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Supporting Information

Ligand-regulated ORR Activity of Au Nanoparticles in Alkaline Medium: the Importance of Surface Coverage of Ligands

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Calculation details:

1. The particle size of each Au/C sample is calculated from XRD using the Scherrer equation based on the Au (111) peak,

$$d = \frac{0.9\lambda}{\Delta(2\theta)cos\theta}$$

where d is the mean size of the ordered primary crystalline domains, λ is the X-ray wavelength, $\Delta(2\theta)$ is the full width at half maximum intensity (FWHM) and θ is the Bragg angle.

2. The surface area of all the samples are calculated from d_{TEM} by TEM (S_{TEM}) and d_{XRD} by XRD (S_{XRD}) using the following equation, and were listed in **Table 1** in the main text.

$$S = \frac{6}{\rho \cdot d} \cdot 10^3$$

Where d is particle size in nm, S is in m^2/g_{Au}, and ρ is the density of gold (19.32 g/cm^3).

3. The electrochemical surface area (ECSA) is calculated by the Au_2O_3 reduction peak through the following equation using a value of 400 μC cm^{-2}.[1]

$$ECSA = \frac{A}{\nu} \cdot \frac{10^6}{400} \cdot \frac{1}{m}$$

Where ECSA is in m^2/g_{Au}, A is the area of the gold oxide reduction peak (mA · V), ν is the scan rate (mV/s), m is the actual load of Au on the electrode (g).

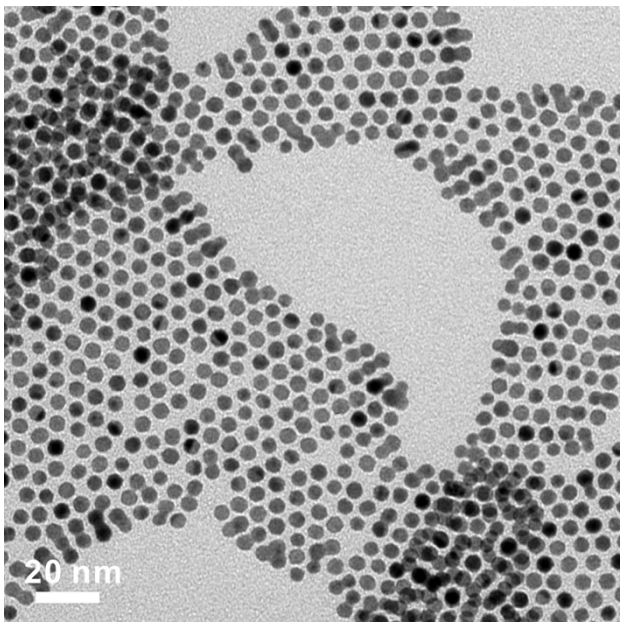

Fig. S1 TEM image of as-synthesized Au(S) NPs.

