Electronic Supplementary Information:

Quantification of electron transfer rates of different facets on single gold nanoparticles during catalytic reaction

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Supplementary Methods

1. Materials.

Gold(III) chloride trihydrate, sodium borohydride, silver nitrate, and L-ascorbic acid were obtained from Aldrich. Cetyltrimethylammonium bromide (CTAB) and hydrochloric acid (HCl) were purchased from Acros and Samchun, respectively. All chemicals were used as received and were not purified further.

2. Synthesis of gold nanoparticles.

Gold seeds were prepared by rapidly adding ice-cold $NaBH_4$ (0.01 M, 0.6 ml) to a solution of $HAuCl_4$ (0.01 M, 0.25 ml) and CTAB (0.1 M, 9.75 ml). To prepare gold nanorods, the growth solution was composed of CTAB (0.1 M, 40 ml), $HAuCl_4$ (0.01 M, 2.0 ml), $AgNO_3$ (0.01 M, 0.06 ml) and ascorbic acid (0.0788M, 0.21 ml). Finally, 25 μl of the seed solution which, diluted fifty times with CTAB (0.1 M), was injected into the growth solution. For elongated THH gold nanoparticle, the growth solution was prepared by adding $AgNO_3$ (0.01 M, 0.3 ml), $HAuCl_4$ (0.01 M, 2.0 ml), HCl (1.0 M, 0.8 ml) and ascorbic acid (0.1 M, 0.32 ml) to CTAB (0.1 M, 40 ml). Lastly, a 100 μl aliquot of the seed solution, was diluted fifty times with CTAB (0.1 M), was injected into the growth solution.

3. Physicochemical characterization.

Bright-field TEM image was collected by high-resolution TEM (HR-TEM, JEOL, JEM-3010). High-resolution TEM (HR-TEM, JEOL, JEM-3000F) was used to collect electron diffraction patterns. The surface morphology of the gold nanoparticles were characterized using a scanning electron microscopy (SEM, Carl Zeiss, SUPRA 55VP). The UV-Vis spectra were recorded using a Hewlett-Packard 8453 spectrophotometer.

4. Immobilization of gold nanoparticles on cover glass.

The cover glass was cleaned and oxidized with a piranha solution ($H_2SO_4 : H_2O_2 = 7 : 3$, v/v) and the glass was then rinsed with D.I. water several times. The cover glass was then immersed in a 1 mM (3-aminopropyl) triethoxysilane (APTES) solution to develop a positive charge. The APTES functionalized cover glass was introduced to 0.1 mg/mL sodium poly (styrene sulfonate) (PSS) for being functionalized negatively and subsequently, the positively charged gold nanorod and elongated THH gold nanoparticles were immobilized, respectively. It should be noted that the synthesized gold nanoparticles are positively charged due to the presence of amine groups in CTAB as a surfactant surrounding gold nanoparticle surface. The prepared cover glass was integrated with a homemade microfluidic system as shown in Fig. S3 and the 4-NIP reduction reaction was monitored by collecting time-resolved scattering spectra of distinct single nanoparticles with the DFM system. The reaction chamber was equipped with a thermal couple and the temperature of the bath was maintained at a constant temperature of 35 ºC throughout the entire experimental process.

5. Dark-field microspectroscopy.

The dark-field micro-spectroscopic system is a combination of a commercial Axio Observer Z1 inverted microscope (Carl Zeiss, Germany), a true-color digital camera, a 1024 pixel 256 pixel cooled spectrograph CCD camera (Andor Technology PLC, UK) and a home-built micro-fluidic chamber[S1]. The spectrophotometer (Monora320i, Dongwoo Optron Co., Korea) had dual-turret holding gratings of 1200 grooves/mm and 300 grooves/mm. A programmable shutter was mounted internal to an adjustable entrance slit, the width of which could be opened to retain only a single nanoparticle in the region of interest.

