Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for: In situ identification of crystal facet-mediated chemical reactions on tetrahexahedral gold nanocrystals using surface-enhanced Raman spectroscopy

S1. Calculations of the total number of the Au atoms on the surfaces and turnover frequency (TOF) for the Au nanospheres and THH Au NCs

1.1 Number of surface Au atoms for Au nanospheres

We assumed that the Au nanospheres used in this work has a smooth surface. The Au nanosphere has a diameter of 140 nm. Its surface area is $3.1415 \times (70\ \text{nm})^2 = 1.54 \times 10^4\ \text{nm}^2$.

Au has the face-centered-cubic structure with a lattice constant of 0.4078 nm. Smallest repeating unit cell on a two-dimensional (111) facet is a triangle with three vertex Au atoms. It contains 0.5 Au atom and its area is $1.732 \times (0.2883\ \text{nm})^2 / 4 = 0.036\ \text{nm}^2$.

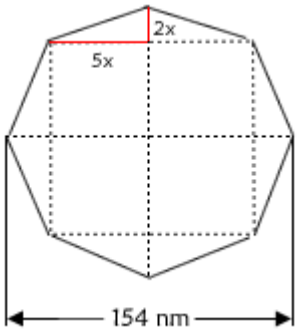
The number of the surface Au atoms on a single Au nanosphere is

$(1.54 \times 104\ \text{nm}^2) / (0.036\ \text{nm}^2) \times 0.5 = 2.14 \times 10^5$.

Number of the Au atoms involved in the catalytic reaction is about 40, which was counted from the SEM image in Fig. 3b of the main text. Thus, the total number of surface Au atoms on the Au nanospheres used in the catalytic reaction is

$40 \times 2.14 \times 105 = 0.86 \times 10^7$.

1.2 Number of surface Au atoms for the THH Au NCs



Scheme S1. Schematic showing of projection from a THH Au NC. The nanocrystal is viewed along the [001] axis.

The THH Au NC sample has an average length of 154 nm. The Au NC is exposed with {520} facets, so the length ratio between the two perpendicular sides of the triangle indicated in red in Scheme S1 is 5:2. Suppose that one side is 5*x*, and the other side is then 2*x*. The third side is calculated to be $\sqrt{29}x$. The value of x can be calculated from the nanocrystal length to be

x = (154 nm) / (2 + 5 + 5 + 2) = 11 nm.

The total number of the surface atoms on the high-index {520} facets is equal to that of the surface atoms on the {010} planes that are projected from the {520} facets.[1] Smallest repeating unit cell on a two-dimensional (010) facet is a square with four vertex Au atoms and one central Au atom. It contains 2 Au atoms and corresponding area is

(0.4078 nm) × (0.4078 nm) =0.166 nm^2.

A THH NC can be decomposed into a cuboid and six pyramids. The total surface area of the cuboid is

(10 × 11 nm) × (10 × 11 nm) × 6 = 7.26 × 10^4 nm^2.

The number of the surface Au atoms on a single THH Au NC is

7.26 × 104 nm^2/ (0.166 nm^2) × 2 = 8.74 × 10^5.

Number of the Au atoms involved in the catalytic reaction is about 20, which could be counted from the SEM image in Fig. 3a. The total number of the surface Au atoms on the THH NCs in the catalytic reaction is 20 × 8.74 × 105 = 1.74 × 10^7.

1.3 TOF for the THH Au NCs and the sphereical Au NCs

TOF for a nanoparticle catalyst = (relative Raman intensity of product) / (number of catalyst surface atoms × acquisition time for the SERS spectrum)

The relative Raman intensities of the 1142 cm^{-1} band with respect to the 1076 cm^{-1} band in the SERS spectra of PATP adsorbed on the THH Au NCs and Au nanospheres are about 0.95 and 0.2, respectively (see SERS spectra in Fig. 3c). The acquisition times used for the SERS measurement on the Au nanoparticles are both 20 s. Thus,

TOF for the THH Au NC: 0.95 / (1.74 × 107 × 20 s) = 2.73 × 10^{-9} s^{-1},

TOF for the Au nanosphere: 0.2 / (0.86 × 107 × 20 s) = 1.16 × 10^{-9} s^{-1}.