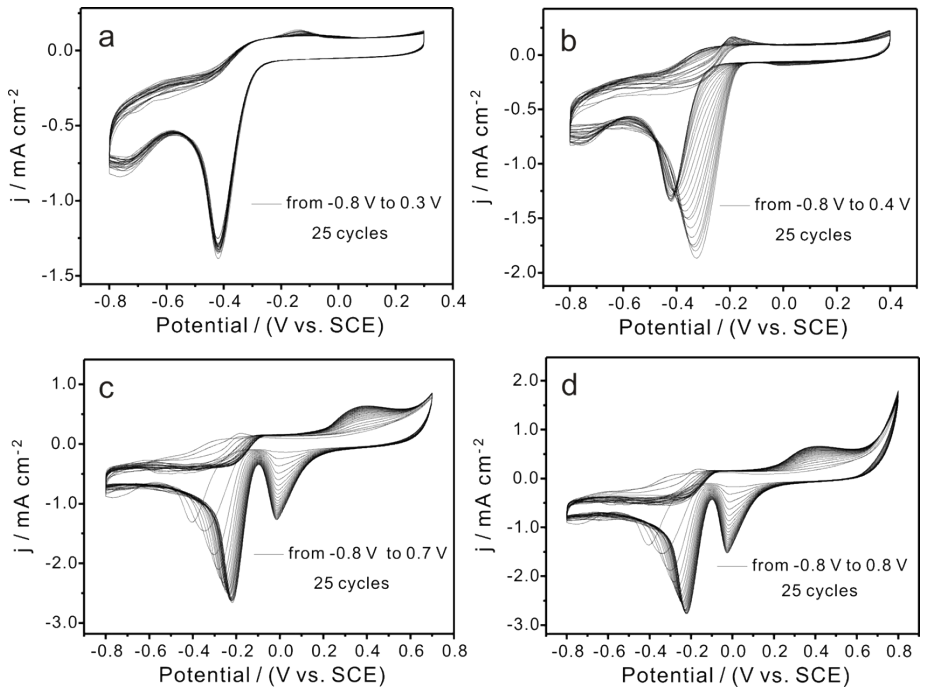

Fig. S2 CV curves of Au(S)/C scanning from -0.8 V to different up potentials for 25 cycles in O_2-saturated 0.1 M KOH.

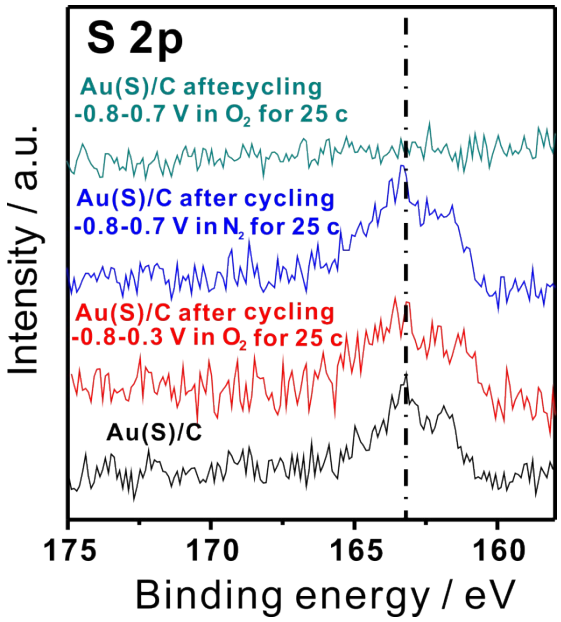

Fig. S3 XPS (S 2p) spectra of different samples.

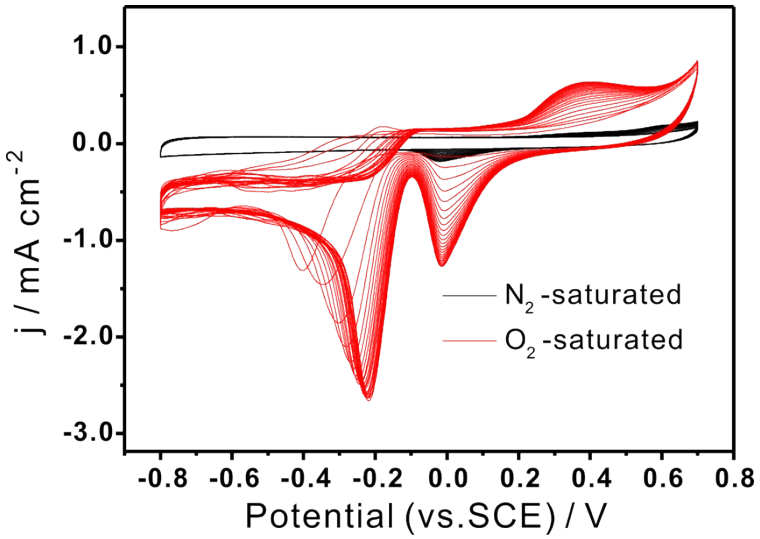

Fig. S4 CV curves of Au(S)/C in N_2 or O_2-saturated 0.1 M KOH solution for 25 cycles.

