

Supporting Information

Shape- and Size-Dependences of Gold Nanostructures on Electrooxidation of Methanol under Visible Light Irradiation

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Electrochemically active surface area analysis (ECSA)

The ECSA was calculated according to the following Eq.

$$\text{ECSA} = Q / (m \times C)$$

Whereas 'Q' integral coulomb charges (mC cm^{-2}) to resultant oxides of reduction peak or CO-stripping oxidation peak, 'm' is loading of Au (mg cm^{-2}) catalyst on surface of GCE, and 'C' is proportionality constant charge required to reduction of Au or oxidation of CO (0.42 mC cm^{-2}) monolayer. According to the oxides of Au reduction peak, the ECSA values obtained.

Preparation of spherical Gold nanoparticles with 20 nm diameter (Au NS20s)

150 μL of 0.1 mol L^{-1} HAuCl_4 solution was mixed with 50 mL of water in flask, the flask was heated to boiling under reflux condition. Finally, 0.5 mL of 0.24 mol L^{-1} sodium citrate solution was added and kept the solution boiling and stirring for 20 minutes. At the end of the reaction, 10 mL of 0.1 mol L^{-1} CTAB solution was added and stirred for 6 hours. After purification through several centrifugations, the Au NSs were dispersed in deionized water.

Preparation of Gold nanorods with SPR Peak of 850nm (Au NR850s)

Seed solution: 25 μL of 0.1 mol L^{-1} HAuCl_4 was mixed with 10 mL of a 0.1 mol L^{-1} CTAB solution at room temperature. Next, 60 μL of freshly prepared 0.1 mol L^{-1} NaBH_4 solution was quickly injected into the solution with vigorous stirring. The gold seeds were stirred for 5 min and kept at

room temperature for 30 minutes to remove NaBH_4 .

Growth solution: 50 μL of 0.1 mol L^{-1} HAuCl_4 and 0.1 mL of 10 mmol L^{-1} AgNO_3 were mixed with 10 mL of a 0.1 mol L^{-1} CTAB solution. The solution was then acidified with 20 μL of HCl , followed by the addition of 80 μL of 0.1 mol L^{-1} ascorbic acid. After the solution became colorless, 24 μL of gold seeds were injected into the growth solution. The growth reaction was carried out under gentle stirring at room temperature for 2 h. After purification through several centrifugations, the Au NRs were dispersed in deionized water.

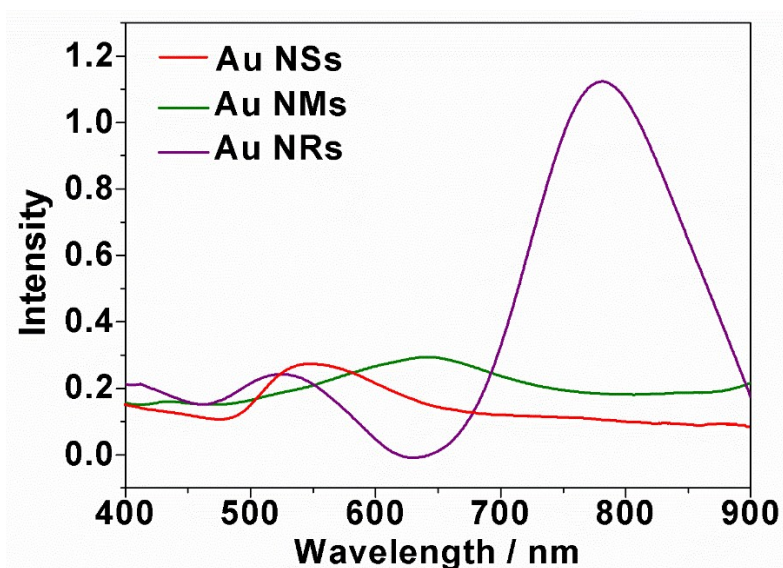


Figure S1. UV-vis spectra of Au NSs, Au NMs and Au NRs.