References:

[1] Wang F.; Li C. H.; Sun L. D.; Wu H. S.; Ming T.; Wang J. F.; Yu J. C.; Yan C. H. Heteroepitaxial Growth of High-Index-Faceted Palladium Nanoshells and Their Catalytic Performance. *J. Am. Chem. Soc.* **2011**, *133*, 1106-1111.

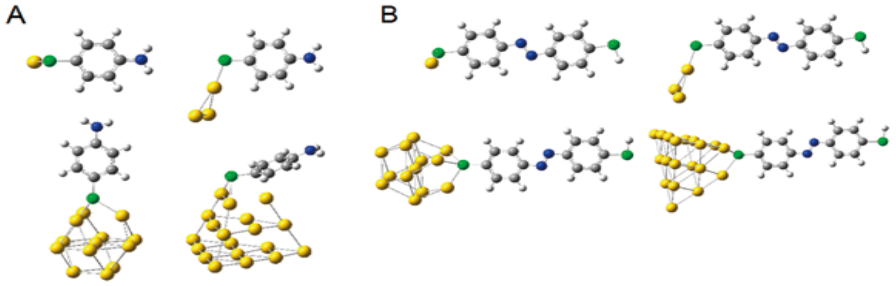


Figure S1 Chemical structures of (A) PATP-Au$_n$ and (B) DMAB-Au$_n$ (n = 1, 3, 13, and 19) complexes. Herein, the N and S atoms are linked by two white H atoms and a white H atom in the PATP, respectively. In the complexes, two Au atoms is connected by the S atom.

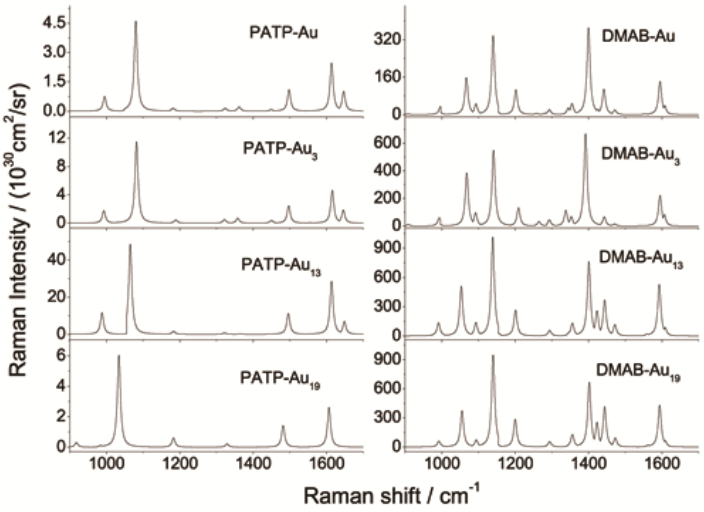


Figure S2 Simulated Raman spectra of PATP-Au$_n$ and DMAB-Au$_n$ (n = 1, 3, 13, 19) complexes. A linewidth of 10 cm^{-1} in Lorentzian line shape were used to calculate the Raman spectra.

