Electronic Supplementary Information for

Intrinsic Insight on Localized Surface Plasmon Resonance Enhanced Methanol Electro-oxidation over Au@AgPt Hollow Urchin-like Nanostructure

Jinglei Bi,^a Pengfei Gao,^b Bin Wang, *a Xiaojing Yu,^c Chuncai Kong,^a Liang Xu,^a Xiaojing Zhang^a and Shengchun Yang^{*a}

^a School of Science, Key Laboratory of Shaanxi for Advanced Materials and Mesoscopic

Physics, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University,

Xi'an, 710049, People's Republic of China

^b Luoyang Electronic Equipment Testing Center of China, Luoyang, Henan, 471003, People's Republic of China

^c School of Materials Science and Engineering, Xi'an University of Technology, Xi'an, 710049, People's Republic of China

*Corresponding Author.

E-mail addresses: bin_wang@xjtu.edu.cn (B.Wang), ysch1209@mail.xjtu.edu.cn (S.C.Yang).

Additional experimental section

Chemicals. Hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O, 99%) was supplied by Acros. Acetonitrile (CH₃CN, ACN, GR), potassium platinochloride (KCl, 99.8%), polyvinylpyrrolidone (PVP K-30, (C₆H₉NO)_x, Mw \approx 58,000), L-ascorbic acid (AA, C₆H₈O₆, 99%), sodium citrate (NaCA, 98%), sodium borohydride (NaBH₄, 98%), silver nitrate (AgNO₃, 99.99%), potassium tetrachloroplatinate (K₂PtCl₄, \geq 99.9% metals basis) and L-dopa ((HO)₂C₆H₃CH₂CH(NH₂)CO₂H, 99%) were purchased from Aladdin. All chemicals were not further purified when they were received and used.

CO stripping test. The CO adsorption/desorption property of Au@AgPt HUSs was characterized by CO stripping experiments. While keeping the potential at 0.1V (vs. RHE) for 20 min in a CO-saturated 0.5M NaOH solution, CO adsorbed on the pre-activated catalyst in a dark or 200 mW cm⁻² lumen light intensity circumstance. The CO stripping curves were tested by sweeping the potential anodically after purging N₂ for 30 min. CO adsorption/desorption property can be represented with the integral from the charge of CO oxidation peak after revising the background charge.^{1,2} Here, the value 0.42 mC cm⁻² was set for surface charge densities for all catalysts in the calculations.^{3,4} As a contrast, the electrocatalytic performances of Au HUSs and commercial J&M Pt black catalyst were conducted under the same experimental condition. Noting that the amount of Pt was equivalently loaded on the L-type GCE.

Detailed description statement for DFT calculation (VASP). To analyze the energetics of reaction intermediates (carbon species), the formation enthalpy is evaluated with respect to methanol. Reuter and Scheffler pointed out that chemical potentials of reacting species with appropriate reservoirs in catalysis can express the reference energies.^{5,6} This approach was developed into electrochemical systems^{7,8} by Nørskov in the concept of the computational

hydrogen electrode. Herein, the hydrogen chemical potential under an applied electrode potential U is expressed as equation (1):

$$\tilde{\mu}_{H}(U) = \tilde{\mu}_{H^{+}(aq)} - e(U + U_{SHE}) = \frac{1}{2}E_{H_{2}(g)} - eU$$
(1)

actually, under standard conditions of the standard hydrogen electrode potential U_{SHE} , the solvated proton exhibits in equilibrium with the gaseous H₂ molecule, which avoids computing solvation energies of ionic species.⁹ When considering the entropic contribution of the proton concentration ($k_BT*ln(10)pH$) in equation (1), the chemical potential will shift approximately 59 meV if the pH is changed by one at room temperature. Meanwhile, solvated methanol and water were employed to define the chemical potentials of carbon and oxygen, as depicted in equation (2) and equation (3), respectively.

$$\mu_0 = E_{H_2 O(aq)} - 2\tilde{\mu}_H(U) \tag{2}$$

$$\mu_{C} = E_{CH_{3}OH(aq)} - \mu_{O} - 4\tilde{\mu}_{H}(U)$$
(3)

DFT total energy of these neutral molecules no mater existed in the form of gas-phase or solvent phase can be calculated with the implicit solvent model, which can expediently derive the chemical potentials. Whereas, the corresponding formation enthalpy of suitable reaction intermediates is defined as equation (4):

$$\Delta H(U) = E_{tot} - E_{slab} - \sum_{i} n_i \mu_i$$
(4)

Where total energies accompanied by the adsorbed reaction intermediate is donated as E_{tot} and the otherwise is donated as E_{slab} . n_i and μ_i represent the number and the chemical potential of species I, respectively. Typically, the formation enthalpies of the species containing carbon are deduced referring to protons in solvate phase, solvated methanol, and liquid water. Because of the ignorable contribution to the vibrational entropy, entropic contributions should be ruled out.

