

## Electronic Supplementary Information (ESI)

### Rational design and synthesis of excavated Au nanocrystals

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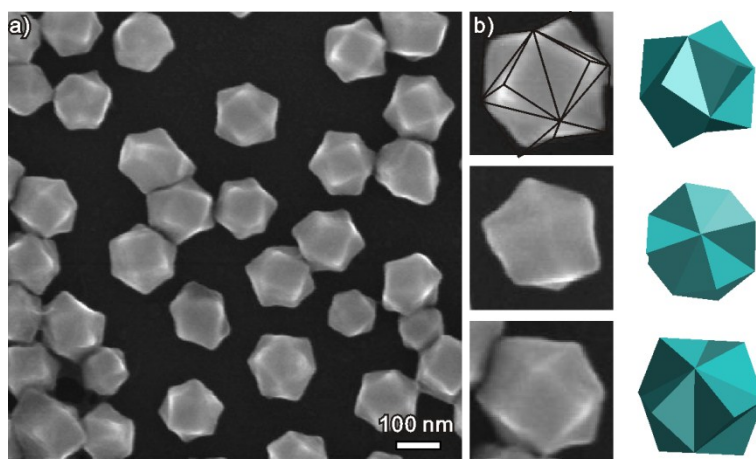
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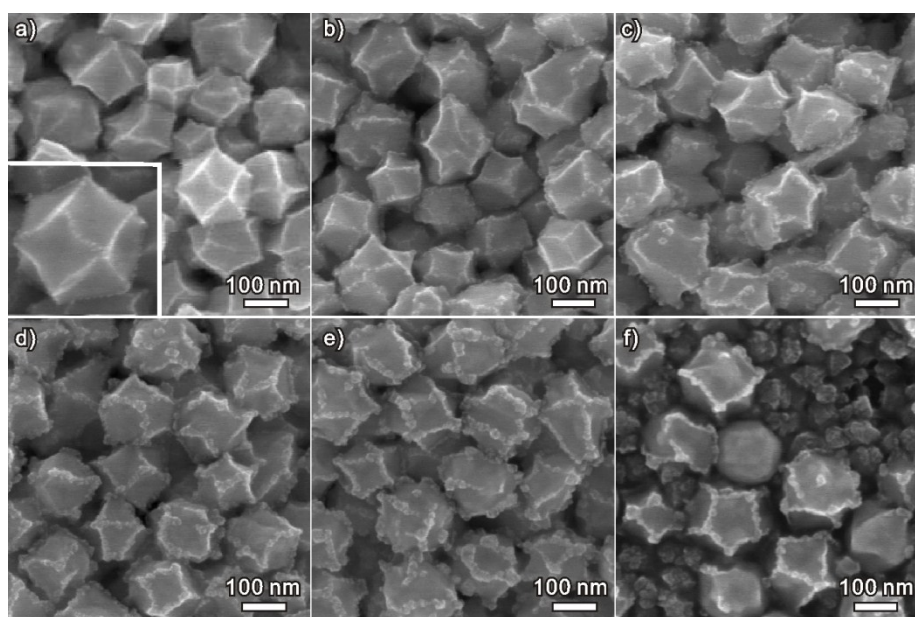
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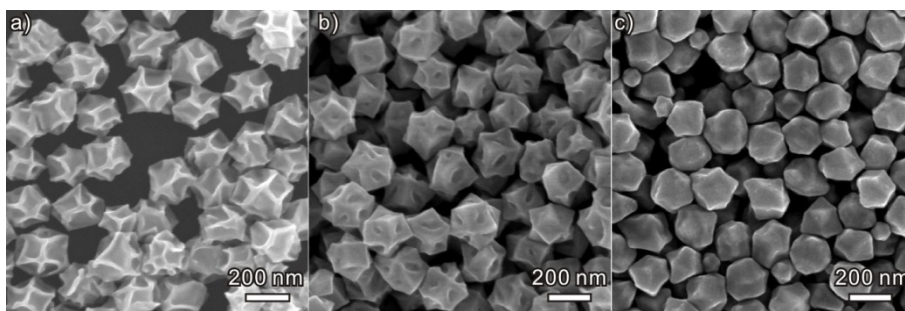
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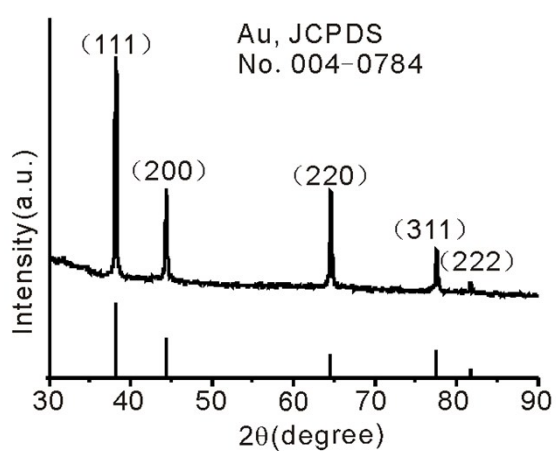
**Figure S1.** a) SEM image of the as-synthesized TOH Au NCs; b) Enlarged SEM images of TOH Au NCs viewing from different directions and their corresponding models, which are bounded by 24 {221} facets.