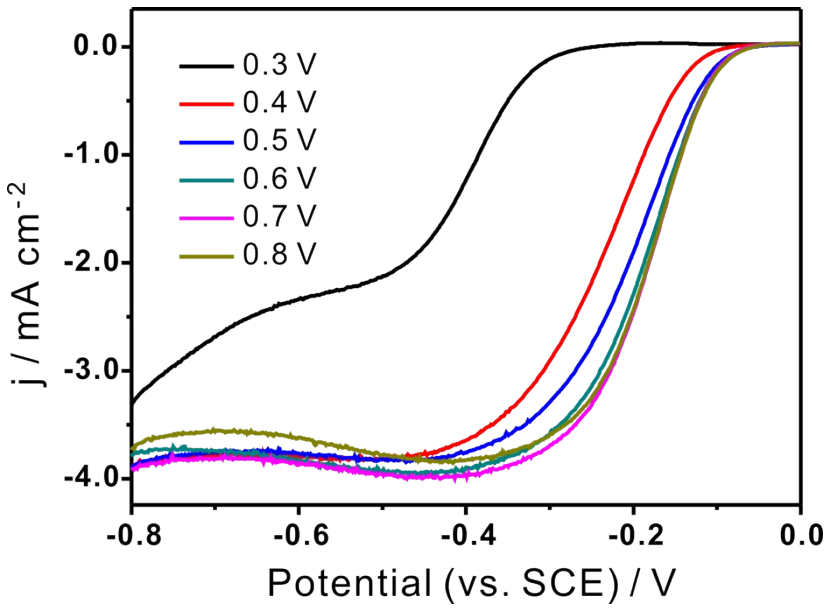

Fig. S5 LSV curves of Au(S)/C in O_2-saturated 0.1 M KOH after activation by CVs from -0.8 V to different up potentials for 25 cycles in O_2-saturated 0.1 M KOH.

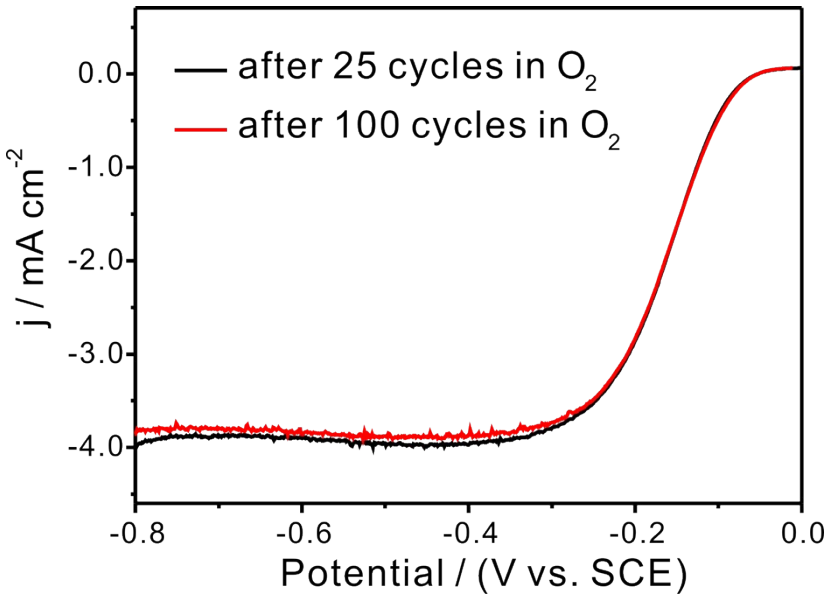

Fig. S6 LSV curves of Au(S)/C in O_2-saturated 0.1 M KOH after activation by CVs from -0.8 V to 0.7 V for 25 cycles or 100 cycles in O_2-saturated 0.1 M KOH.