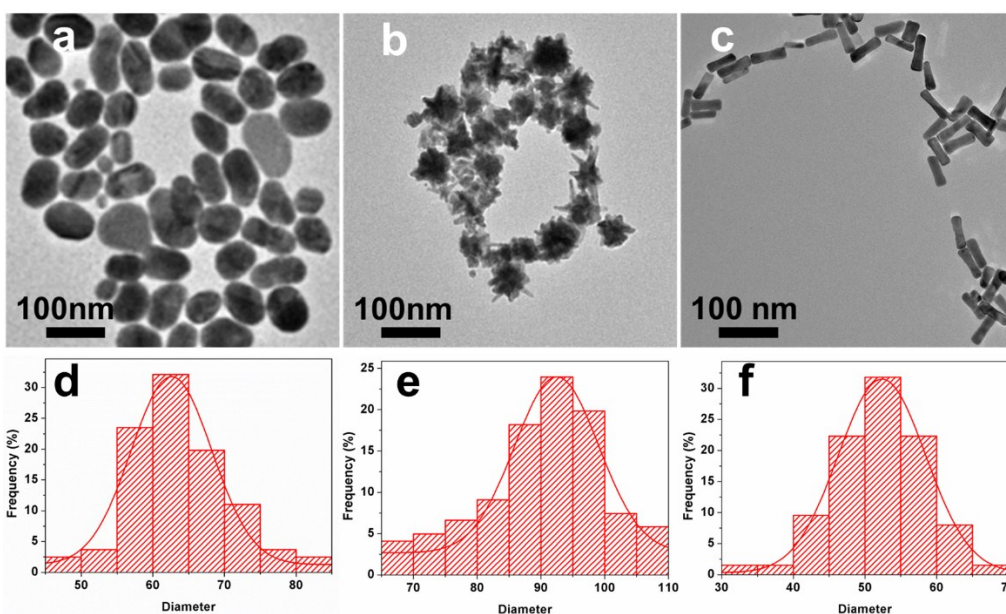


Figure S2. Morphological characterization of Au NSs (a), Au NMs (b) and Au NRs(c); Particle size distribution of Au NSs (d), Au NMs (e), and Au NRs (f). Representative TEM images of Au NSs, Au NMs and Au NRs.

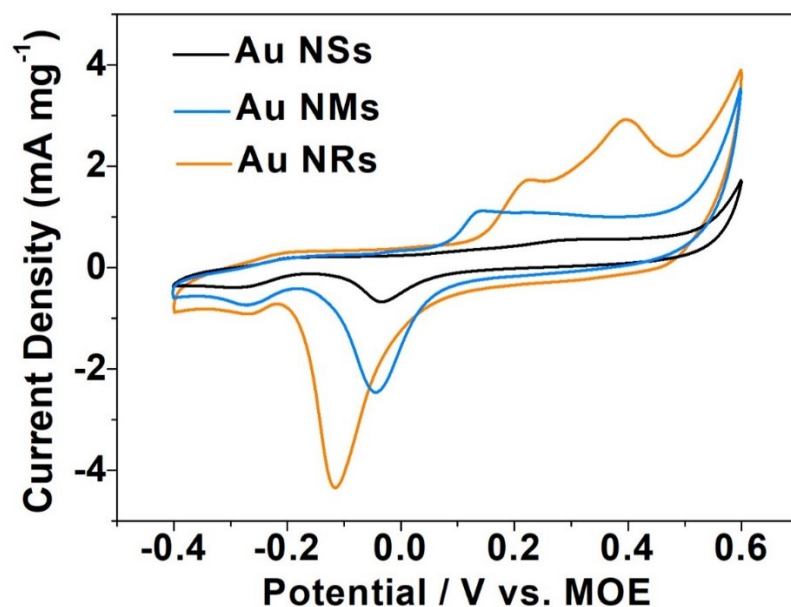


Figure S3. Au NSs, Au NMs and Au NRs recorded in an N₂-saturated 1.0 mol L⁻¹ KOH. The CV curves were measured with a sweep rate of 50 mV s⁻¹, and the MOE (Hg/HgO) electrode was used as the reference electrode.