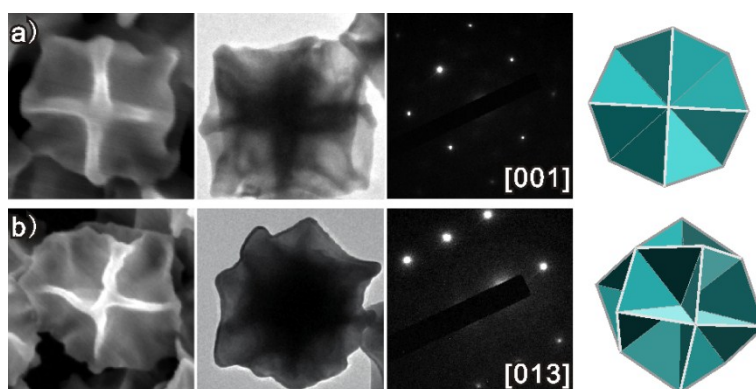
**Figure S2.** SEM images of corresponding Au-Pd heterogeneous NCs synthesized by varying the amount of aqueous solution of  $\text{H}_2\text{PdCl}_4$  ( $1.0 \text{ mmol L}^{-1}$ ): a) 0.10 mL, b) 0.30 mL, c) 0.50 mL, d) 0.70 mL, e) 1.0 mL, f) 3.0 mL, respectively.



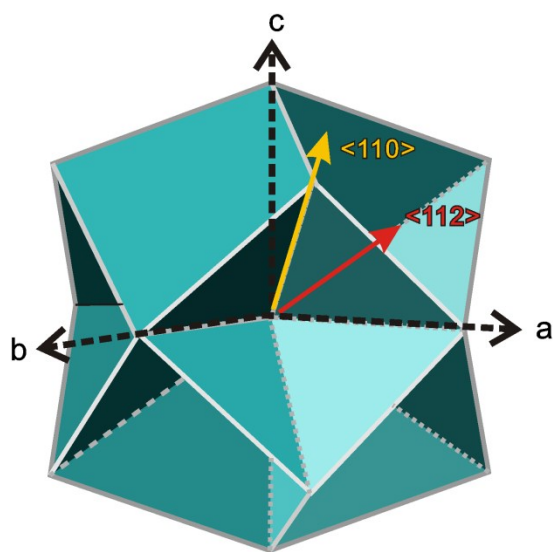
**Figure S3.** SEM images of Au NCs synthesized at different temperatures: a) 6 °C, b) 30 °C, c) 50 °C. The amount of aqueous solution of HAuCl<sub>4</sub> (1.0 mmol L<sup>-1</sup>) was 3.0 mL.



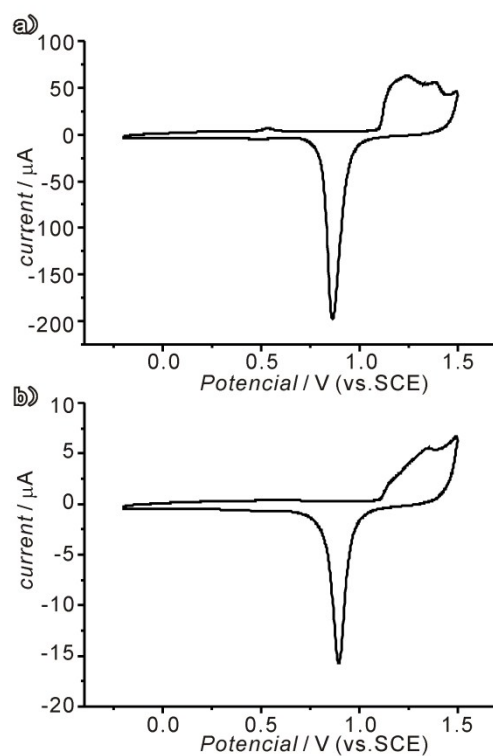
**Figure S4.** XRD pattern of the excavated TOH Au NCs.



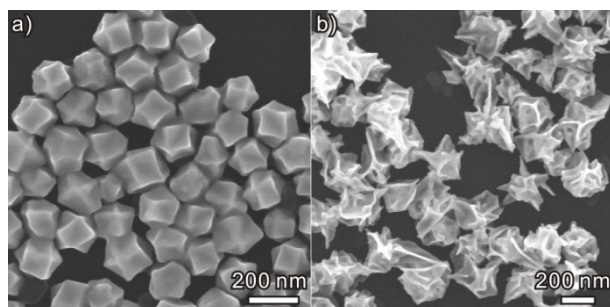
**Figure S5.** SEM images, high-magnification TEM images, corresponding SAED patterns and schematic models of an individual excavated TOH Au NCs viewed along [001] and [013] directions, respectively.



