

Supplementary Information

High-index faceted Au nanocrystals with highly-controllable optical property and electro-catalytic activity

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Chemicals:

Tannic acid, gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), silver nitrate (AgNO_3), cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC), cetylpyridinium chloride (CPC), sodium borohydride (NaBH_4) and ascorbic acid (AA) were purchased from Sigma-Aldrich. Sodium hydroxide (analytical reagent) and benzenethiol (BT) were bought from Rankem and Spectrochem respectively. Sulfuric and formic acid were purchased from Thomas Baker. All chemical were used as such. Milli-Q water (18.2 M Ω) was used for all experiments.

Characterization:

UV-vis spectra were recorded from Chemito SPECTRASCAN UV 2600. FESEM and TEM images were captured through ZEISS Ultra Plus and TECHNAI T30 respectively. Electrocatalytic studies were carried out by Biologic SP-300 potentiostat. Raman spectra were recorded by Horiba JY Labram HR800 micro Raman spectrometer with laser wavelength of 632.8nm, Helium-Neon laser, 20 mW power.

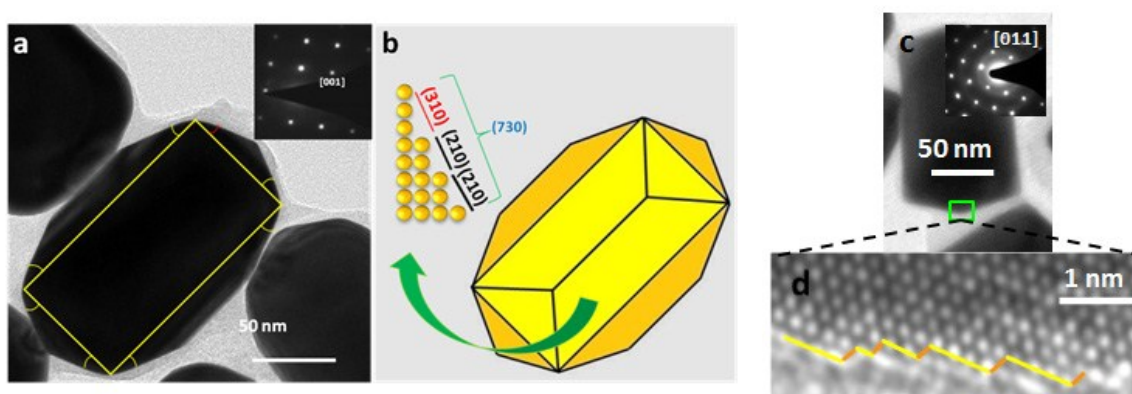


Fig. S1. (a-b) TEM image of ETHH Au NC (yellow box) oriented at [001] zone axis; inset: SAED pattern for the same particle. The angles between bevel and base of ETHH Au NCs were measured to be 26.5, 24.1, 24.1, 24.3, 25.9, 24.2, 26.9, and 24.40 (starting clockwise from marked red colored angle). The average value of all these angles was estimated to be $\sim 25^\circ$ and thereby suggesting that our as synthesized ETHH Au NCs were enclosed with (730) planes (schematically shown in (b)). (c-d) HRTEM of ETHH Au NCs was captured through [011] zone axis.