Thus, when calculating the implicit solvent model, the configurational entropy of the liquid should be adopted.

Table S1 Elemental ICP-MASS analysis of Au@AgPt HUSs before the MOR experiment.

Sample	Ag Conc. /ppm	Pt Conc. /ppm	Au Conc. /ppm	Pt/total_metal_mass
Au@AgPt HUSs	0.480	0.099	5.98	1.5%

Table S2 EDS element analysis of Au@AgPt HUSs before MOR experiment.

Element	Ag L	Pt L	Au L(Ref.)	Pt/total_metal
Mass%	7.33	1.91	90.76	1.91%
Atom%	12.61	1.82	85.57	1.82%

 Table S3 EDS element analysis of Au@AgPt HUSs after MOR experiment.

Element	Ag L	Pt L	Au L(Ref.)	Pt/total_metal
Mass%	4.48	1.34	94.18	1.34%
Atom%	7.89	1.30	90.81	1.30%

Table S4 The enhanced current density (ΔJ), relative enhanced current density ratio ($\Delta J/J$) and current density growth rate ($\Delta J/\Delta t$) in photo-response amperometric i-t curves (Fig. 3d) of Au@AgPt HUSs, Au@Pt HUSs and Pt black under chopped irradiation (200 mW cm⁻²).

Samples	$\Delta J / mA mg$	$\Delta J/J$ / count	$\Delta J/\Delta t / mA s^{-1}$
Au@AgPt HUSs	140.58	12.00%	5.21
Au@Pt HUSs	85.23	9.27%	4.08
J&M Pt black	8.36	7.12%	0.47

Model	Top site	Hollow site		
Au@Pt(111)	1.840 Å	2.092 Å	2.096 Å	2.098 Å
Au@AgPt(111)	1.848 Å	2.095 Å	2.097 Å	2.098 Å

 Table S5 Bond length between the atoms C and Pt calculated by DFT performed on the Au@Pt

 (111) and Au@AgPt (111) facets.

As shown in Fig. S1a and S1b, SEM and TEM image of Au@Ag HUSs represented uniform dimensions and typical urchin-like morphology. The HRTEM image (inset in Fig. S1c) shows the lattice fringes of spacing value ca. 0.24 nm, which matched identically with the d-spacing of the Au (111). The secondary electron information of a single Au@Ag HUS was shown in Fig. S1d. The zoomed-in HAADF-STEM image (Fig. S1f) was acquired from the corresponding HADDF-STEM image of a single Au@Ag HUS (Fig. S1e). As shown in EDS mapping images (Fig. S1g-i), corresponding spatial element distributions of Ag and Au on the targeted Au@Ag HUS (yellow dotted frame in Fig. S1e) provided exact evidence of the core (Au) -shell (Ag) structure. Furthermore, EDS line scan profiles of Ag and Au were collected across three separate nanotips (yellow line in Fig. S1f) of a single Au@Ag HUS, as shown in Fig. S1j. Line scan profile of all three nanotips exhibited higher counts at external and lower counts in inner, while, much higher counts in internal and lower counts at external for that of Ag species, which further demonstrated the core-shell structure of Au@Ag HUSs. The HAADF-STEM image of a single tip of an Au@Ag HUS provided direct evidence of the ultra-thin Ag layer $(1.4 \sim 2.2 \text{ nm})$ deposited on the Au substrate, as shown in Fig. S1k.



Fig. S1 Morphology and Structural Characterization of the precursor Au@Ag urchin-like nanostructure. (a), SEM image, (b), TEM image, (c), HRTEM image e, (d), secondary electron image, (e), STEM image, (f), Zoomed-in STEM image (yellow dotted frame in Fig. S1e) and EDS mapping of (g), Ag, (h), Au and (i), overlayer, (j), EDS line scan profile (yellow line in Fig. S1f, normalized to atomic percentage), (k), magnified HAADF-STEM image.