6. Modified Rayleigh equation

$$\Delta\lambda = \lambda - \lambda_0 = -\frac{\Delta N}{2N}\lambda_p\sqrt{\varepsilon_\infty + \left(\frac{1}{L} - 1\right)\varepsilon_m} \tag{1}$$

Where N is the electron density of the metal (60 electrons / (nm)^3 for gold), ε_∞ the high-frequency dielectric constant of the metal (12.2 for gold), L the shape factor of the nanocrystal (0.17 for both kinds used gold nanoparticles), λ_p the bulk plasma wavelength (131 nm for gold), λ_0 the position of the SP peak for the uncharged nanocrystal and ε_m the medium dielectric permittivity (1.77 for our experimental scheme).

Supplementary Figures

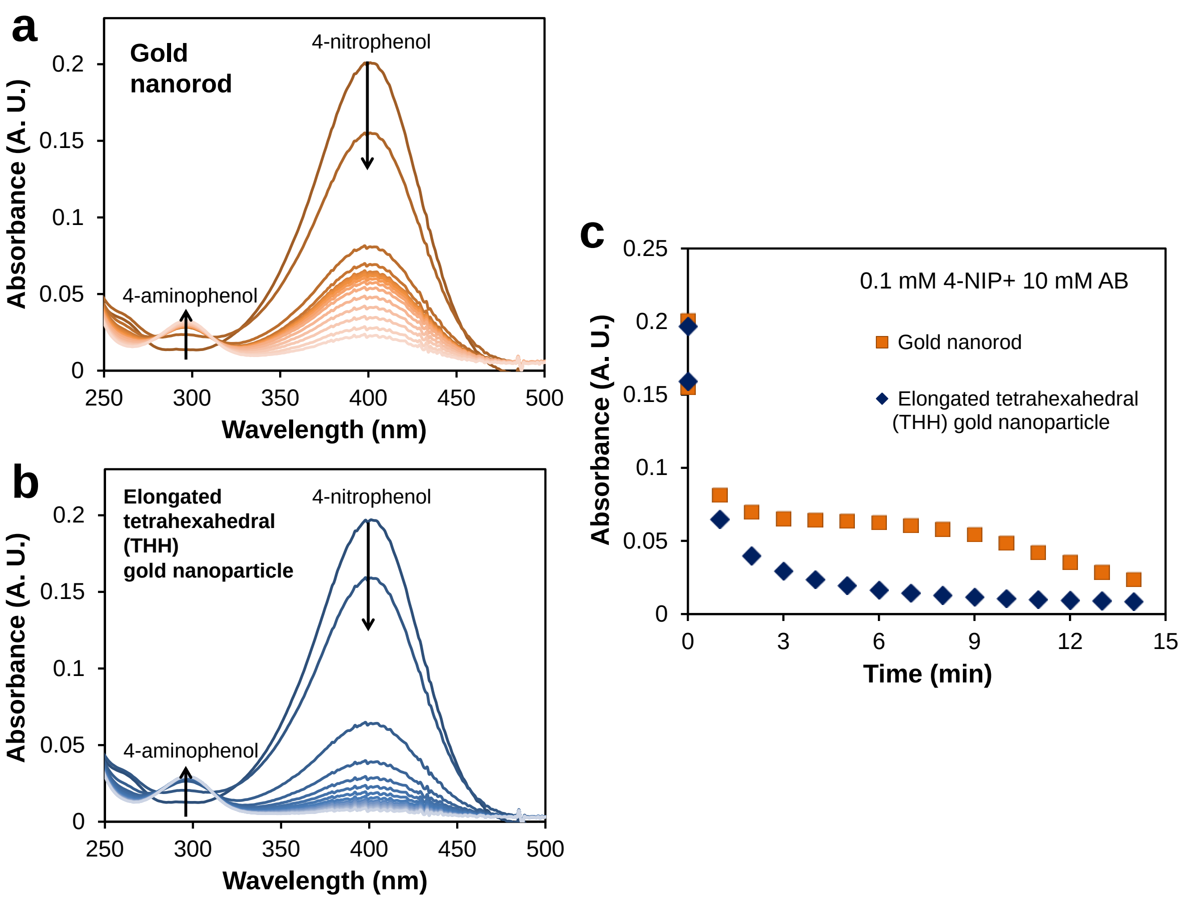