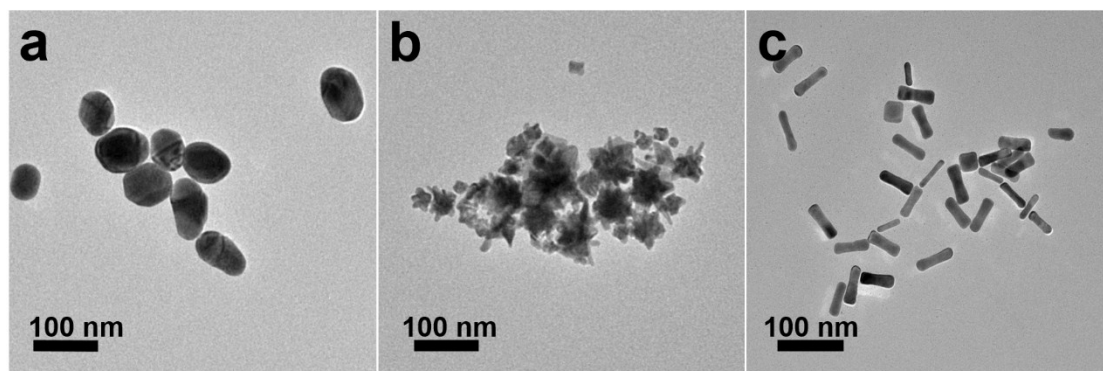


Figure S4. TEM characterization of Au NSs (a), Au NMs (b), and Au NRs (c) catalysts after light irradiation.

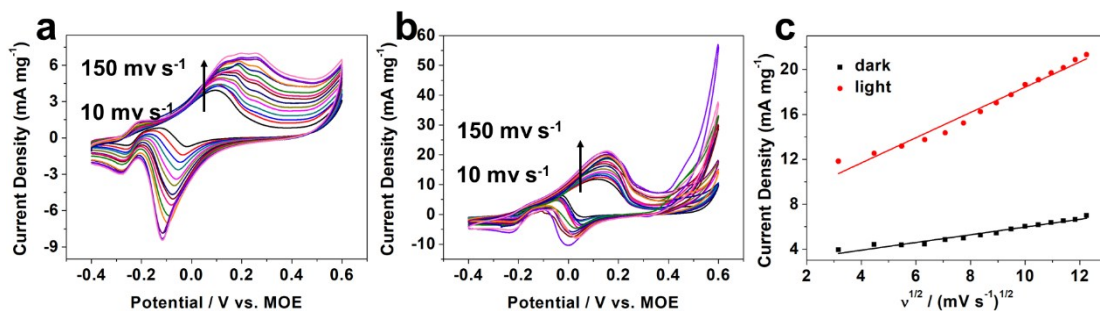


Figure S5. (a) CV curves of MOR on Au NRs modified electrodes at different scan rates under dark; (b) CV curves of MOR on Au NRs modified electrodes at different scan rates under visible light irradiation; (c) The corresponding plot of forward peak current versus the square root of the scan rate ($V^{1/2}$) in the presence and absence of visible light irradiation.

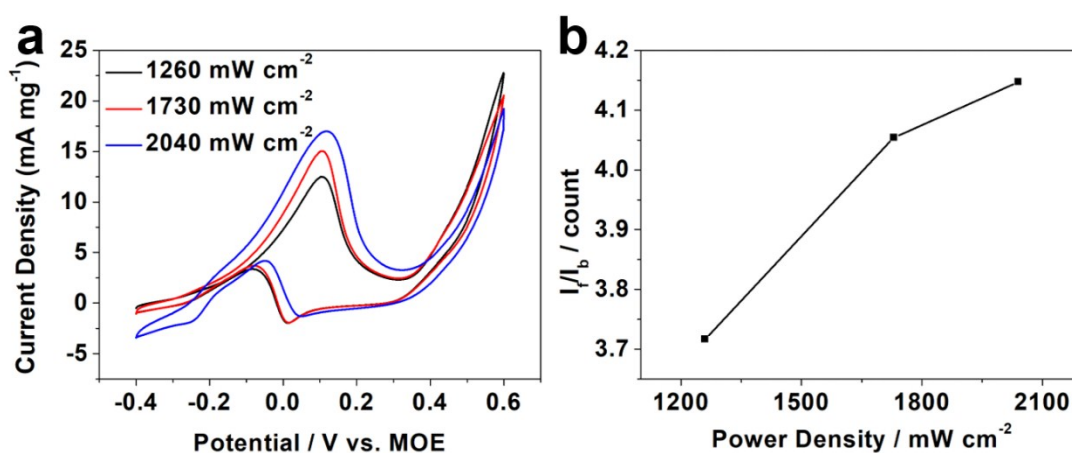


Figure S6. I_f/I_b values of Au NRs irradiated with a series of power

densities.