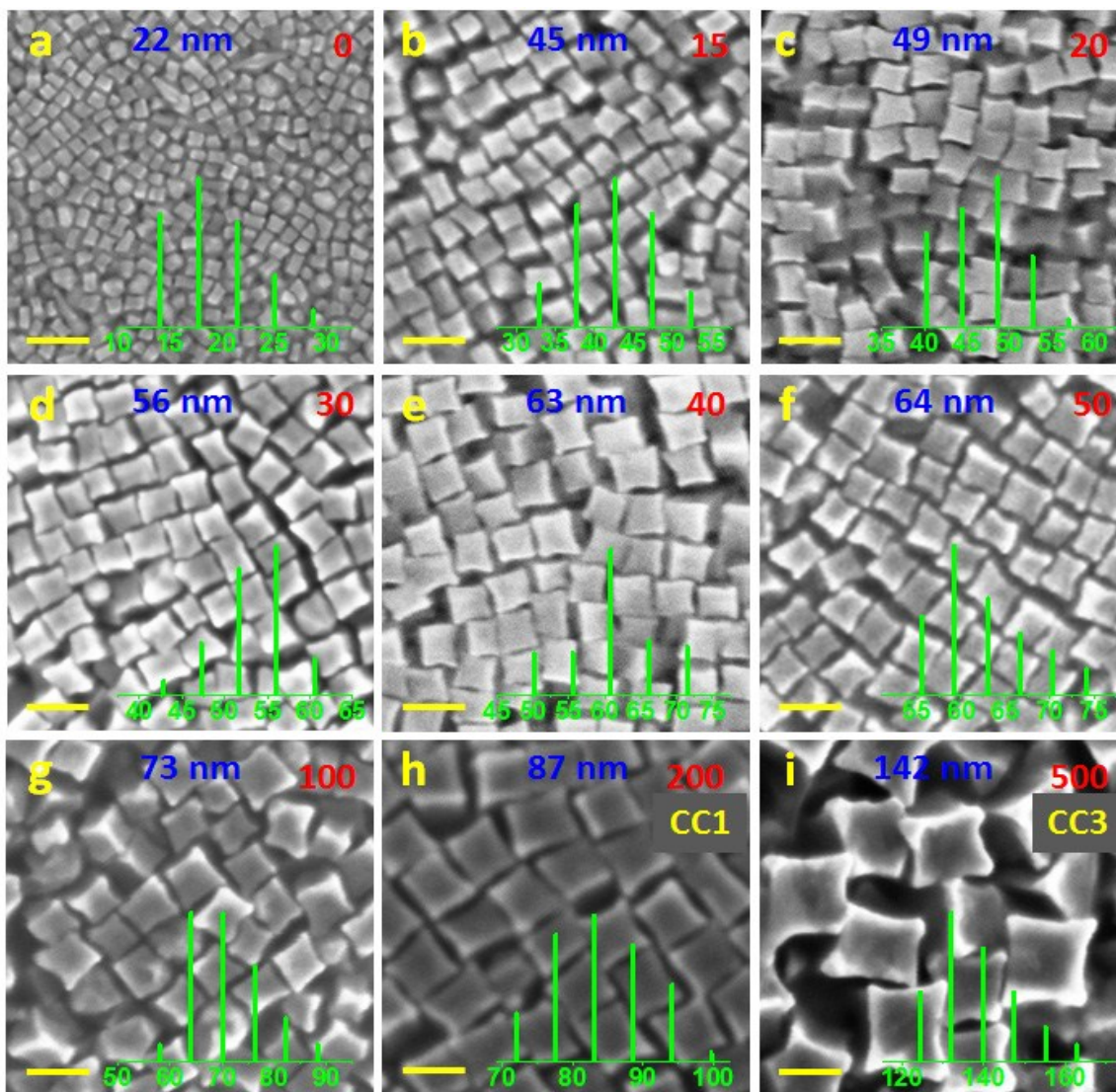


Fig. S2. (a-i) FESEM images of concave cubic Au NCs synthesized by using 0, 15, 20, 30, 40, 50, 100, 200 and 500 times dilution of original seed into the growth solution respectively. Concave cubic Au NCs synthesized by the same procedure used for the ETHH Au NCs, but the CTAC was used instead of CTAB; scale bar is 100 nm for all. Average lengths of edges are labelled with blue colour. Histogram was drawn for each sample (green colour) by surveying above 50 number of particles; scale bar is stand for edge length (nm).

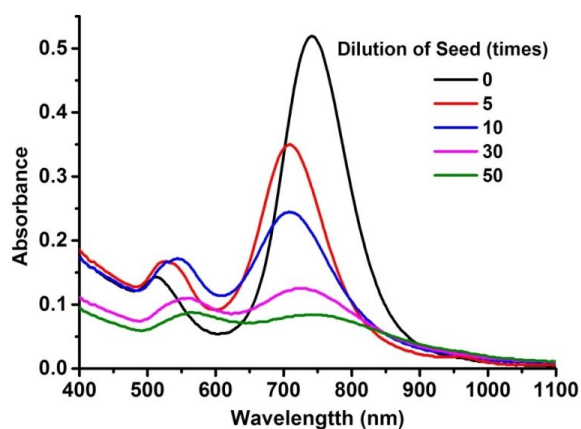


Fig. S3. UV-vis spectra measured for the ETHH Au NCs (Figure 2) synthesized with using 0, 5 (S1), 10 (S2), 30 (S3) and 50 (S4) times dilution of seed solution into the growth solution.