Fig. S1 The UV-Vis spectroscopy results for the reduction of 4-nitrophenol (4-NIP) as a function of time: (a**)** Gold nanorods and (b) Elongated tetrahexahedral (THH) gold nanoparticles for 30 min. The catalytic reaction of elongated THH gold nanocatalysts was faster than gold nanorod catalysts. (c) Absorbance peak of 4-nitrophenolate ions comparison of gold nanorods and elongated THH gold nanoparticles.

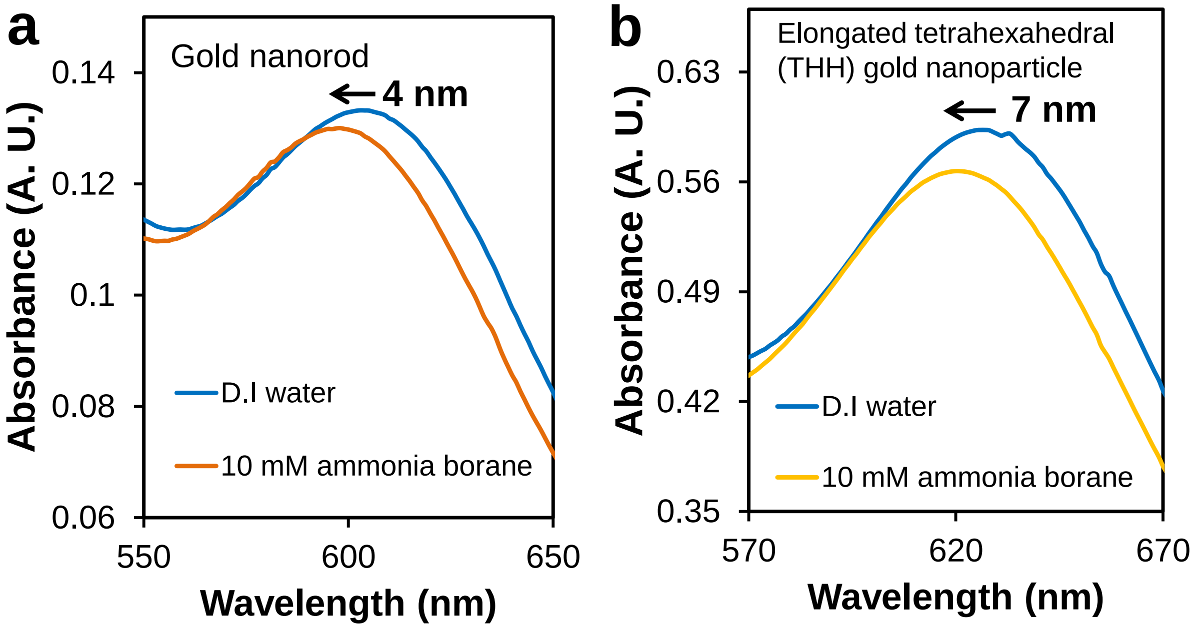

Fig. S2 UV-Vis spectroscopy results representing electron transfer after introducing ammonia borane (AB) into (a) gold nanorods and (b**)** elongated THH gold nanoparticles. The spectral absorption peak of elongated THH gold nanoparticles (high-index facets nanoparticles) was more blue-shifted than that of rod shaped gold nanoparticles (low-index facets nanoparticles).