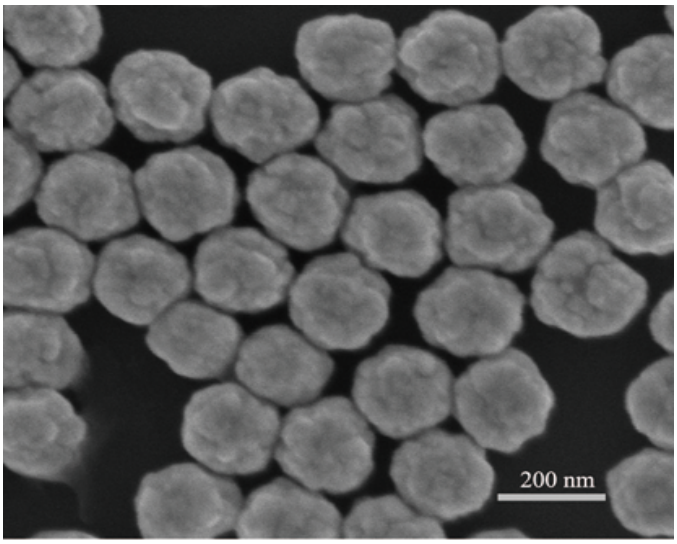


Figure S3 SEM image of the Au nanospheres.

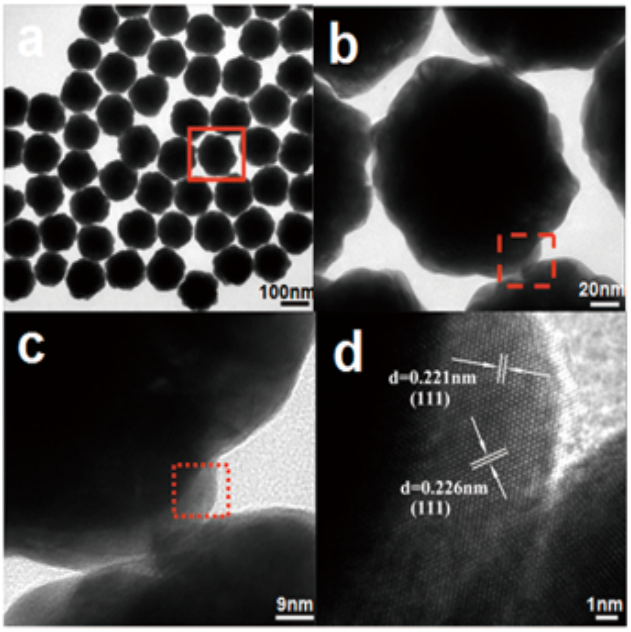


Figure S4 (a) TEM image of Au nanospheres. (b) TEM image of the region indicated by the rectangle in (a). (c) Higher magnification image of the region indicated by the rectangle in (b). (d) High-resolution TEM image recorded from the boxed area marked in (c).

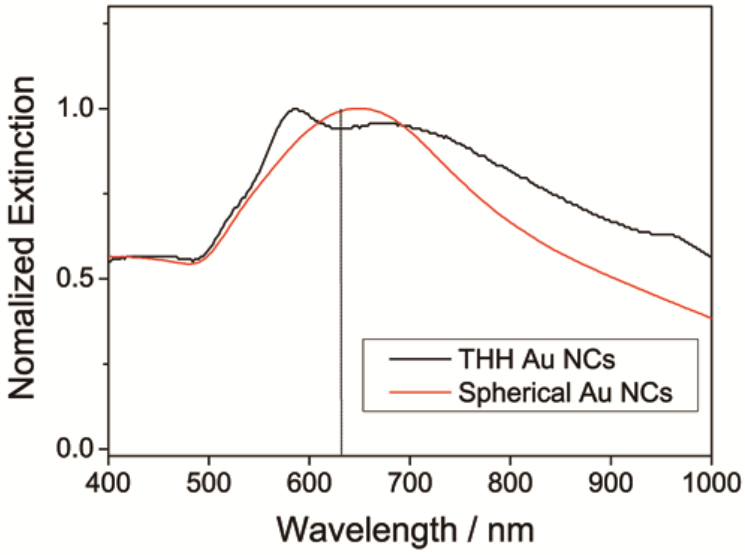


Figure S5 Normalized UV-vis extinction spectra of the THH Au NCs and Au nanospheres. The dashed line represents the laser wavelength used in the SERS measurements.