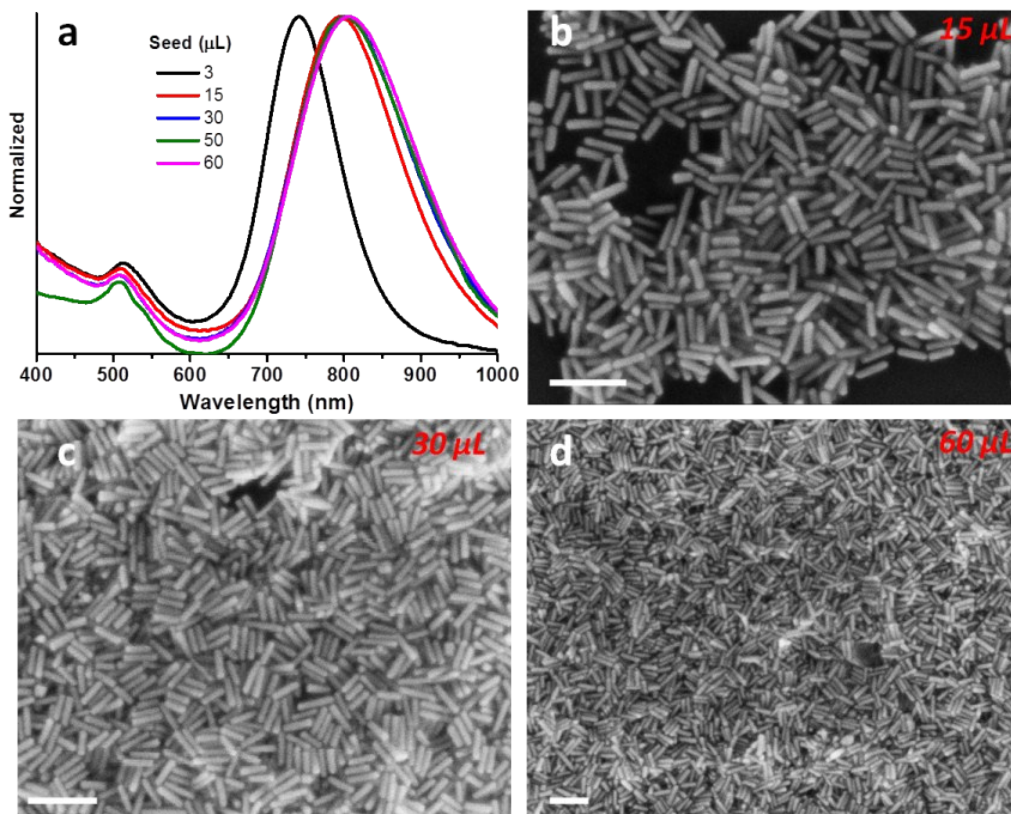


Fig. S4. a) UV-vis spectra recorded for Au NCs synthesized with seed quantities 3, 15, 30, 50 and 60 μL . b), c) and d) FESEM images of 15, 30 and 60 μL seed solutions respectively. For all, scale bar is 100 nm.

Over-growth of Au NRs synthesized using ascorbic acid as mild reducing agent:

Cylindrical Au NRs were synthesized by following reported literature (Ref 1) where ascorbic acid and 150 μL of AgNO_3 (4mM) were used as mild reducing and shape directing agents respectively. After synthesizing Au NRs, centrifuged at 8000 rpm for 7 min and removed the supernatant, followed by re-dispersed into the MQ-Water. Then, Au NRs solution of 200 μL used as seed for the over growth under the similar experimental conditions (Main text).