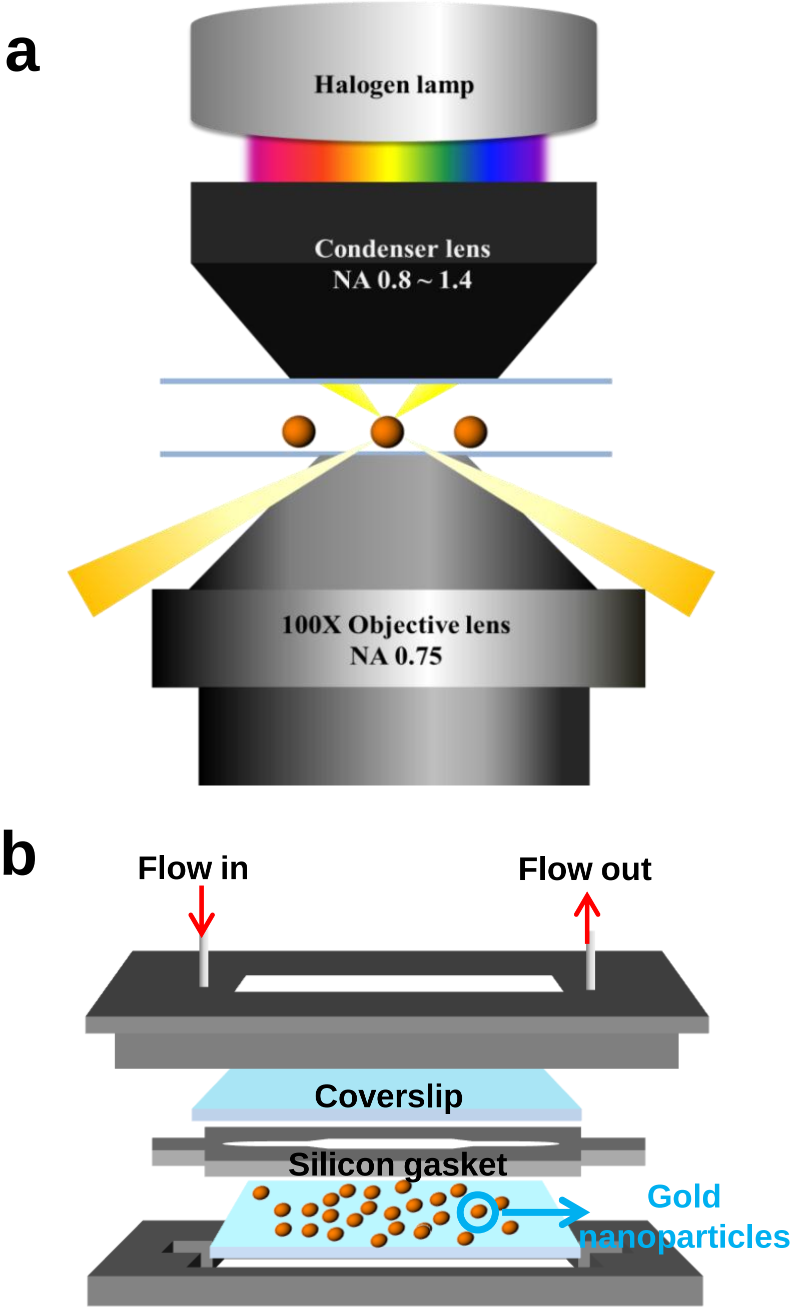

Fig. S3 (a) Schematic illustration of the simultaneous optical monitoring of a catalytic reaction of a single gold nanocatalyst particle. (b) A homemade microfluidic system combined with dark-field microscopy for real time monitoring.