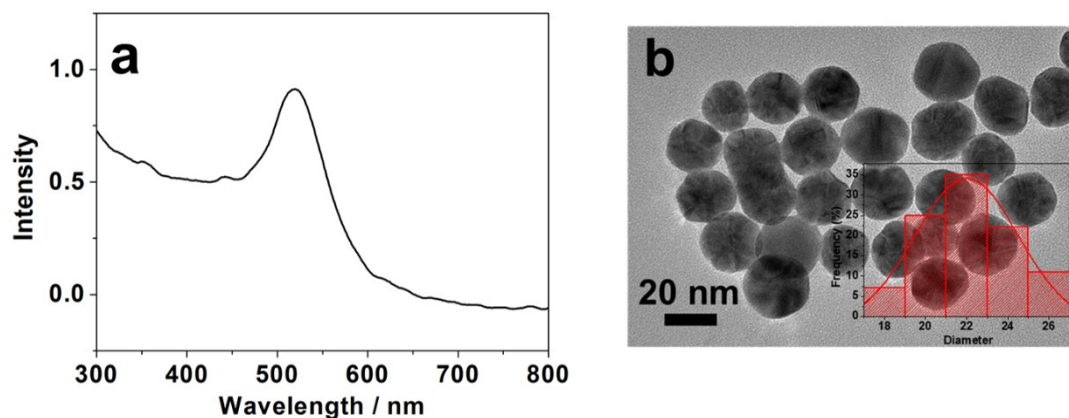


Figure S7. (a) UV-vis spectra of Au NS20s; (b) Representative TEM image and particle size distribution of Au NS20s.

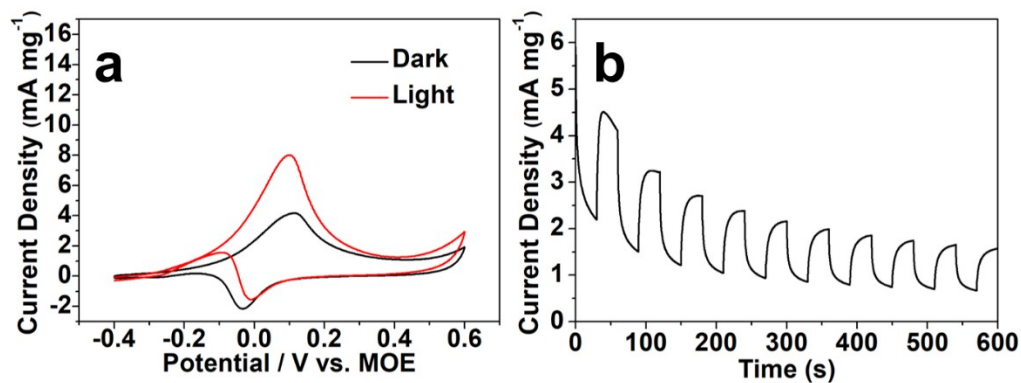


Figure S8. (a) CV curves of Au NS20s in the presence and absence of visible light irradiation; (b) Photocurrent responses of Au NS20s toward MOR in 1.5 mol L⁻¹ CH₃OH and 1.0 mol L⁻¹ KOH solution at a potential of 0.1 V under visible light irradiation (The illumination from a Xe lamp was interrupted every 30 s).