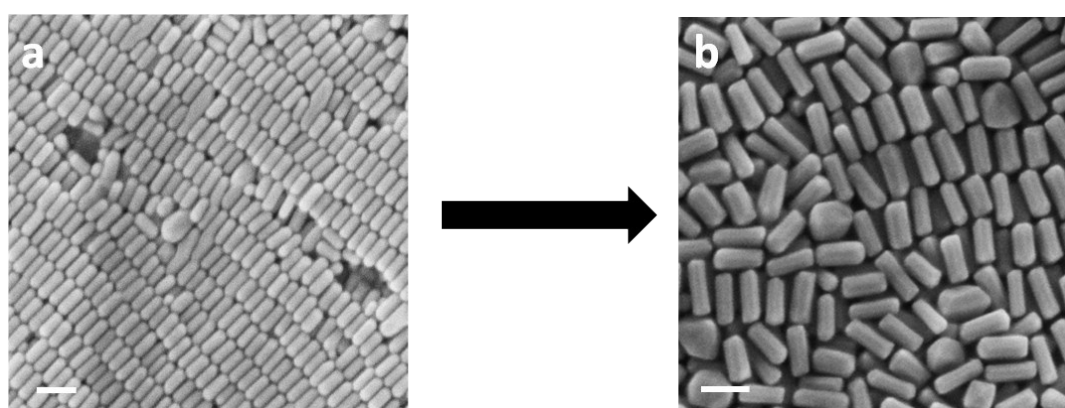


Fig. S5. a) FESEM image of Au NRs synthesized by following the reported literature. b) FESEM image of ETHH Au NCs synthesized by using Au NRs (a) as seed under the similar experimental conditions applied for the ETHH Au NCs synthesis (Fig. 2). For all, scale bar is 100 nm.

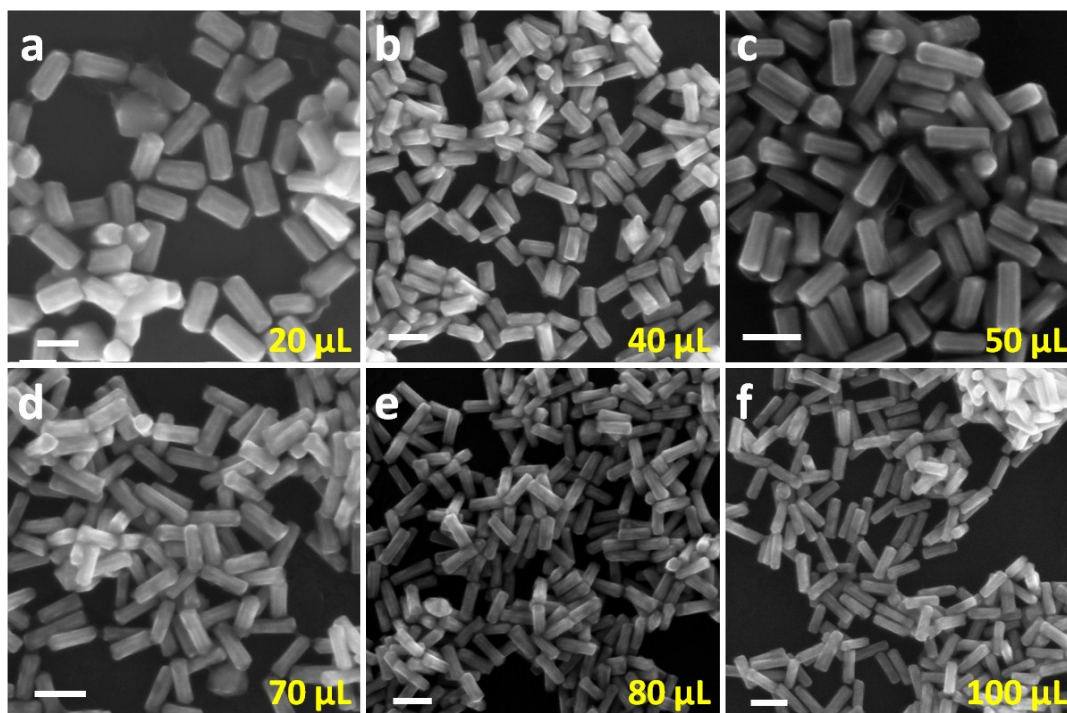


Fig. S6. FESEM images ETHH Au NCs synthesized with AgNO_3 of a) 30, b) 40, c) 60, d) 70, e) 80 and f) 100 μL . For all, scale bar is 100 nm.