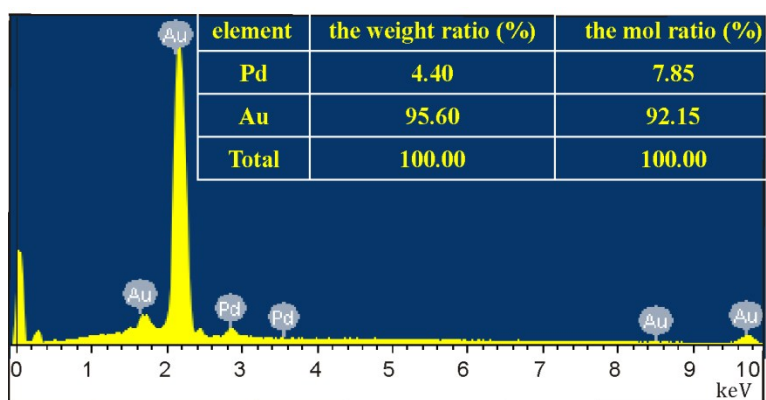
**Figure S6.** Schematic model for the growth orientation of the excavated TOH Au nanocrystal.



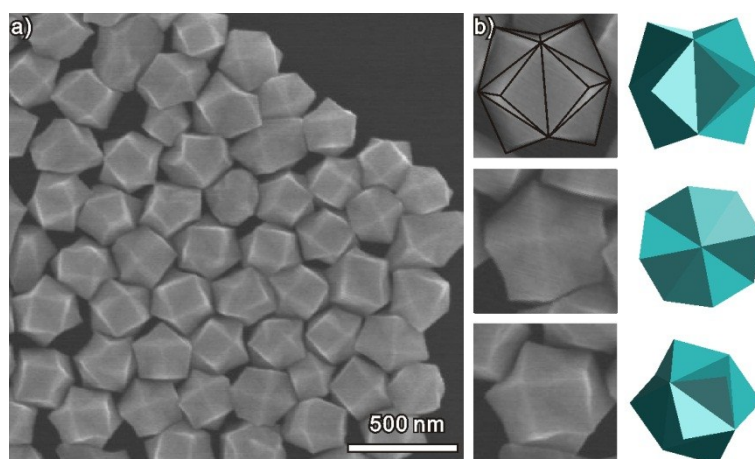
**Figure S7.** a) CV curve of the excavated TOH Au NCs loaded onto a glassy carbon electrode; b) CV curve of a polycrystalline gold electrode. (Tested in 0.1 M H<sub>2</sub>SO<sub>4</sub> at the scan rate of 50 mV s<sup>-1</sup>)



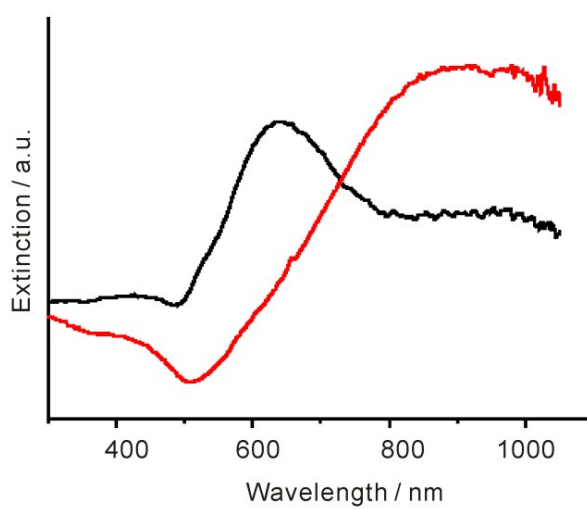
**Figure S8.** SEM images of the Au NCs synthesized in refrigerator: a) original temperature of reaction solution is 30 °C; b) original temperature of reaction solution is 12 °C.



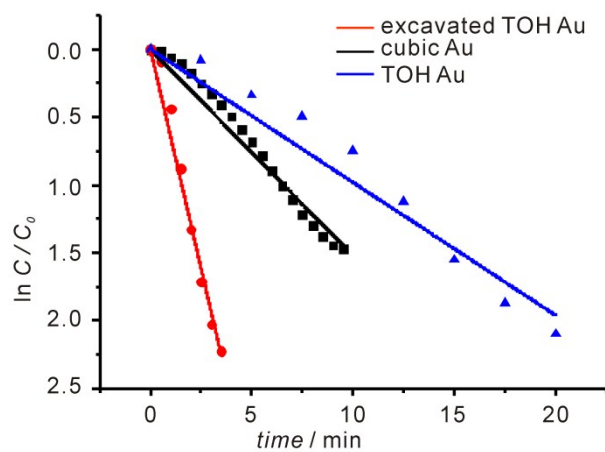
**Figure S9.** EDS of the as-synthesized excavated TOH Au-Pd alloy NCs.



**Figure S10.** a) SEM image of the TOH Au NCs with the same size of the excavated TOH Au NCs; b) Enlarged SEM images of TOH Au NCs viewing from different directions and their corresponding models, which are bounded by 24  $\{221\}$  facets.



**Figure 11.** The comparison of extinction spectra of TOH Au NCs (black line) and excavated TOH Au NCs (red line).



**Figure S12.**  $\ln(C/C_0)$  versus time during the course of reduction of *p*-nitrophenol catalyzed by using excavated TOH Au NCs, cubic Au NCs and TOH Au NCs, respectively.