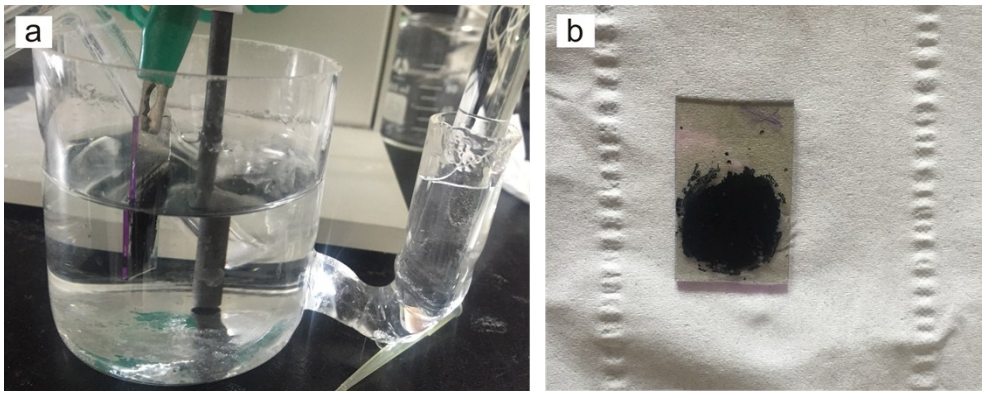

Fig. S7 (a) Photograph of the electrochemical cell that used to remove the ligand on Au(S)/C. About 50 mg of Au(S)/C was deposited on the working electrode (fluorine-doped tin oxide, FTO). (b) Photograph of recovred 50 mg of Au/C catalyst, whose ligand has been removed (evidenced by XPS measurement). The protocol can be used to effectively remove the ligands on high amount of catalyst.

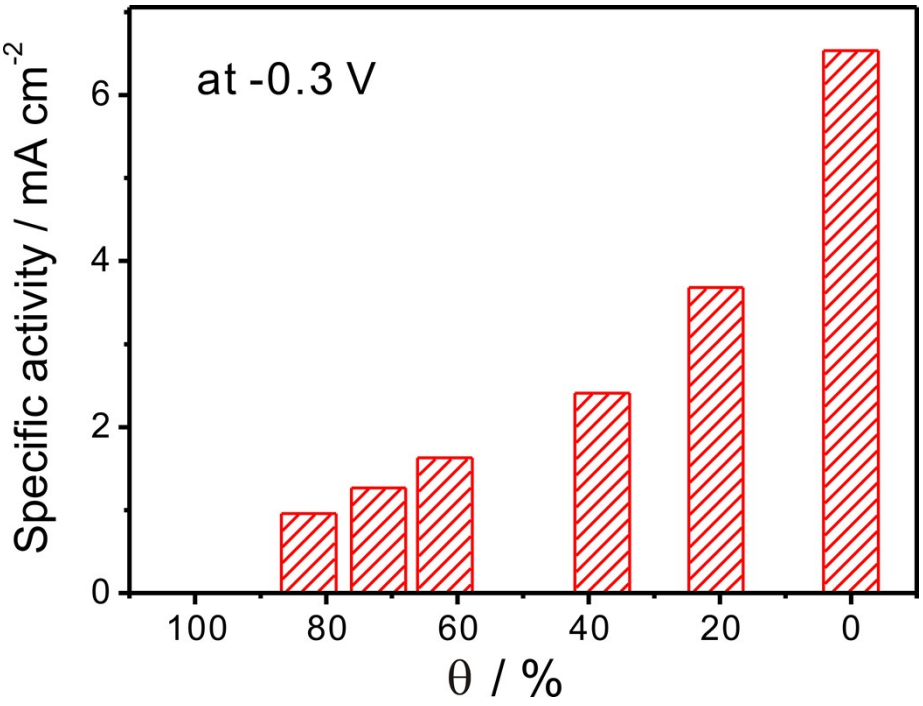

Fig. S8 The kinetic current (-0.3 V) normalized by oxide surface area (specific activity) with different surface coverages of thiol.