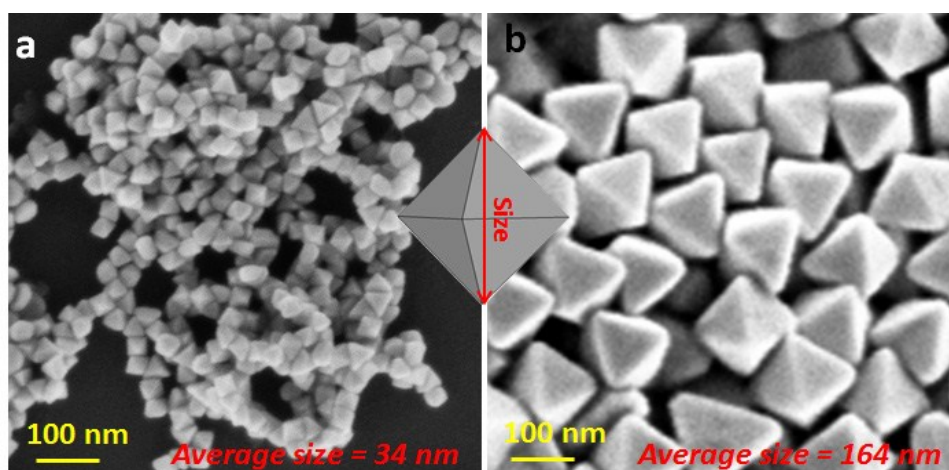


Fig. S7. FESEM images of octahedral Au NCs. a) Synthesized according to reported procedure (Ref. 2). b) Produced by following the existing report (Ref. 3); in the final step 20 μL of CPC capped seed solution was added to the growth solution.

Electro-catalytic activity of ETHH Au NCs:

This experiment was performed as follows, ETHH Au NCs washed twice with water by centrifugation and then loaded the amount of 85 μg on glassy carbon electrode; this electrode used as working electrode. Graphite rod and Hg/HgSO_4 were used as counter and reference electrodes respectively. Electrocatalysis of formic acid (0, 0.25, 0.5, 0.75 and 1M) was performed in H_2SO_4 (0.5 M) solution by applying the voltage scan rate of 50 mVs^{-1} . Nitrogen gas purging was allowed throughout the experiment. The first two cycles of measurements were discarded in order to avoid the interference of absorbed gases in the solution. These measurements were done for the samples S1, S2, S3, S4 (Figure 2) and octahedral Au NCs (Figure S7). Electrochemically active surface area was calculated for the samples S3 and Oh2 based on oxide stripping results (Table S1).