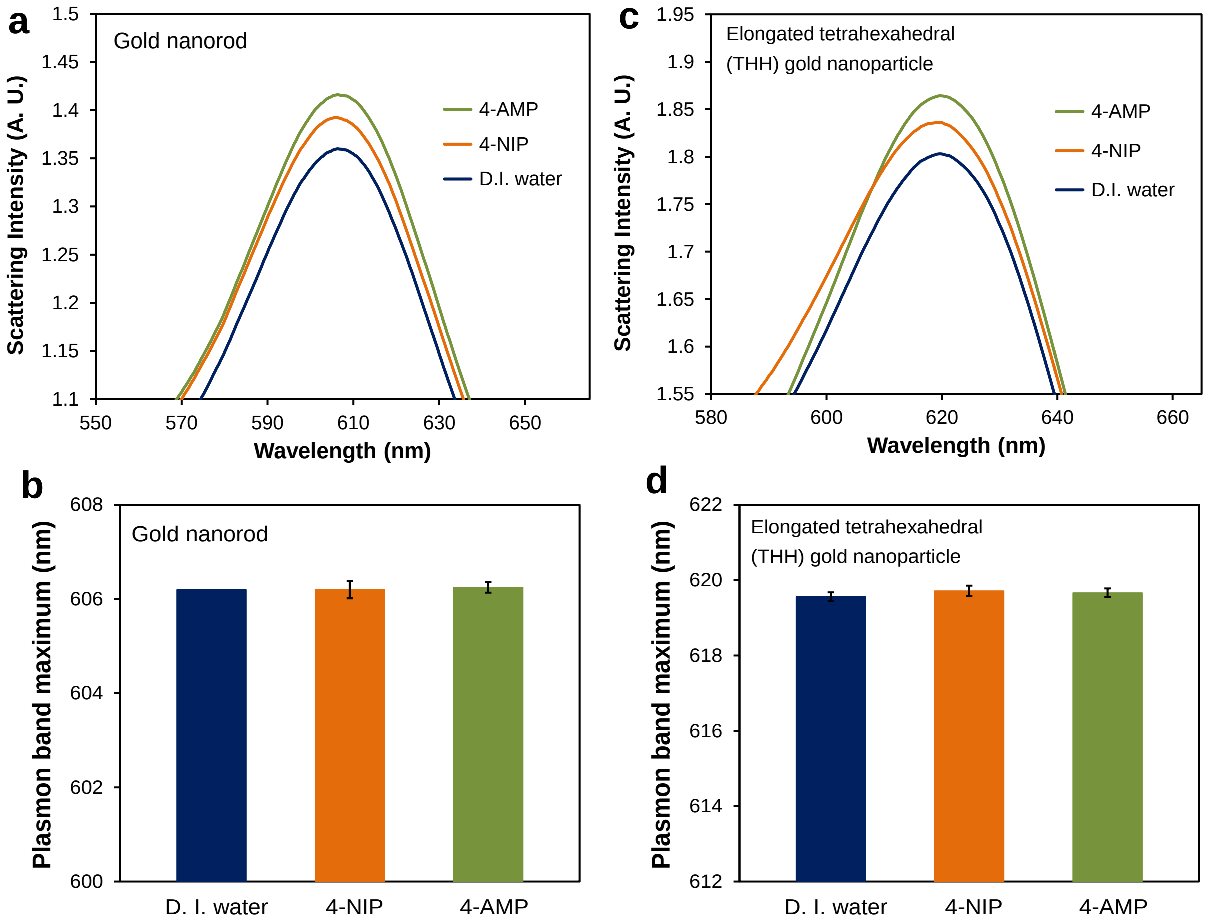

Fig. S4 Normalized plasmon scattering from a single gold nanoparticle in various solvents: (a) Gold nanorods and (c) Elongated tetrahexahedral (THH) gold nanoparticles. Bar graphs summarize the change in responses to three types of solvents. Peak shifts of a single gold nanoparticle when they undergo while in water, in 4-nitrophenol (4-NIP), and in 4-aminophenol (4-AMP) solutions: (b) Gold nanorods and (d) Elongated tetrahexahedral (THH) gold nanoparticles. Error bars correspond to standard deviations measured for five samples.