Fig. S2 XRD patterns of Au@AgPt HUSs, Au@Ag HUSs, Au HUSs, and commercial J&M Pt black. Standard XRD reference patterns are listed as Au (JCPDS NO.04-0784), Pt (JCPDS No. 04-0802), Ag (JCPDS No. 04-0783).



Fig. S3 Morphology and Structural Characterization of Au@AgPt HUSs after MOR test. (a), TEM image, (b), HRTEM image, (c), SAED image, (d), secondary electron image, (e), STEM image, (f), EDAX mapping of Pt L, (g), EDAX mapping of Ag L, (h), EDAX mapping of Au L.

To demonstrate the synergistic effect of the Au-Pt interaction, the electrocatalytic methanol oxidation reaction performance of pure Au HUSs was performed, as shown in Fig. S4. As well known, Au has poor intrinsic catalytic activity in electrocatalytic MOR. In detail, Au HUSs exhibited a much more positive oxidation potential and lower activity compared with that of Au@AgPt HUSs and Pt black, respectively (Fig. 3a). Furthermore, the increased current of Au HUSs was negligible compared with that of Au@AgPt HUSs and Pt black, respectively (Fig. 3a). Furthermore, the increased current of Au HUSs was negligible compared with that of Au@AgPt HUSs and Pt black under irradiation (200 mW cm⁻²). These results demonstrated that Au contained in Au@AgPt HUSs system had an ignorable effect on catalysis MOR. Therefore, Au acted as the light absorber and plasmon donor, while Pt served as the catalytic active site. This can be effective evidence for the synergistic effect of the Au-Pt interaction in the enhanced electrocatalytic methanol oxidation reaction.



Fig. S4 CV curves of Au@AgPtHUSs and Au HUSs performed in an N_2 -saturated electrolyte contained 0.5M NaOH and 1M methanol under irradiation (200 mW cm⁻²) and the dark circumstance. Noting that the total mass of all the catalysts loading on the glassy carbon electrode was kept equivalent.



Fig. S5 Photothermal performance of Au@AgPt HUSs, Au@Pt HUSs, commercial J&M Pt black and bare SiO₂ slide in the electrolyte media with the initial (e, f, g, and h) and stable conditions (i, j, k, and l), respectively. Room temperature was tested as 25.0 ± 0.5 °C.



Fig. S6 Time-dependent surface temperature change curves of Au@AgPt HUSs, Au@Pt HUSs, Pt black, and bare glass slide in the electrolyte media, respectively.

The UV-Vis absorption spectrum showed that no special adsorption peak was observed except that higher light absorption capacity in the near-infrared region. The trace introduction of Ag and

Pt components in Au HUSs did not affect its light absorption capacity evidently. Furthermore, the UV-Vis absorption spectra of Au@AgPt HUSs and Au HUSs in FDTD simulation matched with that of in experiment approximately.



Fig. S7 UV-Vis absorption spectrum and FDTD simulated absorption spectrum of Au@AgPt HUSs and Au HUSs.

The extinction cross-section was calculated with the equation $C_{ext} = C_{scat} + C_{abs}$, where the C_{abs} and C_{scat} represented the absorption cross-section and the scattering cross-section, respectively. The extinction cross-sections, including Au HUSs, Au@Ag HUSs, and Au@AgPt HUSs, were calculated by a 3D-FDTD method. Intraband absorption of Au and Ag determined the LSPR properties of the alloy for UV to 600 nm, as shown in Fig, S8a, S8b, and S8c. The addition of the Ag species in Au@Ag HUSs resulted in a higher extinction efficiency when compared to that of Au HUSs, which was demonstrated by the larger absorption cross-section of Au@Ag HUSs and Au HUSs, as shown in Fig, S8b. Meanwhile, the superior absorption cross-section of Au@Ag HUSs was inherited by Au@AgPt HUSs (Fig, S8b). The enlarged absorption cross-section endowed the higher photothermal efficiency, higher absorption, and energy transfer efficiency for Au@AgPt HUSs. The extinction, scatting and absorption spectrum of all samples(Au HUSs, Au@Ag HUSs, and Au@AgPt HUSs) were presented in Fig, S8a, S8b, and S8c. Owing to the addition of surface Ag species, the absorption peaks in infrared wavelength region (ca. 1100 nm) of Au@Ag HUSs (Fig, S8b right) were enhanced obviously compared with that of Au HUSs (Fig, S8a right). The introduced surface Pt species had a negligible impact on the absorption amplitude of Au@AgPt HUSs at the infrared absorption peaks (1100 nm), even though a slight red-shift of absorption peak was observed.