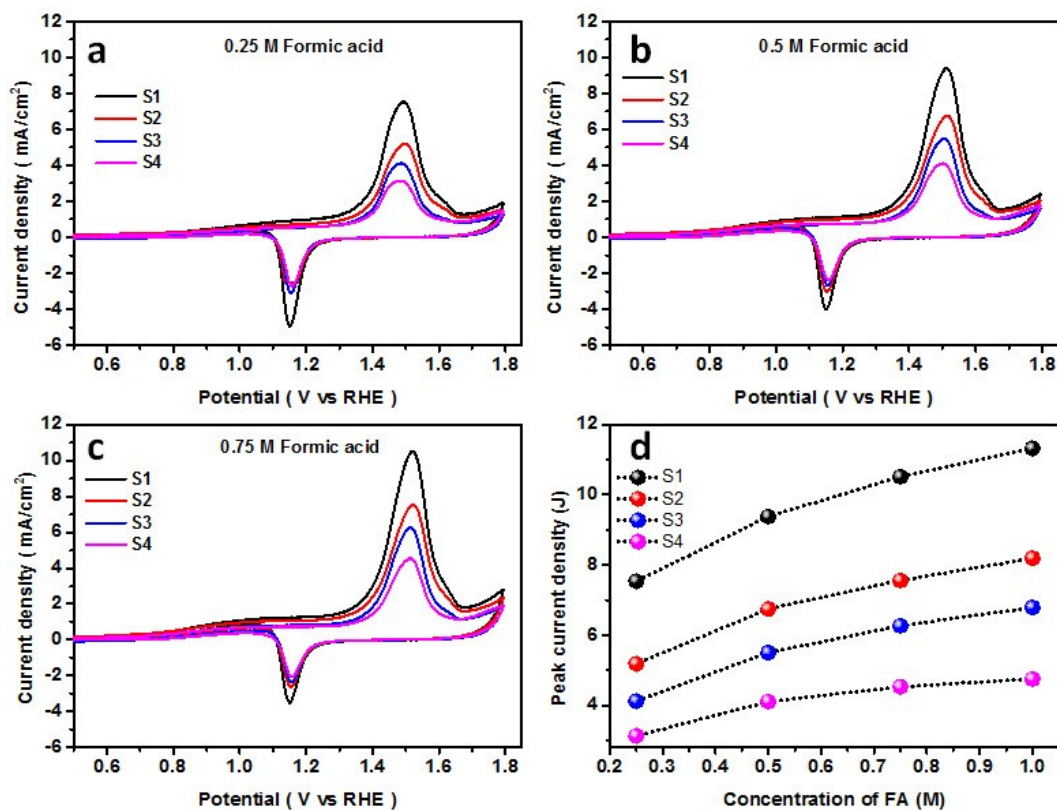


Fig. S8. CVs of a) 0.25 M, b) 0.5 M and c) 0.75 M formic acid (FA) oxidation catalysed by S1, S2, S3 and S4 (Fig. 2). d) Plot of oxidation peak current densities (during the FA oxidation) obtained for ETHH Au NCs versus different concentrations of FA used in the electrolyte solution.

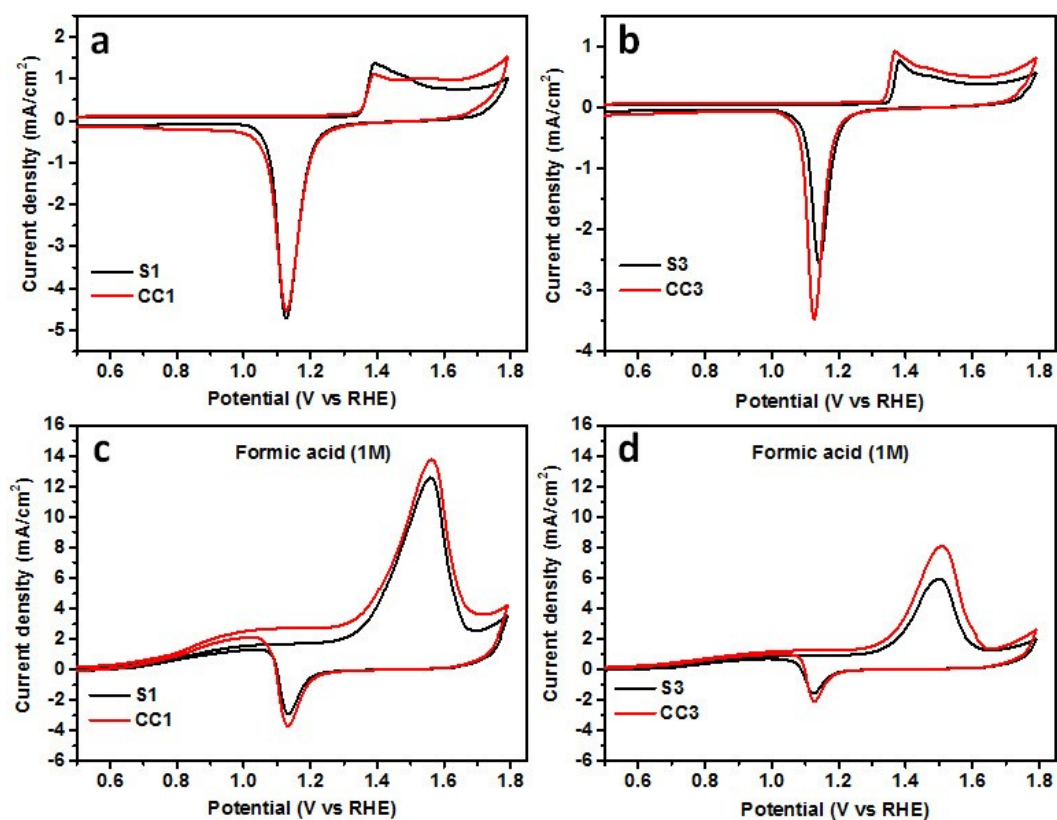


Fig. S9. (a-b) CV traces were recorded for the samples S1, S3 (ETHH Au NCs; Figure 2), CC1 and CC3 (Concave cubic Au NCs; Fig. S2) in H₂SO₄ (0.5 M) solution. (c-d) CVs were recorded for the oxidation of formic acid catalysed by the samples.

