## Electronic Supplementary Information

## Electrocatalytic properties of Au@Pt nanoparticles: effects of Pt shell packing density and Au core size

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**Preparation of working electrodes**: the as-synthesized Au@Pt NPs or the commercial Pt black (courtesy of Johnson-Matthey) were transferred into a mixed solution composed of 1 mL 2-propanol and 5  $\mu$ L 5 wt.% Nafion<sup>®</sup> (Du Pont, Inc) solution. The mixed solution was then sonicated for at least 10 min to form a uniform suspension which was drop-cast onto the surface of the supporting GC electrodes. The electrode surface was air dried under a gentle Ar flow and rinsed with a copious amount of Milli-Q water to eliminate loosely attached NPs.

**Estimation of the Pt PDs:** The Pt packing densities were estimated as follows. For an ideal *n*-layer cubo-octahedral NP of fcc (face-centered cubic) crystal structure, the numbers of total ( $N_{\text{total}}$ ) and surface ( $N_{\text{surf.}}$ ) atoms can be express as<sup>26</sup>:

$$N_{\text{total}} = (10/3)n^3 - 5n^2 - (11/3)n - 1 \ (n \ge 1)$$
(1)

$$N_{\text{surf.}} = 10n^2 - 20n + 12$$
  $(n \ge 2)$  (2)

On the other hand, for a TEM measured NP of diameter *d*, the total number of atoms in the NP can be calculated by

(3)

$$N_{\rm total} = (2\pi/3)(d/a)^3$$

where *a* is the lattice constant (0.408 nm for Au and 0.392 nm for Pt). For the Au core NPs, the layer number *n* was determined by equating Eq. (1) to (3) and solving the equation for *n*. Once the *n* was determined, the corresponding  $N_{surf.}$  was calculated using eq. 2. The dispersion of the NPs,  $N_{surf.}/N_{total}$ , was so calculated respectively for the three Au-seed NPs: 37%, 21% and 7.9% respectively. For a Au@Pt NP of size  $d_{Au@Pt}$ , the number of Pt atoms was estimated by  $N_{Pt} = (2\pi/3)(d^3_{Au@Pt} - d^3_{Au\ core})/a_{Pt}^3$  and the corresponding Pt packing density by  $N_{Pt}/N_{surf.}$ . The so calculated Pt packing densities are collected in Table 1.



*Figure S1*. The TEM images, UV-Vis spectra, and size distributions (~250 counts) of the 3.3 nm (A), the 5.2 nm (B) and the 17.5nm (C) Au NPs. The SPR peak positions are 514 nm, 517 nm, and 519 nm respectively.



*Figure S2.* The TEM images and corresponding size distributions of the Au@Pt NPs with the 3.3nm Au core: (A) Au(S)@Pt-0.24, (B) Au(S)@Pt-0.54, (C) Au(S)@Pt-0.83, (D) Au(S)@Pt-1.07, (E) Au(S)@Pt-1.50, (F) Au(S)@Pt-2.60. The average particle sizes are 3.50nm, 3.49nm, 3.51nm, 3.52nm, 3.59nm and 3.64nm respectively. The scale bars equal to 20nm.



*Figure S3.* The TEM images and corresponding size distributions of the Au@Pt NPs with the 5.2nm Au core: (A) Au(M)@Pt-0.09, (B) Au(M)@Pt-0.34, (C) Au(M)@Pt-0.94, (D) Au(M)@Pt-1.22, (D) Au(M)@Pt-2.00, (D) Au(M)@Pt-2.22. The average particle sizes are 5.23nm, 5.46nm, 5.67nm, 5.97nm, 6.02nm and 6.13nm respectively. The scale bars equal to 20nm.



*Figure S4.* The TEM images and corresponding size distributions of the Au@Pt NPs with the 17.5 nm Au core: (A) Au(L)@Pt-0.74, (B) Au(L)@Pt-0.94, (C) Au(L)@Pt-1.3, (D) Au(L)@Pt-2.0, (E) Au(L)@Pt-3.0, and Au(L)@Pt-3.4. The average particle sizes are 17.9 nm, 18.0 nm, 18.6 nm, 18.7 nm, 18.7 nm and 18.8 nm respectively. The scale bars equal to 50 nm.



*Figure S5.* The CVs of (A) the Au(S)@Pt-0.24 and 3.3nm Au NPs (red curve as a reference), (B) the Au(S)@Pt-0.54 NPs, Au(S)@Pt-0.83 NPs, and (D) Au(S)@Pt-1.07 NPs, (E) Au(S)@Pt-1.50, (F) Au(S)@Pt-2.60 and J-M Pt black(dashed curve). In (F), the arrow highlight the suppression of the formation of Pt oxides on Au(S)@Pt in general.



*Figure S6.* The CVs of (A) the Au(M)@Pt-0.09 and 5.2nm Au NPs (red curve as a reference), (B) the Au(M)@Pt-0.34 NPs, Au(M)@Pt-0.94 NPs, and (D) Au(M)@Pt-1.49 NPs, (E) Au(M)@Pt-2.00, (F) Au(M)@Pt-2.22 and J-M Pt black(dashed curve). In (F), the arrows (red for J-M Pt and black for Au@Pt) highlight the suppression of the formation of Pt oxides on Au(M)@Pt in general.



*Figure S7.* The MOR CVs of (A) the Au(S)@Pt-0.24, (B) the Au(S)@Pt-0.54 NPs, Au(S)@Pt-0.83 NPs, and (D) Au(S)@Pt-1.07 NPs, (E) Au(S)@Pt-1.50, (F) Au(S)@Pt-2.60 and J-M Pt black(dashed curve).



*Figure S8.* The MOR CVs of (A) the Au(M)@Pt-0.09, (B) the Au(M)@Pt-0.34 NPs, Au(M)@Pt-0.94 NPs, and (D) Au(M)@Pt-1.49 NPs, (E) Au(M)@Pt-2.00, (F) Au(M)@Pt-2.22 and J-M Pt black(dashed curve).