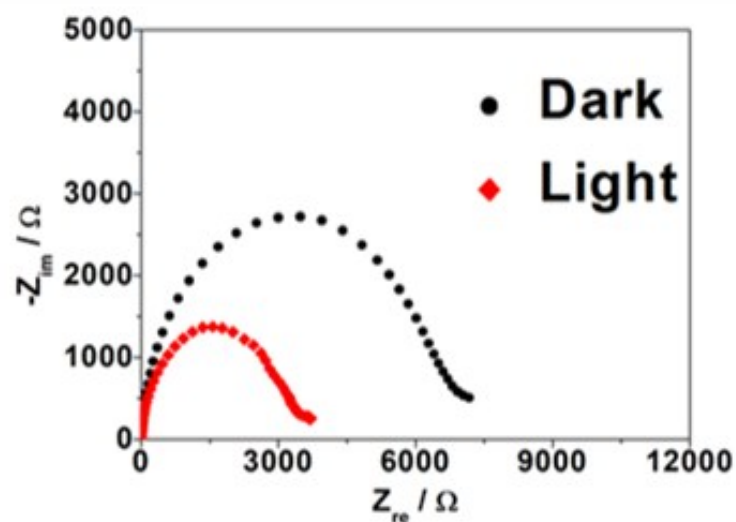


Figure S9. Nyquist plots of Au NS20s toward MOR in the presence and absence of visible light irradiation

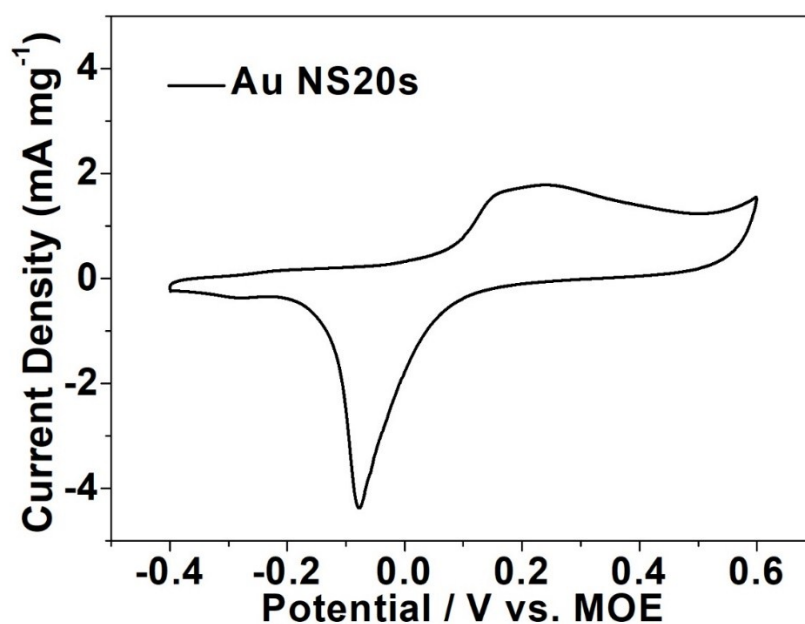


Figure S10. Au NS20s recorded in an N_2 -saturated 1.0 mol L^{-1} KOH. The CV curves were measured with a sweep rate of 50 mV s^{-1} , and the MOE (Hg/HgO) electrode was used as the reference electrode.

