Electronic supplementary information for:

Rationally designed metal nanocluster for electrocatalytic hydrogen production from water

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Materials and Methods

Materials. Hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O, reagent grade), dihydrogen hexachloroplatinate(IV) hydrate (H₂PtCl₆·xH₂O, >99%), 1-hexanethiol (C₆S, 95%), 3-mercaptopropionic acid (MPA, >99%), sodium 3-mercapto-1-propanesulfonic acid (MPS, 90%), sodium borohydride (NaBH₄, 99%), tetraoctylammonium bromide (TOABr, 98%), hydrogen peroxide solution (H₂O₂, 34*wt*%), tetramethylammonium hydroxide pentahydrate (TMAH, >95%), decanoic acid (>99%), potassium chloride (KCl, >99%), tetrabutylammonim hexafluorophosphate (Bu₄NPF₆, >99%), ferrocene (Fc, 98%), and acetic acid (HOAc, 99.5%) were purchased from Aldrich. Extrapure grade methanol, ethanol, toluene and dichloromethane were used. Amicon ultra-4 centrifugal filter units (desalting column) were purchased from Merck Millipore. Water was purified using a Millipore Milli-Q system (18.2 MΩ·cm). All the chemicals were used as received without further purification.

Characterizations of nanoclusters. The molecular formula of the synthesized nanocluster was analyzed by an ESI mass spectrometer (compact Q-TOF, Bruker) in negative-ion mode (flow rate, 5.0 μ L/min; capillary voltage, 3.0 kV; capillary temperature, 180 °C; m/z range, 0-3500). The samples were prepared in water at a concentration of 1 mg/mL and directly injected into the mass spectrometer. Absorbance spectra of nanoclusters were acquired using a UV-Vis-NIR spectrophotometer (UV-3600, Shimadzu). Square wave voltammetry (SWV) was carried out at room temperature with an electrochemical workstation (Model 660 B, CH Instruments). Aqueous metal nanocluster solutions (10 mM) containing 0.5 M KCl were degassed and blanketed with high-purity Ar atmosphere during measurement. A Pt disk (0.4 mm diameter) was used as the working electrode, a Pt disk (0.4 mm diameter) as the counter electrode and Ag/AgCl (3M NaCl) reference electrode as the reference electrode for the voltammetric measurements. Voltammetry in non-aqueous solution was carried out by using a Pt disk (0.4 mm diameter) as the working electrode, a Pt disk (0.4 mm diameter) as the counter electrode and Ag/Ag⁺ reference electrode (-0.23 V vs. ferrocene couple). SWV scans were conducted with pulse amplitude of 50 mV and potential increment of 4 mV at the frequency of 30 Hz.

Synthesis hexanethiolate-protected Au₂₅ (C₆S-Au₂₅). C₆S-Au₂₅ nanoclusters were synthesized according to the procedure reported elsewhere.^{S1} The synthesis was very reproducible and the purity of the synthesized nanoclusters was confirmed by mass spectrometry and absorption spectrometry.

Synthesis of MPA-protected Au₂₅ (MPA-Au₂₅). MPA-Au₂₅ nanoclusters were synthesized according to a reported procedure.^{S2} In a typical synthesis of MPA-Au₂₅ clusters, 4 mg of HAuCl₄·3H₂O (0.01 mmol) and 2.1 mg of MPA (0.018 mmol) were mixed in ultrapure water (4.7 mL) under mild stirring, followed by the addition of 0.6 mL of NaOH solution (1.0 M). The solution color was changed from yellow to pale yellow. 0.2 mL of NaBH₄

solution (0.1 M) was then added dropwise to the solution (the solution color was changed to yellowish-brown). After 2 h of vigorous stirring, the unreacted MPA and other impurities were removed by using a 3k Da cut off desalting column, resulting in highly pure MPA-protected Au₂₅ nanoclusters. The nanocluster was identified as Au₂₅(MPA)₁₈ by ESI mass spectrometry and UV-vis-NIR absorption spectrometry.

