Supplementary Information

Surface plasmon-enhanced activity and stability for methanol oxidation on gold caviar-like assembly under solar light

Yaxing Liu^{a,b}, Fuyi Chen^{a,b,c,*}, Qiao Wang^{a,c}, Junpeng Wang^{a,c}, Jiali Wang^{a,c}, and Tesfaye Tadesse

Gebremariam^c

^a State Key Laboratory of Solidification Processing, Northwestern Polytechnical University

Xi'an 710072, China

^b School of Electronics and Information, Northwestern Polytechnical University

Xi'an 710072, China

^c School of Materials Science and Engineering, Northwestern Polytechnical University

Xi'an 710072, China

Corresponding author:

*Fuyi Chen
a 127 West Youyi Road Xi'an Shaanxi, 710072 P. R. China. Tel/Fax: +86-29-88492052
E-mail address: <u>fuyichen@nwpu.edu.cn</u>



Figure S1 Morphology characterisation of gold caviar-like assembly (Au-CA). SEM images of Au-CA under the following deposition times: (a) 1T, (b) 2T, (c) 3T, (d) 4T, (e) 5T, (f) 6T, (g) 8T, (h) 10T and (i) 12T. The insets indicate the corresponding size distributions obtained using the Digital Micrograph analysis software from SEM images.



Figure S2 Morphology characterisation of Au-CA. Tapping-mode AFM images of Au-CA under the following deposition times: (a) 1T, (b) 2T, (c) 3T, (d) 4T, (e) 5T, (f) 6T, (g) 8T, (h) 10T and (i) 12T.



Figure S3 XRD patterns for the Au-CA and glass carbon. XRD patterns of Au-CA 2T, Au-CA 5T and Au-CA 10T compared with that of glass carbon. The insets indicate the details of the corresponding diffraction peaks. Bar diagram: Au #04-0784.



Figure S4 Effect of simulated solar irradiation on the methanol electrooxidation performance of commercial Pt/C catalyst in a deoxygenated solution of 1.0 M KOH mixed with 1.5 M CH₃OH.



Figure S5 Effect of the natural light on the methanol electrooxidation performance of Au-CA 5T in a deoxygenated solution of 1.0 M KOH mixed with 1.5 M CH₃OH.



Figure S6 ECSA characterization. CV curves for glassy carbon and Au-CA under the following deposition times (1T, 2T, 3T, 4T, 5T, 6T, 8T, 10T and 12T) are recorded in N₂-saturated 0.5 M H_2SO_4 solution with a sweep rate of 50 mV s⁻¹ and the Hg/HgO electrode used as reference electrode.



Figure S7 ECSA values of various Au-CA samples deposited for 1 to 12 times, which are calculated from corresponding CV curves from Figure S6.



Figure S8 Diffuse reflectance UV–vis absorption for the Au-CA and glass carbon. Diffuse reflectance UV–vis absorption spectra of glass carbon and Au-CA with various deposition times (1T, 2T, 3T, 4T, 5T, 6T, 8T, 10T and 12 T.).



Figure S9 Effect of the various wavelength light (simulated solar light, LED: 468 nm and LED: 640 nm on the methanol electrooxidation performance of Au-CA 5T.



Figure S10 Effect of the UV light of 385 nm on the methanol electrooxidation performance of Au-CA 5T in a deoxygenated solution of 1.0 M KOH mixed with 1.5 M CH₃OH.



Figure S11 Effect of the pH value on the methanol electrooxidation capacities of Au-CA 5T in the deoxygenated solutions of 1.0 M KOH, 1.0 M Na₂SO₄ and 0.5 M H₂SO₄ mixed with 1.5 M CH₃OH, respectively.



Figure S12 Effect of simulated solar irradiation on the methanol electrooxidation reaction of Au-CA 5T in deoxygenated solution of 1.0 M KOH with different methanol concentrations. CV curves of Au-CA 5T measured in the absence (a) and presence (b) of simulated solar irradiation in a deoxygenated solution of 1.0 M KOH with different methanol concentrations (0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 M).



Figure S13 Solar light effect on the long-term electrooxidation performance of Au-CA under various deposition times. Chronoamperograms of Au-CA under various deposition times (1T, 2T, 3T, 4T, 5T, 6T, 8T, 10T and 12T) in a deoxygenated solution of 1.0 M KOH and 1.5 M CH₃OH at their oxidation potentials for 40 min in the absence (a) and presence (b) of simulated solar irradiation.



Figure S14 Effect of simulated solar irradiation on the stability of Au-CA 5T for methanol electrooxidation. CV curves of methanol electrooxidation reaction on Au-CA 5T in the absence (a) and presence (b) of simulated solar irradiation in a deoxygenated solution of 1.0 M KOH and 1.5 M CH₃OH.