

## Electronic Supplementary Information

### **A novel trimeric cationic surfactant as a high-efficient capping agent for the synthesis of trisoctahedral gold nanocrystals**

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## Experimental Section

### Materials

Chloroauric acid ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ) was purchased from Shenyang Jinke Reagents Plant. Ascorbic acid (AA), cetyltrimethylammonium chloride (CTAC), and NaCl of analytical grade were obtained from Sinopharm Chemical Reagent Co., Ltd. Rhodamine 6G (R6G) was purchased from Aldrich. Trimeric cationic surfactant tri(Dodecyldimethylammonioacetoxyl)diethyltriamine, trichloride (DTAD) was synthesized using our previously reported method (ref 10) and was used after repeated recrystallization from acetone/ethanol mixed solution. Milli-Q deionized water ( $18 \text{ M}\Omega \text{ cm}$ ) was used to prepare all the solutions.

### Synthesis and characterization of gold nanocrystals

As a typical procedure,  $100 \mu\text{L}$  of DTAD solution ( $10 \text{ mM}$ ) and  $500 \mu\text{L}$  of  $\text{HAuCl}_4$  aqueous solution ( $20 \text{ mM}$ ) was added into  $4.3 \text{ mL}$  of water in sequence and mixed. After that,  $100 \mu\text{L}$  of freshly prepared AA ( $50 \text{ mM}$ ) was rapidly injected into the above mixture with vigorously stirring for  $30 \text{ s}$ , and the reaction mixture was kept at  $25 \text{ }^\circ\text{C}$  under static condition for at least  $1 \text{ h}$ . The product was collected by centrifugation. Subsequently, the supernatant was removed and pure water was added to the precipitate. The residue was dispersed by sonication for  $1 \text{ min}$ . The rinsing procedure was repeated at least three times to obtain the final gold nanocrystals.

The obtained gold products were characterized by scanning electron microscopy (SEM, Hitachi S-4800,  $10 \text{ kV}$ ), transmission electron microscopy and selected area electron diffraction (TEM and SAED, JEM-2100F,  $200 \text{ kV}$ ). SEM and TEM specimens were prepared by placing one drop of the aqueous dispersion of gold product on a silicon wafer and a carbon-coated copper grid, respectively, allowing water to evaporate at ambient temperature.

### Electrochemical measurements

An electrochemical workstation (CV, CHI660B, Chenhua, China) with a three-electrode cell was used to perform electrocatalytic experiments. An Ag/AgCl electrode (KCl-saturated) and a platinum wire were used as reference electrode and auxiliary electrode, respectively. The working electrode was a glassy carbon electrode ( $4 \text{ mm}$ ) modified with TOH Au NCs. The glassy carbon electrode was first polished with  $0.05 \mu\text{m}$  alumina powders and then washed in water and ethanol by ultrasonic treatment. Afterwards,  $10 \mu\text{L}$  suspension of TOH Au NCs was dropped on the glassy carbon electrode surface and dried under an infrared lamp. Finally,  $4 \mu\text{L}$  of  $0.5 \text{ wt } \%$  Nafion alcohol solution was cast on the surface of the electrode and dried naturally in the air. For comparison purposes, commercialized polycrystalline Au electrode was used for electrochemical experiments. The electrolyte was an aqueous solution of  $0.5 \text{ M H}_2\text{SO}_4$ . Before each measurement, the solution was

bubbled with nitrogen for 30 min to remove dissolved oxygen gas.

### **X-ray Photoelectron Spectroscopy (XPS)**

X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlK $\alpha$  radiation. The base pressure was about  $3 \times 10^{-9}$  mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. Each spectrum was curve-fitted using the Xpspeak95 version 4.1 software. In the curve fitting, the widths (FWHM) of Gaussian peaks were maintained constant for all components in a particular spectrum.