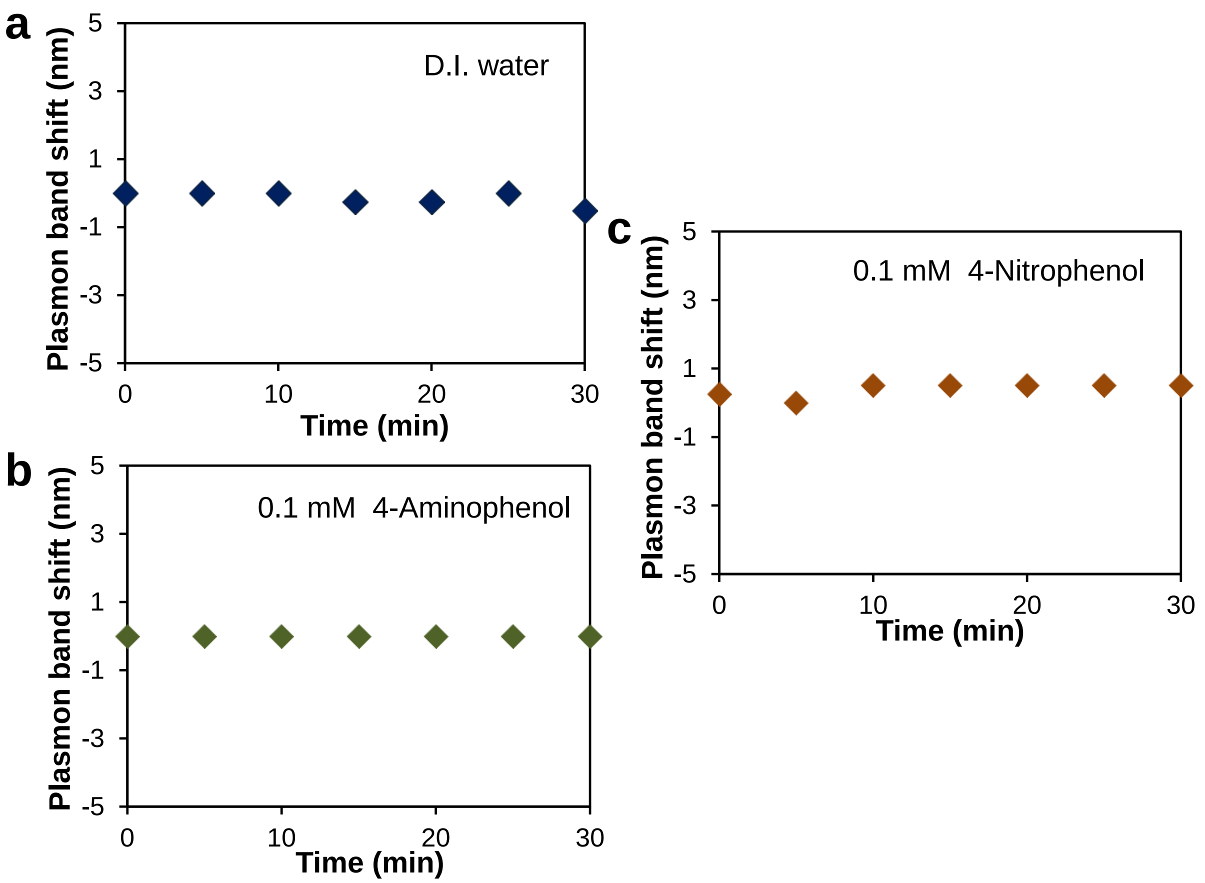

Fig. S5 SP band position as a function of time after introducing (a) D.I. water, (b**)** 0.1 mM 4-AMP and (c**)** 0.1 mM 4-NIP for control test.