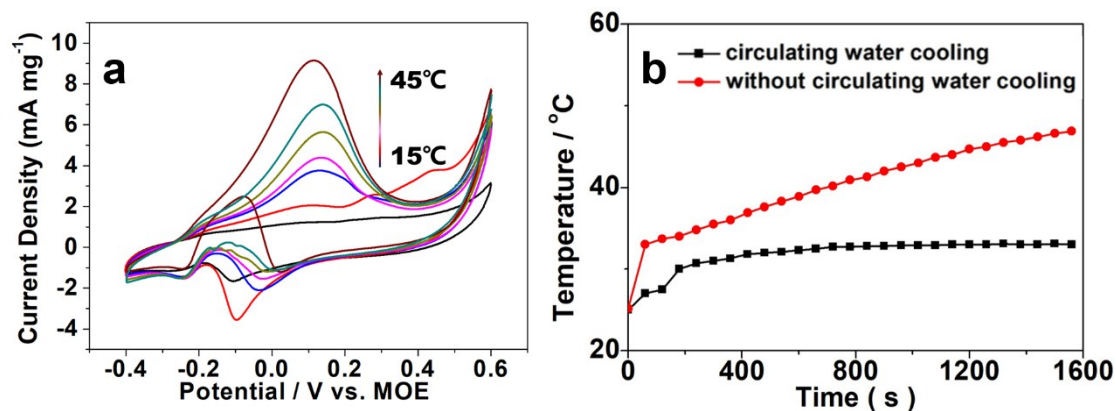


Figure S11. (a) Taking the Au NRs as an example, the CV curve of methanol oxidation at different temperatures. (b) Temperature variation curve of experimental device with or without circulating water in the presence of visible light irradiation.

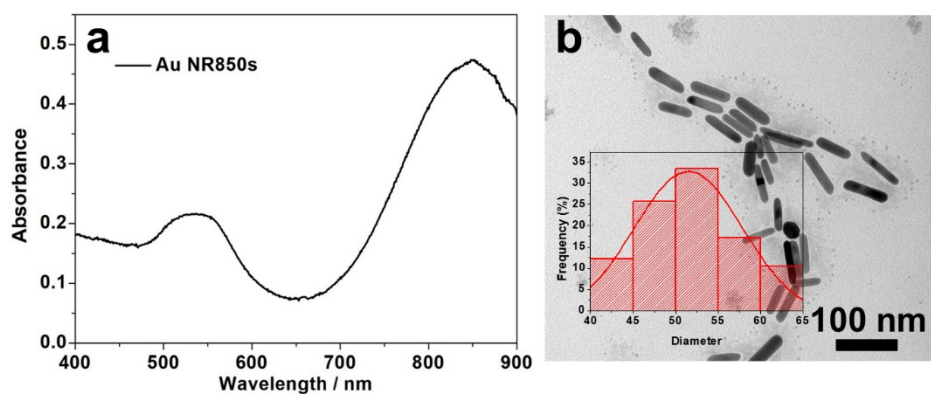


Figure S12. (a) UV-vis absorption spectra of Au NR850s; (b) TEM and particle size distribution of Au NR850s.

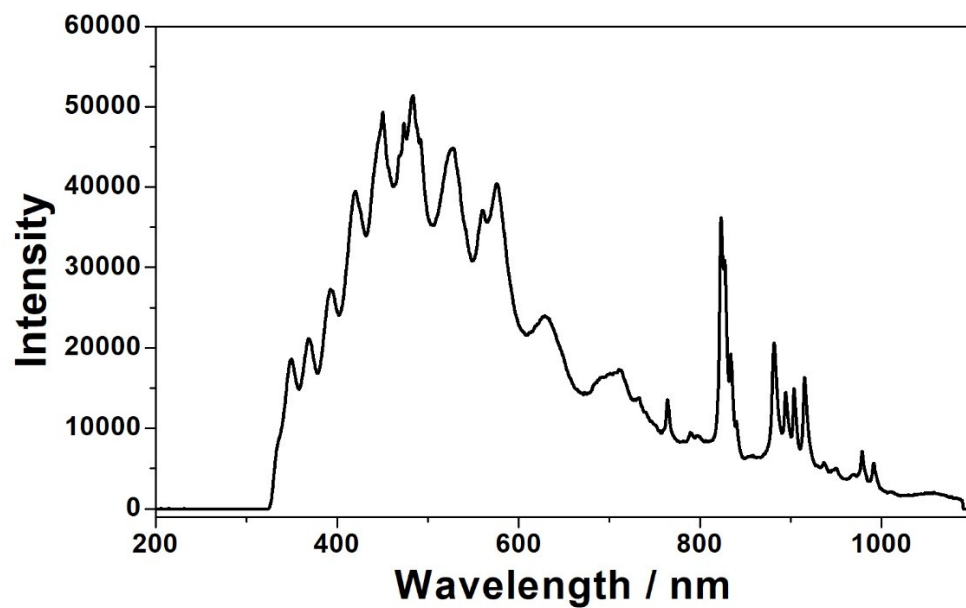


Figure S13 Spectral intensity Distribution of Xe lamp used in experiment.