### **Fourier Transform-Infrared Spectroscopic (FTIR)**

FTIR spectra were measured with a Bruker Optics TENSOR-27 spectrophotometer. The samples were prepared by vacuum evaporation of a 10  $\mu$ L drop of TOH Au NCs solution on CaF $_2$  glass slides.

### **Surface enhanced Raman scattering (SERS) measurements**

Herein, Rhodamine 6G (R6G) was used as a probe molecule for the SERS measurements. In a typical procedure, silica wafers were first cleaned with aqua regia and then rinsed thoroughly with water prior to use. The SERS substrate was prepared by drop-casting 30  $\mu$ L of Au TOH nanocrystals dispersions on a 5 mm  $\times$  5 mm silica wafer and dried in atmosphere to form the nanocrystal films. Then 10  $\mu$ L of R6G ethanol solution ( $10^{-5}$  M) was spread onto the prepared gold substrate. SERS measurements were carried out on a Renishaw inVia Plus Raman microscope with excitation from a 785 nm laser in one scan. The laser power was 10 mW. Spectra were collected by focusing the laser beam onto the sample using a 50  $\times$  objective, providing a spatial resolution of approximately 1  $\mu$ m. The data acquisition time was 50 s for one accumulation. To test the reproducibility, measurements were performed at different positions on each sample.

### **The calculation of enhancement factor (EF)**

The enhancement factor (EF) value was calculated using the equation (1)<sup>S1</sup>:

$$EF = (I_{\text{SERS}}/N_{\text{ads}}) / (I_{\text{bulk}}/N_{\text{bulk}}) \quad (1)$$

$I_{\text{SERS}}$  and  $I_{\text{bulk}}$  are the vibration intensity in the SERS and normal Raman spectra, respectively.  $N_{\text{bulk}}$  and  $N_{\text{ads}}$  are the number of molecules of solid and number of molecules of adsorbed R6G on the SERS substrate in the laser spot volume, respectively.

$N_{\text{ads}}$  can be calculated according to the equation (2):

$$N_{\text{ads}} = N_{\text{d}} A_{\text{laser}} A_{\text{N}} / \sigma \quad (2)$$

Where  $N_{\text{d}}$  is the number density of the Au TOH nanocrystals,  $A_{\text{laser}}$  is the area of the focal spot of laser,  $A_{\text{N}}$  is the Au TOH nanocrystals footprint area, and  $\sigma$  is the surface area occupied by an

adsorbed R6G molecule, which is about  $4 \text{ nm}^2$ .<sup>S2</sup> The surface area of Au TOH nanocrystal was calculated as  $S = 7.09D^2$ ,<sup>S3</sup> where  $D$  is particle size of the nanocrystal (inset, Table S1).  $A_N$  and  $D$  can be estimated from SEM image, and the surface area of the Au nanocrystals is about  $1.32 \times 10^6 \text{ nm}^2$ , then the total number of surface adsorbed molecules ( $N_{\text{ads}}$ ) within the illuminated laser spot is about  $3.3 \times 10^5$ .

$N_{\text{bulk}}$  can be calculated according to the equation (3):

$$N_{\text{bulk}} = (V\rho/M)N_A \quad (3)$$

$V$  is the effective laser excitation volume ( $V = \pi r^2 \delta$ , where  $r$  being radius of laser spot,  $\delta$  being depth of focus),  $\rho$  and  $M$  represent the density and molar mass of R6G molecules respectively, and  $N_A$  is Avogadro number. In our experiment, the laser spot diameter  $r$  is  $\sim 2 \mu\text{m}$  and the penetration depth  $\delta$  is  $\sim 10 \mu\text{m}$  estimated by finely controlling the height of the stage during the Raman measurements. Therefore,  $N_{\text{bulk}}$  of R6G was estimated to be  $4.98 \times 10^{10}$ .

