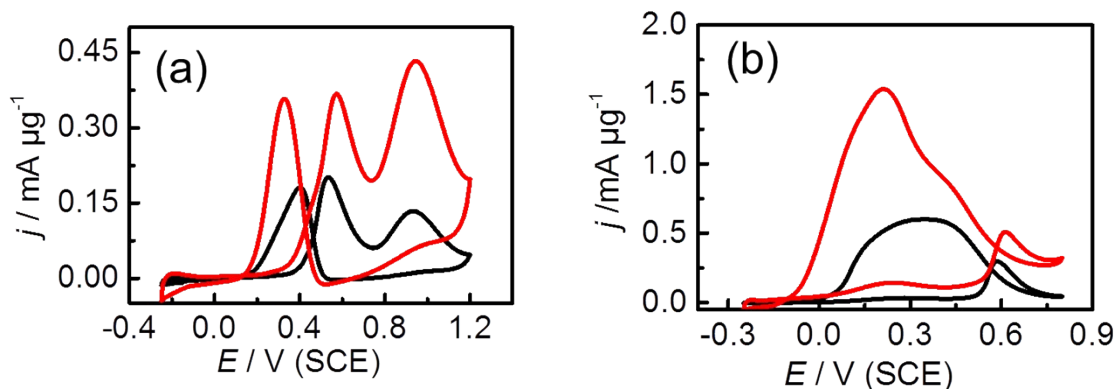
Fig. S8 CV curves of electrooxidation of ethanol (a) and formic acid (b) on Pt concave nanocubes and commercial Pt/C in solutions of 0.1 M CH_3CH_2OH + 0.1 M $HClO_4$ and 0.25 M $HCOOH$ + 0.1 M $HClO_4$, respectively, scan rate: 50 mVs^{-1}. Black and red lines correspond to Pt concave nanocubes and commercial Pt/C catalyst, respectively.
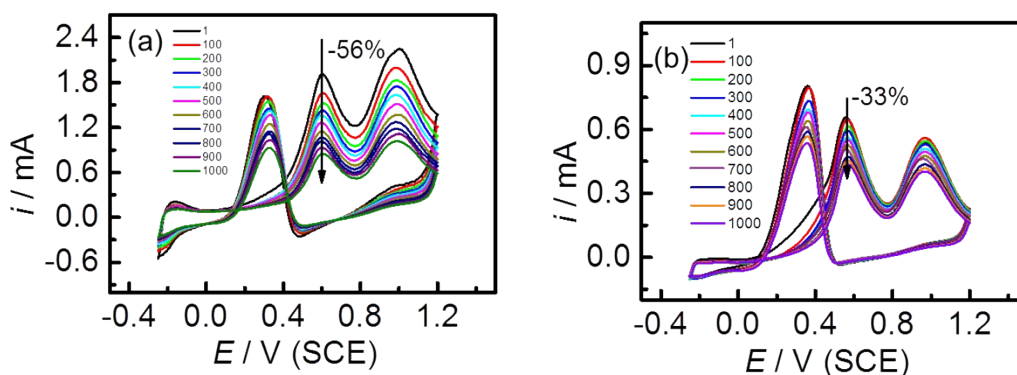

Fig. S9 The stability test of commercial Pt/C (a) and Pt concave nanocubes (b) by 1000 consecutive potential cycles between -0.25 and 1.20 V at 200 mV s^{-1} in 0.1 M CH_3CH_2OH + 0.1 M $HClO_4$. The scans of every 100 scans are given.
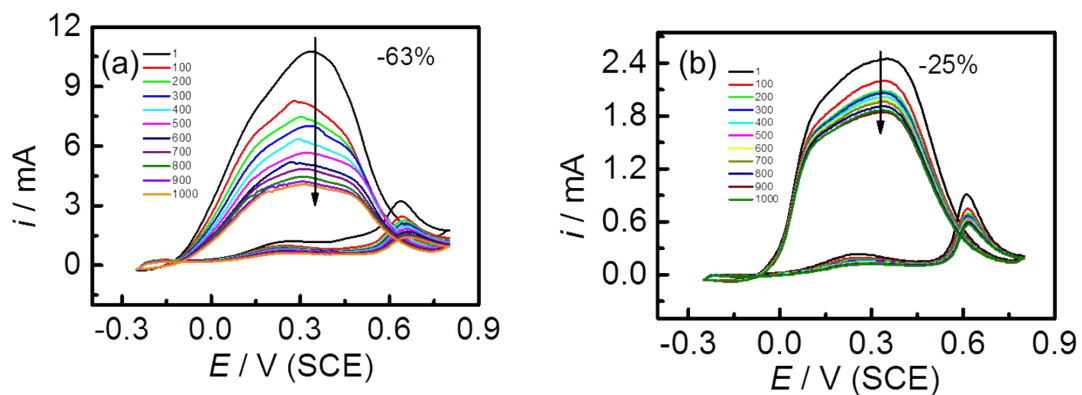
Fig. S10 The stability test of commercial Pt/C (a) and Pt concave nanocubes (b) by 1000 consecutive potential cycles between -0.25 and 0.80 V at 200 mV s^{-1} in 0.25 M HCOOH + 0.1 M HClO$_4$. The scans of every 100 scans are given.
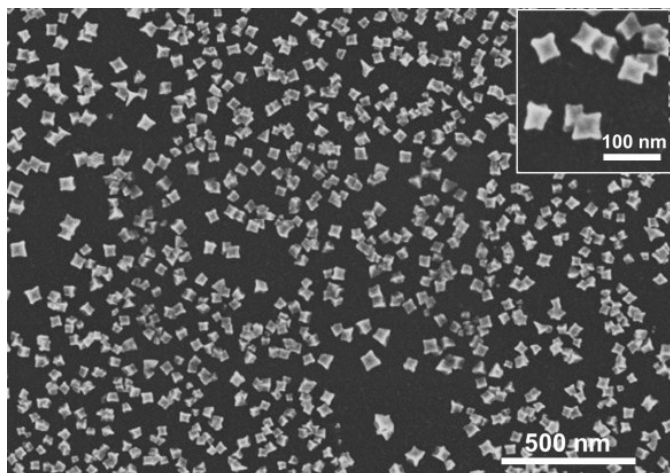

Fig. S11 SEM images of Pt concave nanocubes after the stability test.