Synthesis of MPS-protected Au₂₅ (MPS-Au₂₅). Synthesis of MPS-Au₂₅ was carried out at room temperature according to a reported procedure^{S3} with some modifications. In a typical synthesis, 0.777 g of MPS (3 mmol) was dissolved and stirred in 60 mL of water. 0.394 g of HAuCl₄·3H₂O (1 mmol) in 30 mL of methanol was slowly added to the above solution and stirring was continued for ~30 min until the whitish yellow solution turned colorless. To the above solution, 0.112 g of NaBH₄ (3 mmol) in 10 mL of water was added. The solution turned brown immediately, indicative of particle formation. After stirring of 1 h, 0.0748 g of NaBH₄ (2 mmol) in 2 mL of water was added additionally with rapid stirring. After additional stirring of 30 min, the solution was rotary evaporated to near dryness and washed thoroughly with copious amounts of acetonitrile. To isolate Au₂₅ nanoclusters from the product mixture, recrystallization was carried out using water-acetonitrile mixtures. The product was dissolved in 10 mL of water and then 2 mL of acetonitrile was added to induce precipitation of larger particles. The precipitate was separated by centrifugation and more acetonitrile was added to the supernatant to induce additional precipitation. The precipitate was separated by centrifugation again. This recrystallization step was repeated until a clear supernatant was obtained. Precipitates containing monodisperse MPS-Au₂₅ were obtained in the middle fractions of recrystallization and identified by using UV-vis-NIR absorption spectrometry and ESI mass spectrometry. The total yield of MPS-Au₂₅ was typically ~150 mg.

Synthesis of MPS-protected PtAu₂₄ (MPS- PtAu₂₄). In a typical reaction, 0.777 g of MPS (3 mmol) was dissolved and stirred in 60 mL of water. 0.315 g of HAuCl₄·3H₂O (0.8 mmol)

and 0.0820 g of H_2 PtCl₆ (0.2 mmol) in 30 mL of methanol was slowly added to the above solution and stirring was continued for 15 min until the whitish yellow solution turned colorless. To the above solution, 0.112 g of $NaBH_4$ (3 mmol) in 15 mL of water was added. The solution turned brown immediately, indicative of particle formation. After stirring of 1 h, 0.0748 g of NaBH₄ (2 mmol) in 3 mL of water was added under vigorous rapid stirring. After additional stirring of 30 min, the solution was rotary evaporated to near dryness and washed thoroughly with copious amounts of methanol. To isolate a mixture of MPS-Au₂₅ and MPS-PtAu₂₄ nanoclusters from the product, recrystallization was carried out using water-methanol mixtures. The product was dissolved in 6 mL of water and then 2 mL of methanol was added to induce precipitation of larger particles. The precipitate was separated by centrifugation and more methanol was added to the supernatant to induce additional precipitation. The precipitate was separated by centrifugation again. This recrystallization step was repeated until a clear supernatant was obtained. Precipitates containing a mixture of MPS-Au₂₅ and MPS-PtAu₂₄ nanoclusters were obtained in the middle fractions of recrystallization and identified by using UV-vis-NIR absorption spectrometry.

To isolate MPS-PtAu₂₄ from the nanocluster mixture, the mixture of MPS-Au₂₅ and MPS-PtAu₂₄ was dissolved in 10 mL of water in a 30 mL scintillation vial. 3 mL of 10 mM TOABr in toluene was added to make an immiscible layer above the water phase. The mixture was then vigorously hand-shaken. Phase transfer of water-soluble nanoclusters to toluene phase occurred within 30 s, as noticed by the color changes of the water and toluene phases. After the phase transfer reaction, the aqueous phase was replaced with fresh water and then the mixture was shaken again to remove water-soluble impurities. This step was repeated several times. The toluene solution was then rotary evaporated to near dryness and washed thoroughly with a mixture of ethanol and water. Separation of MPS-PtAu₂₄ was achieved in organic solution by selectively decomposing Au₂₅ nanoclusters using concentrated H_2O_2 . Unlike the Au₂₅, the PtAu₂₄ was found to be very robust in the oxidation environment, which allowed us to decompose Au₂₅ selectively by reacting with concentrated H_2O_2 . Typically, to the phase-transferred nanocluster