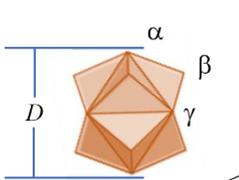
Finally, the EF values were estimated by considering the  $1510 \text{ cm}^{-1}$  Raman band using the equation (1). The calculated EF values were range from  $2.13 \times 10^6$  to  $4.67 \times 10^6$ .

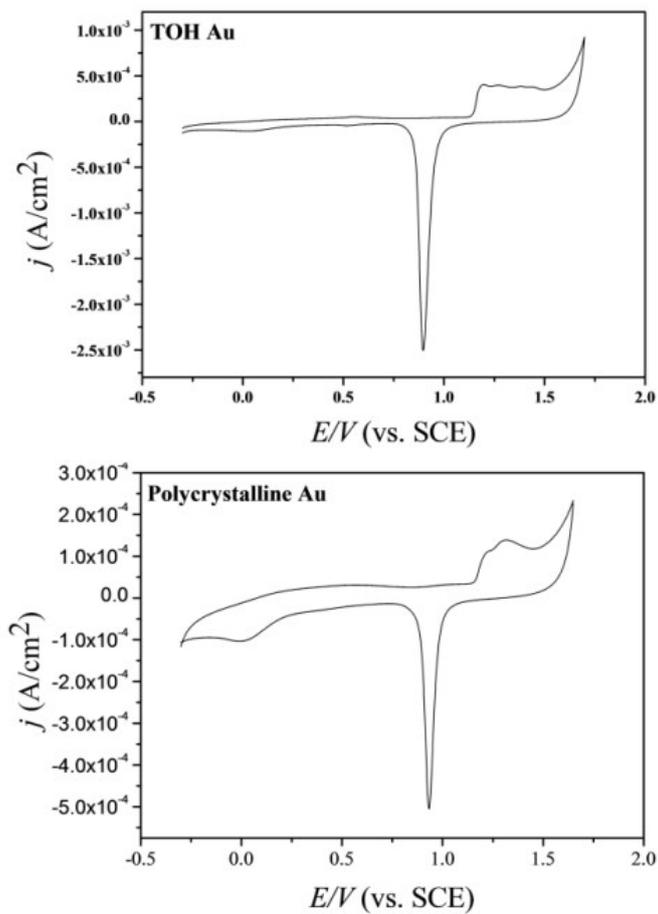
## References

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 S3. Q. Zhang, N. Large and Hui Wang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 17255.

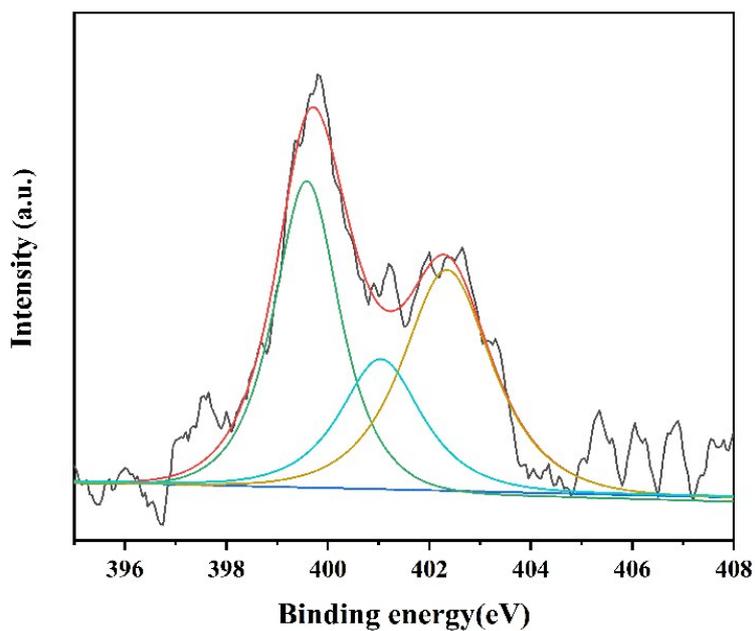
## Additional Results

**Tab. S1** The geometrical model of TOH geometry and the relations between the projection angles and Miller indices of TOH NC in the  $\langle 110 \rangle$  direction based on the TOH geometry.