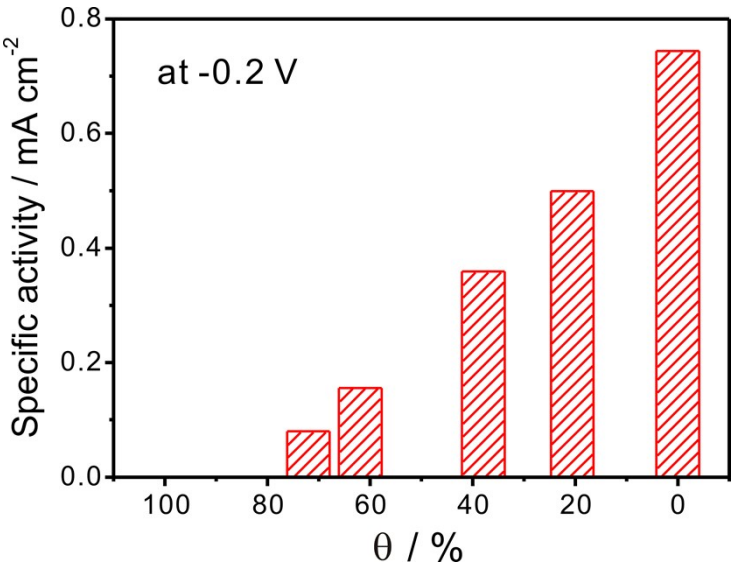

Fig. S9 The kinetic current (-0.2 V) normalized by oxide surface area (specific activity) with different surface coverages of thiol.

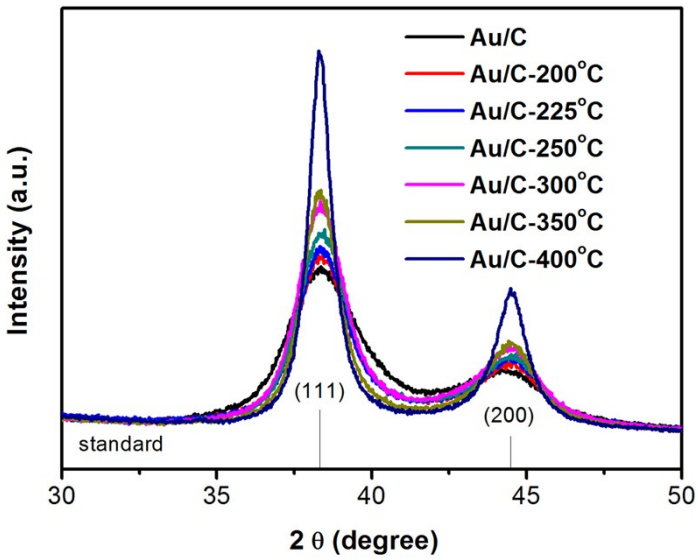

Fig. S10 XRD patterns of Au(S)/C and Au(S)/C annealed at different temperatures.