Fig. S8 FDTD simulated cross-sections (left) and absorption, scatting and extinction spectrum (right) of Au HUSs, Au@Ag HUSs, and Au@AgPt HUSs.



Fig. S9 FDTD simulation model (a) and spatial localized electric field in XY plane (b) and XZ plane (c) of Au@Ag HUSs.



Fig. S10 XPS spectra of Au@Ag HUSs: (a) overall survey spectrum, (b) Au 4f spectrum, (c) Ag 3d spectrum.

To verify the influence of irradiation on the adsorption behavior of CO molecule, a set of CO stripping tests were conducted on Au@AgPt HUSs, Au HUSs, and commercial J&M Pt black, as shown in Fig. S11. Under irradiation (200 mW cm⁻²), it showed that the peak intensity of Au@AgPt HUSs at ca. -0.06 V (vs Ag/AgCl) was associated with the CO oxidation and evidently decreased when compared with that of dark circumstance. The integral from the charge of CO oxidation peak after revising the background charge can directly evaluate the CO coverage ratio, which can characterize the CO adsorption/desorption property. The integral of the charge in the CO oxidation process on Au@AgPt HUSs showed a significant reduction compared with that of Au HUSs and commercial J&M Pt black under irradiation, which clearly demonstrated that the Ag species in Au@AgPt HUSs can reduce the CO coverage ratio under irradiation.



Fig. S11 CO stripping of samples performed in 0.5M NaOH saturated with pure CO and N_2 , respectively under irradiation (beam power density 200 mW cm⁻²) and dark circumstance. (a), Au@AgPt HUSs, (b), Au HUSs, and (c), Pt black.



Fig. S12 Schematic illustration of HOMO-LUMO of CO molecule immersing in the applied electric field performed in the Gaussian calculation.



Fig. S13 Schematic representation of the HOMO-LUMO calculation and energy gaps of CO under a series of external electric fields.



Fig. S14 Schematic representation of the reaction scheme accompanying with intermediates in methanol electro-oxidation on Au@Pt (111) plane.



Fig. S15 Schematic representation of the reaction scheme accompanying with intermediates in methanol electro-oxidation on Au@AgPt (111).



Fig. S16 Morphology and Structural Characterization of Au@Pt HUSs. (a), TEM image, (b), zoomed-in HRTEM image, (c), SAED image of the special particle in (a), (d), secondary electron image (e), EDS mapping of Pt L, (f), EDS mapping of Au L.



Fig. S17 Schematic diagram of the synthesis process of Au@Ag HUSs.



Fig. S18 Schematic diagram of the synthesis process of Au@AgPt HUSs.



Fig. S19 Schematic diagram of the Au@Pt HUSs synthesis process.



Fig. S20 XPS spectrum analysis of Au@AgPt HUSs after MOR experiment. (a), total spectrum and refinement spectrum of (b), Pt 4f, (c), Au 4f and (d), Ag 3d.

References

1 H. Lv, D. Xu, L. Sun, J. Henzie, A. Lopes, Q. Gu, Y. Yamauchi and B. Liu, *Nano Lett.*, 2019, **19**, 3379–3385.

2 H. Lv, Y. Wang, A. Lopes, D. Xu and B. Liu, *Appl. Catal. B Environ.*, 2019, 249, 116–
125.

3 J. E. Sulaiman, S. Zhu, Z. Xing, Q. Chang and M. Shao, *ACS Catal.*, 2017, 7, 5134–5141.

4 S. Wang, L. Xiong, J. Bi, X. Zhang, G. Yang and S. Yang, *ACS Appl. Mater. Interfaces*, 2018, **10**, 27009–27018.

5 K. Reuter, D. Frenkel and M. Scheffler, *Phys. Rev. Lett.*, 2004, **93**, 116105.

6 K. Reuter and M. Scheffler, *Phys. Rev. B* - *Condens. Matter Mater. Phys.*, 2006, **73**, 045433.

J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jónsson, *J. Phys. Chem. B*, 2004, **108**, 17886–17892.

8 E. Skúlason, G. S. Karlberg, J. Rossmeisl, T. Bligaard, J. Greeley, H. Jónsson and J. K. Nørskov, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3241–3250.

9 F. Gossenberger, T. Roman and A. Groß, *Surf. Sci.*, 2015, **631**, 17–22.