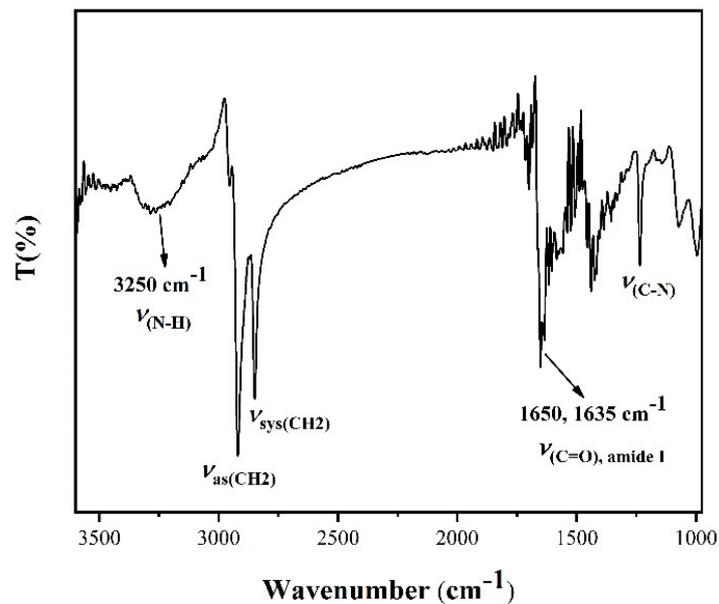
Geometrical model of TOH	{hhl}	$\alpha$	$\beta$	$\gamma$
	{221}	$141^\circ$	$90^\circ$	$141^\circ$
	{331}	$129.5^\circ$	$102^\circ$	$153.5^\circ$
	{441}	$124^\circ$	$108^\circ$	$160^\circ$
	{552}	$134^\circ$	$97^\circ$	$148.5^\circ$