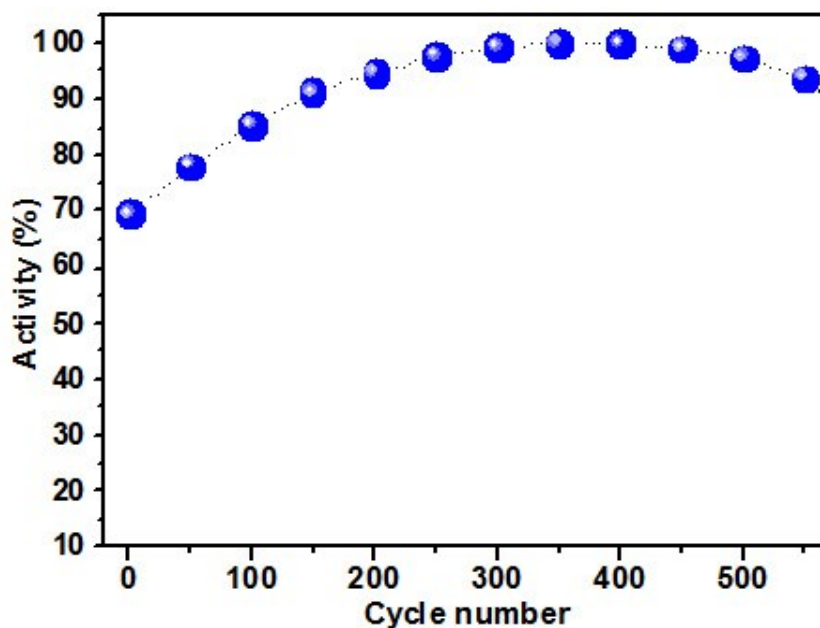


Fig. S10. Electrocatalytic durability test was performed for the sample S3 in HCOOH (1M) + H₂SO₄ (0.5 M) electrolyte solution.

Table S1

Au NCs	Mass activity (A mg⁻¹)	ECSA (cm² mg⁻¹)	Specific activity (mA cm⁻²)
S3	15.64X10 ⁻³	76.95	2.02X10 ⁻²
Oh2	10.03X10 ⁻³	70.83	1.41X10 ⁻²

SERS Measurement:

Raman measurement was carried out through the following way. As synthesized ETHH Au NCs (S2 and S4) solutions of 1mL were centrifuged at 6000 rpm for 7 min and removed the supernatant and subsequently the precipitate re-dispersed into the 1mL MQ-water. These solutions were centrifuged again with the same parameters and re-dispersed the precipitate into 50 μ L MQ-water with sonication (after discarding the supernatant). Subsequently these solutions were treated with 50 μ L of benzenethiol (BT) (10 μ M, in ethanol) and kept for incubation for 12 hrs (the resultant concentration of BT is 5 μ M). After drop-casting these sample on glass slide, dried under the incandescent lamp (200 W) for 20 min. Raman spectra were recorded for these samples along with neat BT (9.676 M) at 2 mW with acquisition time of 5s by using 632.8 nm lasers as source.

Table S2a

ETHH Au NCs	I_{SERS} of 1070 cm^{-1}	C_{SERS} (M)	I_{RS} (BT)	C_{RS} (M)	$I_{\text{SERS}}/I_{\text{RS}}$	AEF = $I_{\text{SERS}}/I_{\text{RS}} * C_{\text{RS}}/C_{\text{SERS}}$
S4	668642.361	5×10^{-6}	7326.8677	9.676	91.259	1.76×10^8
S2	125486.691	5×10^{-6}	7326.8677	9.676	17.127	3.31×10^7