mixture dissolved in 10 mL of dichloromethane, 5 mL of H_2O_2 (34*wt%*) solution was added to react with the nanoclusters for 90 min. After decanting the aqueous phase, the toluene solution was rotary evaporated at room temperature. The dried product was washed with ethanol and collected by centrifugation. To convert the toluene-soluble PtAu₂₄ nanocluster to water-soluble one, the PtAu₂₄ nanoclusters in toluene were phase transferred back to water using tetramethylammonium decanoate (TMAD). 5 mL of chloroform and 5 mL of water were added to 5 mL of toluene solution of phasetransferred MPS-PtAu₂₅. 5 mL of TMAD (100 mM) solution was then added to the mixture under rapid stirring. TMAD solution was prepared by dissolving 1.7 g of decanoic acid (10 mmol) and 1.8 g of TMAH (10 mmol) in 100 mL of methanol. The mixture was left to stand and the upper (aqueous) phase was collected after washing with a copious amount of toluene. The MPS-PtAu₂₄ nanocluster was identified by using UV-vis-NIR absorption spectrometry and ESI mass spectrometry. The typical yield of MPS-Au₂₅ was ~5 mg.

Determination of k_{obs} .⁵⁴⁻⁵⁷ The relationship between the catalytic current (I_c), the catalyst concentration ([cat]), and the acid concentration ([H⁺]) for a catalytic reaction is given by eq. S1 when the acid concentration is sufficiently high that it is unchanged during the course of the reaction and at potentials sufficiently negative that electron transfer is fast. In eq. S1, *n* is the number of electrons involved in the catalytic reaction, *F* is Faraday's constant, *A* is the area of the electrode, *D* is the diffusion coefficient of the catalyst, and *k* is the third order rate constant.

$$I_c = nFA[cat]\sqrt{Dk[H^+]^2}$$
(S1)

For a reversible, one-electron wave, the peak current of catalyst (I_p) is related with [cat] and the sweep rate (v) by eq. S2, where *R* is the ideal gas constant and *T* is the absolute temperature.

$$I_p = 0.4463FA[cat]\sqrt{\frac{F\nu D}{RT}}$$
(S2)

The ratio of I_c/I_p is then given by eq. S3.

$$\frac{I_{\rm c}}{I_{\rm p}} = \frac{n}{0.446} \sqrt{\frac{RTk[H^+]^2}{F\nu}} = \frac{2}{0.446} \sqrt{\frac{RTk_{obs}}{F\nu}}$$
(S3)

For HER in which two electrons are passed for each H₂ molecule (*n*= 2) and at sufficiently high acid concentration relative to the catalyst, the pseudo first-order rate constant ($k_{obs} = k[H^+]^2$) can be calculated by eq. S3 from the slope of the I_c/I_p vs. $v^{-1/2}$ plot.

Determination of Turnover Frequency (TOF).^{S7-S9} The amount of H₂ gas evolved was quantified from the analysis of the headspace with Agilent 7890B gas chromatograph using a thermal conductivity detector, a 5 μ m molecular sieve column (0.53 mm × 30 m) and with N₂ as a carrying gas. The TOF was calculated by eq. S4 using moles of H₂ produced, the reaction time and moles of the catalyst. HER data were averaged for at least two paralleled experiments.

$$TOF = \frac{(\text{mole of } H_2)}{(\text{mole of catalyst}) \times (\text{time})}$$
(S4)

TOF has also been estimated by k_{obs} in a number of reports.^{S10-S12} In this case, however, there are significant uncertainties in the estimation of the H₂ production and the catalyst concentration by I_c and I_p, respectively.

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Fig. S1 Negative-mode ESI mass spectra of (a) C_6S-Au_{25} , (b) MPA-Au₂₅ and (c) MPS-Au₂₅. The assignment coding x, y, and z in parentheses represent, respectively, the number of H^+ ions, Na⁺ ions, and charge of cluster anions. Assignments of all mass peaks observed in Figs. S1b and c are provided in Table S1 and S2, respectively. The insets show the comparisons between the experimental data of $[Au_{25}(SC_6H_{13})_{18}]^-$ (black lines), $[Au_{25}(S(CH_2)_2COO^-)_{18}(H^+)_{14}]^{5-}$ (red lines) and $[Au_{25}(S(CH_2)_3SO_3^-)_{18}(Na^+)_{10}]^{9-}$ (blue lines), and their simulated isotope patterns (grey bars).