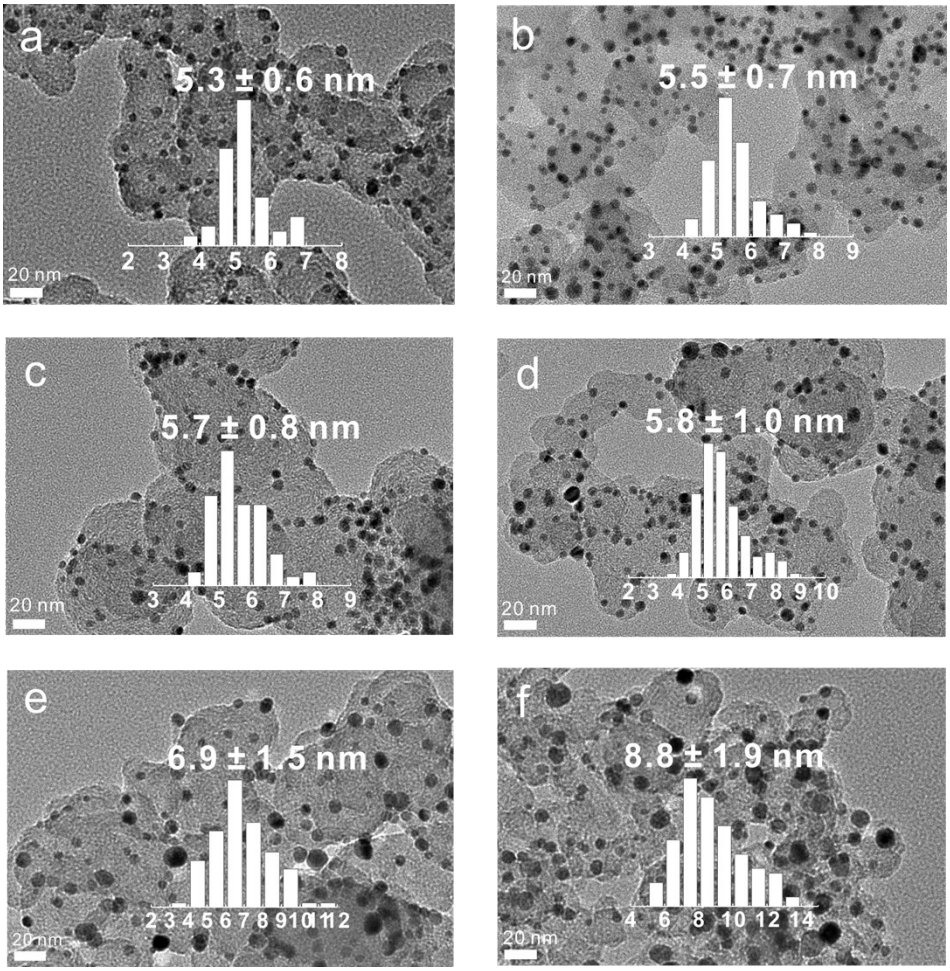

Fig. S11 TEM images of (a) Au(S)/C-200, (b) Au(S)/C-225, (c) Au(S)/C-250, (d)Au(S)/C-300, (e) Au(S)/C-350, and (f) Au(S)/C-400. Insets are the histograms of particle size distribution for the corresponding samples counted over 100 particles.