Table S2b

ETHH Au NCs	I_{SERS} of 1570 cm^{-1}	C_{SERS} (M)	I_{RS} (BT)	C_{RS} (M)	$I_{\text{SERS}}/I_{\text{RS}}$	AEF = $I_{\text{SERS}}/I_{\text{RS}} * C_{\text{RS}}/C_{\text{SERS}}$
S4	528136.6848	5×10^{-6}	10428.131	9.676	50.645	4.9×10^8
S2	81729.8874	5×10^{-6}	10428.131	9.676	7.837	7.58×10^7

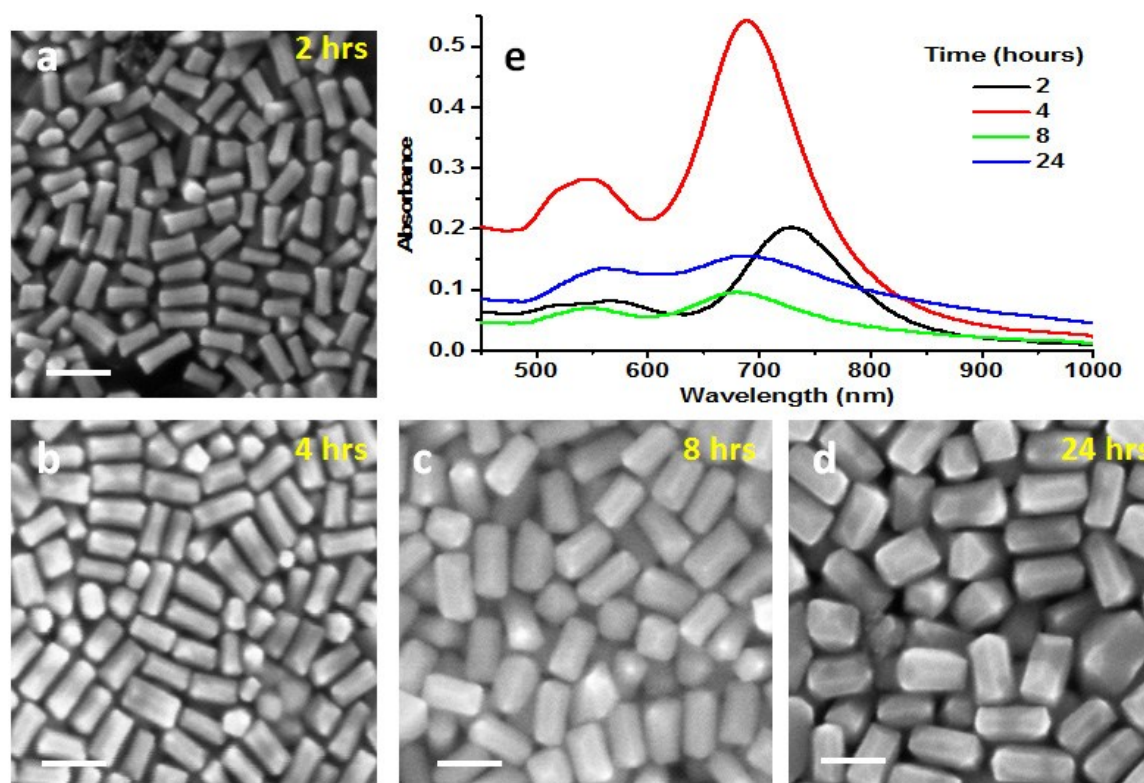


Fig. S11. (a-d) FESEM images were captured during evolution of ETHH Au NCs (S2) with time after 2, 4, 8 and 24 hrs respectively. e) UV-vis spectra were recorded during the growth of ETHH Au NCs (S2) with time after addition of seed to the growth solution. Scale bar is 100 nm for all.

References:

1. B. Nikoobakht, M. A. El-Sayed, *Chem. Mater.*, 2003, **15**, 1957-1962.
2. F.-R. Fan, D.-Y. Liu, Y.-F. Wu, S. Duan, Z.-X. Xie, Z.-Y. Jiang, Z.-Q. Tian, *J. Am. Chem. Soc.*, 2008, **130**, 6949-6951.
3. W. Niu, S. Zheng, D. Wang, X. Liu, H. Li, S. Han, J. Chen, Z. Tang, G. Xu, *J. Am. Chem. Soc.*, 2009, **131**, 697-703.