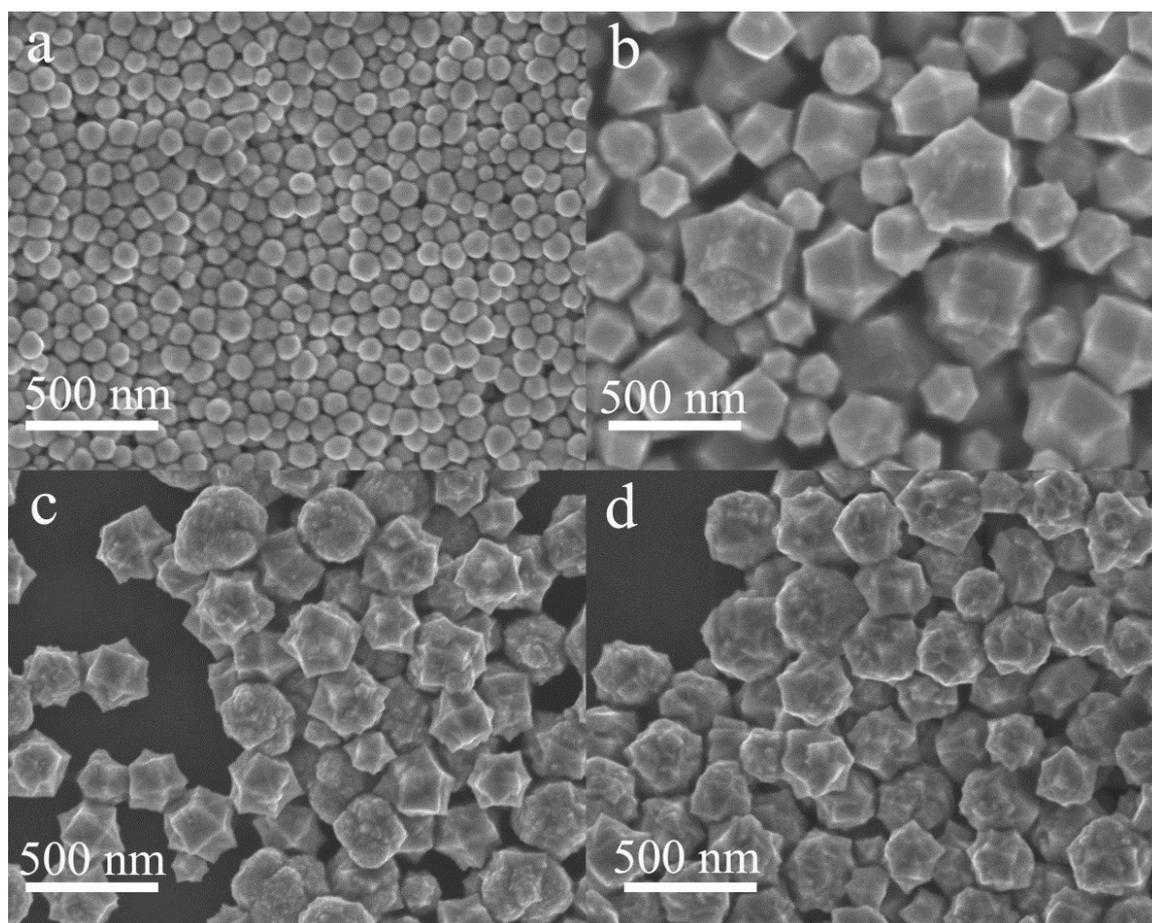
**Fig. S1** Cyclic voltammograms (CVs) of TOH Au NCs modified electrode and the commercialized polycrystalline Au electrode.



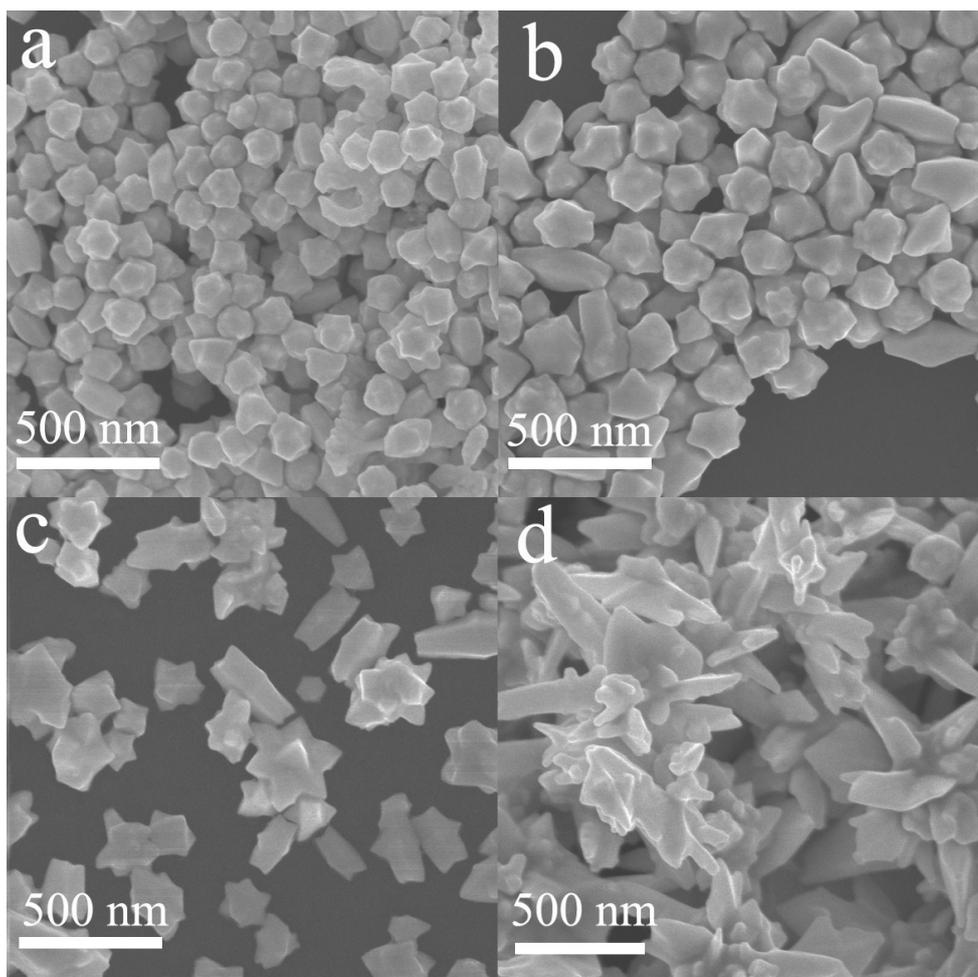
**Fig. S2** XPS spectrum of N 1s of the DTAD adsorbed on the TOH Au NCs.