Fig. S2 LSVs of (a) 1 mM MPA-Au₂₅ and (b) 1 mM MPS-Au₂₅ in water containing 0.1 M KCl at 50 mVs⁻¹ in the presence of 0, 10, 16, 24, 32, 40, 47, 91, 120, 160, and 180 mM of HOAc. The blank current values (black lines) were multiplied by 100 to show the nanocluster peaks more clearly. (c) Dependence of the catalytic current observed in Figs. S2a and b on the concentration of proton in the presence of 1 mM MPA-Au₂₅ (red) and 1 mM MPS-Au₂₅ (blue) at -0.7 V (versus RHE). [H⁺] was calculated by [H⁺]= ([HOAc]·K_a)^{1/2}, where pK_a= 4.76.



Fig. S3 Plots of I_c/I_p versus $v^{-1/2}$ (v= 0.05 - 10 Vs⁻¹) for a 0.1 M KCl aqueous solution containing 1.8 mM [H⁺] (or 180 mM HOAc) in the presence of 1 mM MPA-Au₂₅ (red) and 1 mM MPS-Au₂₅ (blue) at -0.7 V (versus RHE).



Fig. S4 Dependence of the catalytic current on the pH in the presence of 1 mM MPA- Au_{25} (red) and 1 mM MPS- Au_{25} (blue) at -0.7 V (versus RHE). HOAc was used as the proton source.



Fig. S5 UV-vis-NIR absorption spectra of MPS-Au₂₅ (blue) and MPS-PtAu₂₄ (green) in water. The wavelength scale absorption spectra, Abs (λ), were converted to the energy scale spectra, Absorbance (E), according to the relation Absorbance(E) \propto [Abs(λ)] λ^2 .



Fig. S6 Plots of I_c/I_p versus $v^{-1/2}$ (v= 0.05 - 10 Vs⁻¹) for a 0.1 M KCl aqueous solution containing 1.8 mM [H⁺] (or 180 mM HOAc) in the presence of 1 mM MPS-PtAu₂₄ at -0.7 V (versus RHE). [H⁺] was calculated by [H⁺]= ([HOAc]·K_a)^{1/2}, where pK_a= 4.76. The catalytic current was saturated when [H⁺] > 1.8 mM.



Fig. S7 (a) LSVs of MPS-PtAu₂₄ (1 mM) in water containing 0.1 M KCl at 50 mVs⁻¹ in the presence of 0, 10, 16, 24, 32, 40, 47, 91, 120, 160, and 180 mM of HOAc. The blank current values (black lines) were multiplied by 100 to show the cluster peaks more clearly. (b) Dependence of the catalytic current observed in Fig. S7a on the concentration of proton in the presence of 1 mM MPS-PtAu₂₄ at -0.7 V (versus RHE). [H⁺] was calculated by [H⁺] = ([HOAc]·K_a)^{1/2}, where pK_a= 4.76.



Fig. S8 TOF-potential plots before the blank correction. TOFs obtained at various potentials after 5 min CPE in water (3.0 M KCl) containing 180 mM HOAc with a glassy carbon plate (1 cm²) in the presence of 2.5 μ M MPA-Au₂₅, MPS-Au₂₅, and MPS-PtAu₂₄. Potentials measured vs. Ag/AgCl in aqueous solution were converted to the RHE scale.