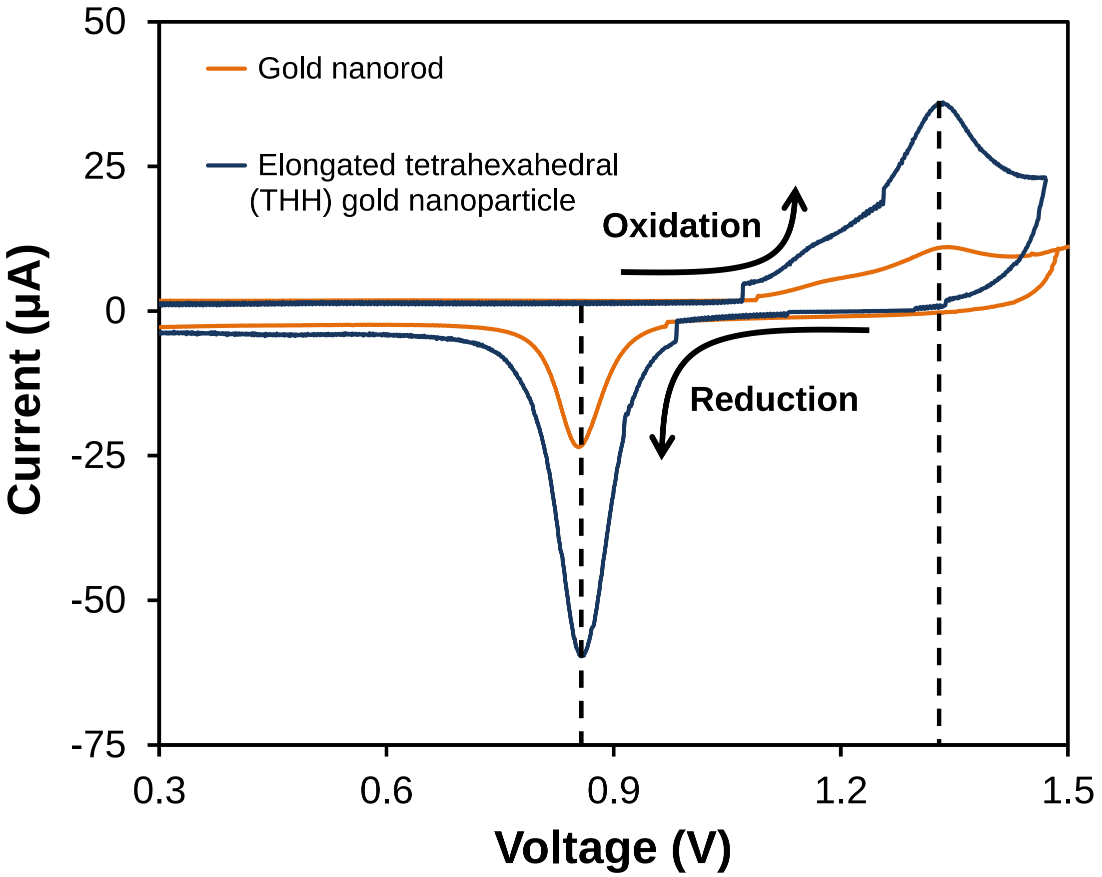

Fig. S6 CV traces of the different shaped gold nanocrystals. The same amounts of gold nanoparticles were spin casted on indium tin oxide glass and the CV measurements were carried out at a scan rate of 20 mVs^{-1}. A Pt wire and Ag/AgCl (in saturated NaCl) served as the counter and reference electrodes, respectively. An aqueous solution of H_2SO_4 (0.1 M) was employed as the electrolyte solution and was purged with high-purity N_2 gas for 30 min before the measurement. This result suggests that the electron movement rate is faster on gold nanoparticles enclosed by {730} high-index facets than gold nanorods enclosed by low-index facets.

Reference

S1. Y. I. Yang, E. Jeong, I. Choi, S. Lee, H. D. Song, K. Kim, Y. Choi, T. Kang and J. Yi, *Angew. Chem. Int. Ed.*, 2011, **50**, 4633-4636.