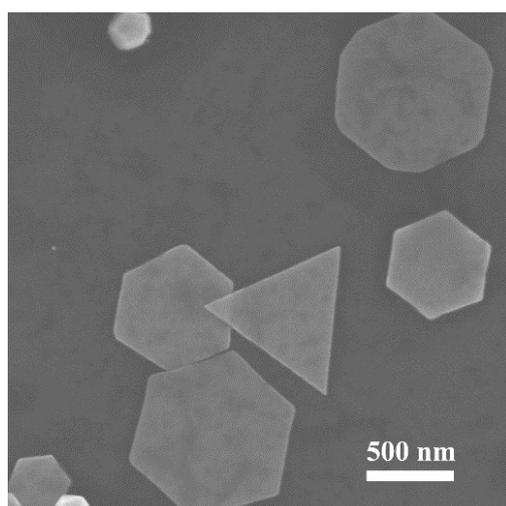
**Fig. S3** FTIR spectrum of the DTAD adsorbed on the TOH Au NCs.



**Fig. S4** SEM images of Au NCs prepared in the presence of different DTAD concentrations in the growth solution: 0.1 mM (a), 0.4 mM (b), 1.0 mM (c), and 2.0 mM (d).



**Fig. S5** SEM images of Au NCs prepared in the presence of different NaBr concentrations in the growth solution containing 0.2 mM DTAD: 0.1 mM (a), 0.2 mM (b), 0.4 mM (c), and 1.0 mM (d).



**Fig. S6** SEM image of the obtained Au NCs from the reduction of 0.2 mM  $\text{HAuCl}_4$  by 0.2 mM AA in the presence of 0.2 mM DTAD.

**Tab. S2** Brief summary of literature reported EF of the Au NCs with high-index facets.

shape of the NCs	structure of the exposed surface	EF for R6G	probe molecule	Ref.
TOH Au NCs	{hkl} (h > 1)	$10^6 \square 10^7$	Rhodamine 6G (R6G)	S1
TOH Au NCs	---	$10^6 \square 10^7$	4-aminothiophenol (4-ATP)	S2
TOH Au NCs	{331}	$\square 10^9$	4-ATP	S3
TOH Au NCs	---	$\square 10^7$	lindane	S4
TOH Au NCs	{221}	$\square 10^5$	4-ATP	S5
TOH Au NCs	{221}, etc	$\square 10^6$	R6G	present work
Au Nanostars	{321}	$\square 10^8$	4-mercaptobenzoic acid	S6
Au nanopunchions	{250}, {301}, and 2{010}	$4 \times 10^8$	R6G	S7
dendritic Au	{211}, {110}, etc	$7.15 \times 10^5$	R6G	S8

## References

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