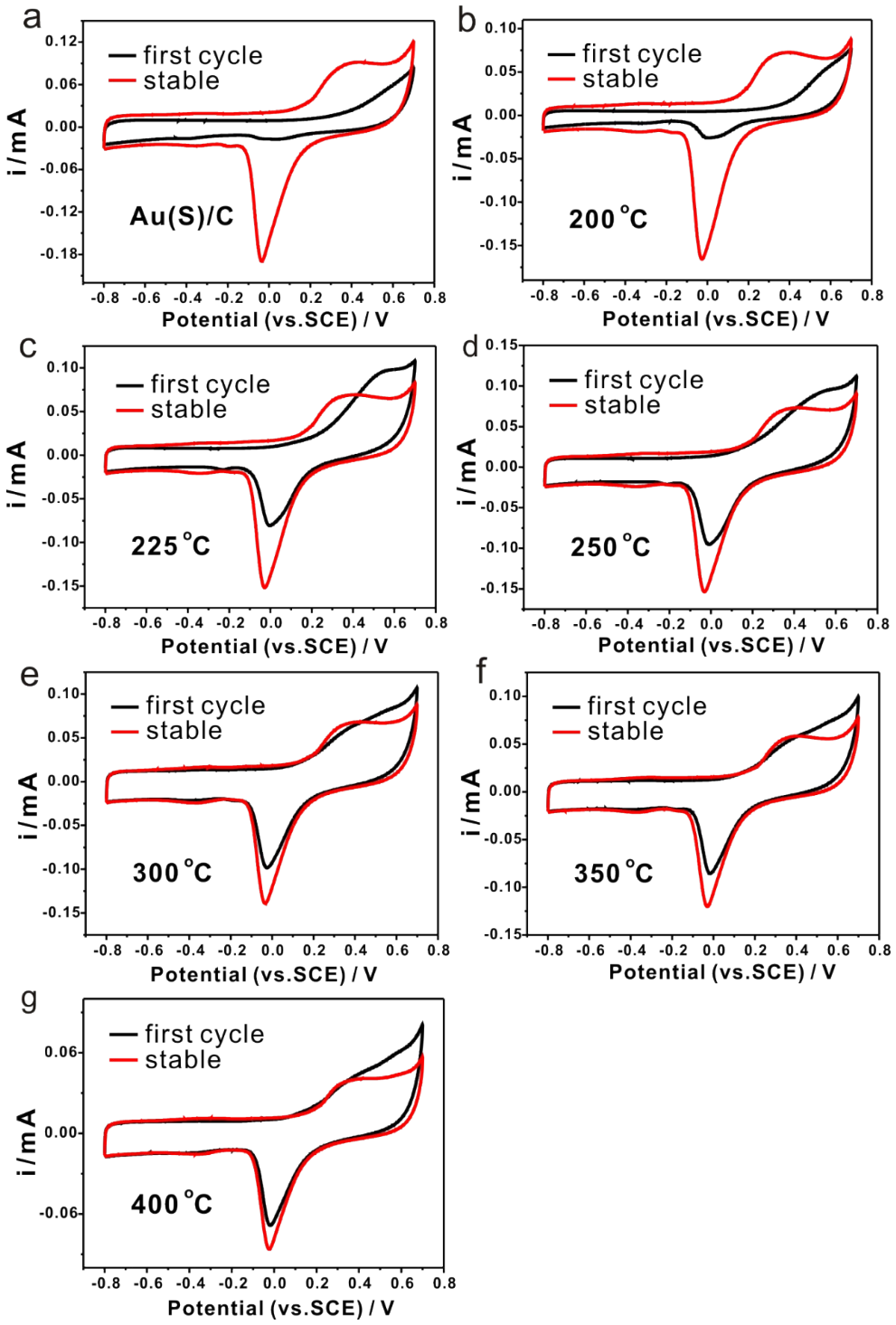

Fig. S12 CV curves of first cycle (not activated by potential cycling, black) and stable cycle (activated by potential cycling, red) of Au(S)/C and Au(S)/C-T (T is the temperaure) in N_2 saturated 0.1 M KOH.

Table S1 Physico-chemical properties for Au(S)/C annealed at different temperatures.

Sample	d (nm)		S (m^2 g_{Au}^{-1})		
	XRD	TEM	XRD	TEM	EC-25
Au(S)/C-25	4.7	4.8±0.5	55.3	54.2	52.9
Au(S)/C-200	5.1	5.3±0.6	51.0	49.1	51.8
Au(S)/C-225	5.4	5.5±0.7	48.1	47.3	46.0
Au(S)/C-250	5.5	5.7±0.8	47.2	45.6	43.6
Au(S)/C-300	5.9	5.8±1.0	44	44.8	41.0
Au(S)/C-350	6.7	6.9±1.5	38.8	37.7	33.9
Au(S)/C-400	9.2	8.8±1.9	28.3	29.5	26.0

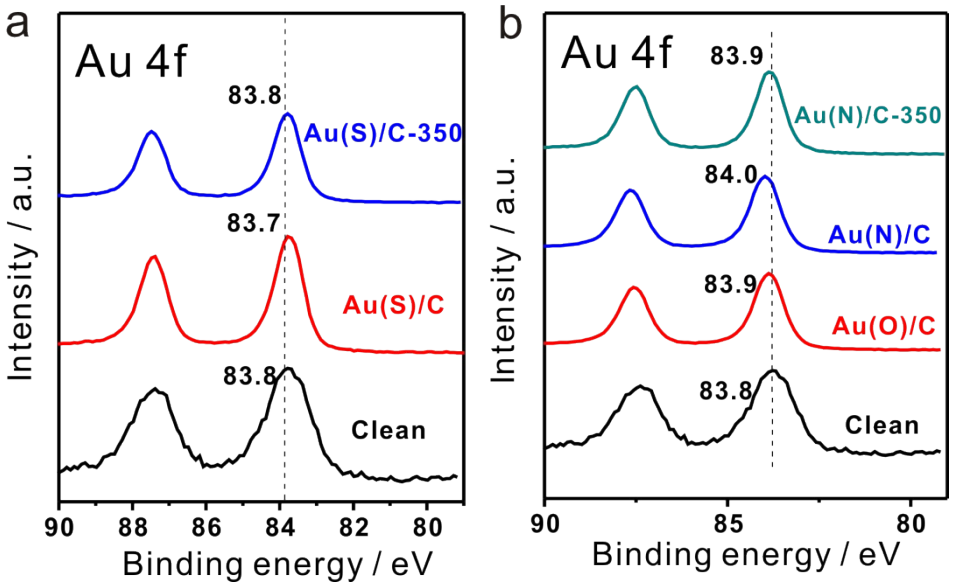

Fig. S13 XPS spectras: (a) Au 4f spectra of clean (black), Au(S)/C (red) and Au(S)/C-350 (blue). (b) Au 4f spectra of clean (black), Au(O)/C (red), Au(N)/C (blue) and Au(N)/C-350 (green).