Number of			Cluster	Calculated	Experimental Relative error		
Au	MPA	H^{+}	charge	m/z (Da)	m/z (Da)	(%)	
25	18	15	-4	1707.92	1702.79	-0.30	
25	17	14	-4	1681.38	1676.54	-0.29	
24	16	13	-4	1605.60	1601.05	-0.28	
23	16	13	-4	1556.36	1551.81	-0.29	
23	15	12	-4	1529.83	1525.56	-0.28	
25	18	14	-5	1366.13	1362.03	-0.30	
25	17	13	-5	1344.90	1341.03	-0.29	
24	16	12	-5	1284.28	1280.64	-0.28	
23	16	12	-5	1244.89	1241.24	-0.29	
23	15	11	-5	1223.66	1220.24	-0.28	
25	18	13	-6	1138.27	1134.86	-0.30	
25	17	12	-6	1120.58	1117.36	-0.29	
24	16	11	-6	1070.07	1067.03	-0.28	
23	16	11	-6	1037.24	1034.20	-0.29	
23	15	10	-6	1019.55	1016.70	-0.28	
25	18	12	-7	975.52	972.59	-0.30	
25	17	11	-7	960.36	957.59	-0.29	

Table S1. Comparison of experimental and calculated m/z values of peaks observed in Fig. S1b, MPA-Au₂₅.

Number of			Cluster	Calculated	Experimental Relative error	
Au	MPS	Na^+	charge	m/z (Da)	m/z (Da)	(%)
25	18	12	-7	1139.41	1139.09	-0.028
25	17	11	-7	1114.10	1113.81	-0.026
24	16	10	-7	1060.64	1060.39	-0.024
25	18	11	-8	994.11	993.83	-0.029
25	17	10	-8	971.96	971.71	-0.026
24	16	9	-8	925.19	924.96	-0.024
23	16	9	-8	900.57	900.34	-0.025
23	15	8	-8	878.42	878.22	-0.022
25	18	10	-9	881.10	880.85	-0.029
25	17	9	-9	861.41	861.18	-0.026
24	16	8	-9	819.84	819.64	-0.024
23	16	8	-9	797.95	797.75	-0.025
23	15	7	-9	778.26	778.09	-0.022
25	18	9	-10	790.69	790.46	-0.029
25	17	8	-10	772.97	772.77	-0.026
24	16	7	-10	735.55	735.37	-0.024
23	16	7	-10	715.86	715.68	-0.025
23	15	6	-10	698.14	697.98	-0.022
25	18	8	-11	716.72	716.51	-0.029
25	17	7	-11	700.61	700.43	-0.026
24	16	6	-11	666.59	666.43	-0.025

Table S2. Comparison of experimental and calculated m/z values of peaks observed in Fig. S1c, MPS-Au₂₅.

	Num	ber of		Cluster charge	Calculated m/z (Da)	Experimental m/z (Da)	Relative
Pt	Au	MPS	Na^+				error (%)
1	24	18	12	-6	1329.00	1328.60	-0.030
1	24	17	11	-6	1299.46	1299.11	-0.028
1	23	16	10	-6	1237.10	1236.78	-0.026
1	22	16	10	-6	1204.28	1203.96	-0.027
1	22	15	9	-6	1174.74	1174.46	-0.024
1	24	18	11	-7	1135.86	1135.66	-0.018
1	24	17	10	-7	1110.54	1110.24	-0.028
1	23	16	9	-7	1057.09	1056.82	-0.026
1	22	16	9	-7	1028.95	1028.68	-0.027
1	22	15	8	-7	1003.64	1003.40	-0.024
1	24	18	10	-8	991.00	990.70	-0.030
1	24	17	9	-8	968.85	968.58	-0.028
1	23	16	8	-8	922.08	921.84	-0.026
1	22	16	8	-8	897.46	897.22	-0.027
1	22	15	7	-8	875.31	875.10	-0.024
1	24	18	9	-9	878.34	878.07	-0.030
1	24	17	8	-9	858.65	858.52	-0.015
1	23	16	7	-9	817.07	816.86	-0.026
1	22	16	7	-9	795.19	794.97	-0.027
1	22	15	6	-9	775.50	775.31	-0.024
1	24	18	8	-10	788.20	787.96	-0.030
1	24	17	7	-10	770.48	770.27	-0.028
1	23	16	6	-10	733.07	732.87	-0.026

Table S3. Comparison of experimental and calculated m/z values of peaks observed in Fig. 3a, MPS-PtAu₂₄.