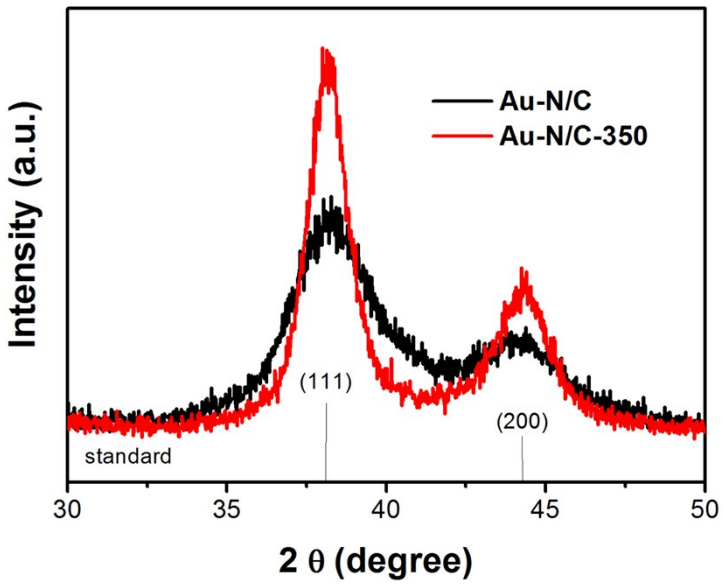

Fig. S14 XRD patterns of Au(N)/C and Au(N)/C calcinated at 350 °C.

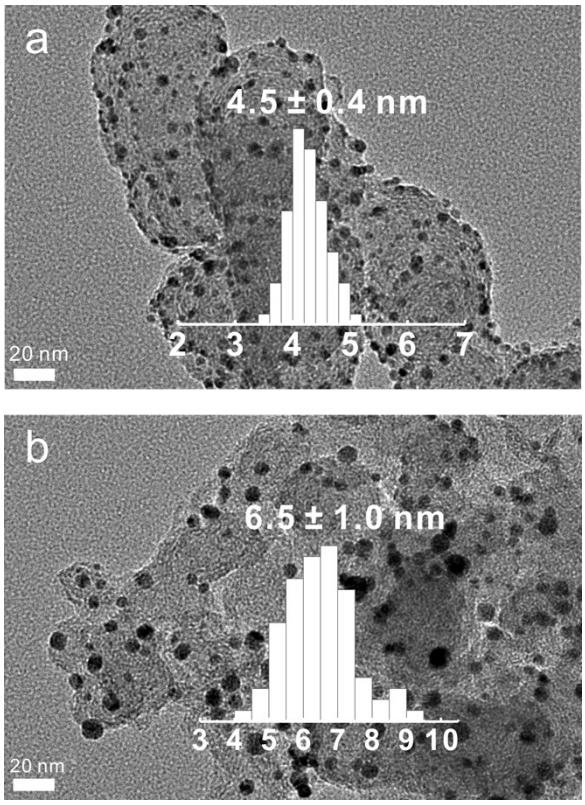

Fig. S15 TEM images of (a) Au(N)/C and (b) Au(N)/C-350. Insets are the histograms of particle size distribution for the corresponding samples counted over 100 particles.

Table S2 Physico-chemical properties for Au(N)/C and Au(N)/C-350.

Sample	d (nm)		S (m^2 g_{Au}^{-1})		
	XRD	TEM	XRD	TEM	EC-25
Au(N)/C-25	4.6	4.5±0.4	56.5	57.8	53.0
Au(N)/C-350	6.5	6.5±1.0	40.0	40.0	34.1
Au(O)/C-25	4.8	4.6±0.5	54.1	56.5	55.1

References

S. Trasatti and O. A. Petrii, *Pure Appl. Chem.*, 1991, **63**, 711−734.