Electronic Supplementary Material (ESI) for Nanoscale Advances.

Rapid controllable synthesis of branched Au superparticles：formation mechanism of toggling the growth mode and their applications of optical broadband absorption

Shichuan Zhong,[a] *LiFeng Hang,*[b] *Lulu Wen,*[a] *Tao Zhang,*[a,c] *An Cao,*[a] *Pan Zeng,*[a] *Hanlin Zhang,*[a] *Dilong liu,*[a] *Weiping Cai* [a] *and Yue Li**[a]

[a] Key Lab of Materials Physics, Anhui Key Lab of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, Anhui, P. R. China

[b] The Department of Medical Imaging Guangdong Second Provincial General Hospital, Southern Medical University, Guangzhou 518037, P. R. China

[c]School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore

Experimental Section

Materials. Poly-(diallyldimethylammonium) chloride (PDDA, MW=100000-200000, 20% in the water) was purchased from Sigma-Aldrich. Ethylene glycol (ACS reagent), cetyltrimethylammonium chloride (CTAC, 99%), chloroauric acid ($HAuCl_4$, 99.9%), silver nitrate (>99.8%), ascorbic acid (99.5%), sodium borohydride (99%), dopamine (98%), hydrochloric acid (37%) were obtained from Sinopharm Chemical Reagent Co., Ltd. 4-Aminothiophenol (98%) was purchased from Shanghai Macklin Biochemical Co., Ltd. 2-Aminophenol (98%), 3-Aminophenol (98%), 4-Aminophenol (98%), o-Phenylenediamine (98%), m-Phenylenediamine (99%), p-Phenylenediamine (99%), Catechol (99%), Resorcinol (99%), Hydroquinone (99%) and acetonitrile (ACS, >99%) were purchased from Aladdin Co. Ltd.Deionized (DI) water was achieved by a Milli-Q integral water purification system (18.2 MΩ•cm resistivity at 25 °C).

Characterization. Transmission electron microscopy (TEM) was performed on a JEOL-2010 system operated at 200 kV. The samples for TEM examination were prepared by dropping the suspension on a copper grids with thin carbon coating and then drying at room temperature. The morphologies of the products were characterized by field-emission scanning electron microscopy (FESEM, Sirion 200). The optical extinction data was collected by the Shimadzu UV-2600. The Raman spectra were examined by a confocal microprobe Raman spectrometer (Renishaw in Via Reflex) with a laser beam wavelength of 785 nm, a power of 1 mW, and an integration time of 10 seconds. The concentrations of branched Au superparticles solution were measured by the inductively coupled plasma-mass spectrometry (ICP-MS) from thermofisher scientific.

Synthesis of Au seeds nanoparticles. This method is referred to our previous work.[1] Simply, a 100 mL glass bottle as a container, adding into 60 mL ethylene glycol, 30 μL 1 M $HAuCl_4$ solution, 1.2 mL PDDA and 12 μL 0.1 M $AgNO_3$ solution, the mixed solution was gently stirred at room temperature. After thorough mixing, the bottle was transferred to an oil bath at 220 °C for reacting 2 h. The colour of solution was changed from yellow to red after the reaction. Subsequently, the uniform Au seeds nanoparticles (about 60 nm diameter) were obtained by centrifugation with DI water 3 times at 10000 rpm. Finally, the volume of Au seeds solution was adjusted to 5 mL.

Synthesis of branched Au superparticles. In a 10 mL glass bottle, 100 μL 0.01 M $HAuCl_4$, 20 μL PDDA and 100 μL Au seeds solution were dropped into 4.64 mL DI water under stirring, respectively. Then, 140 μL of 0.1 M 3-Aminophenol was quickly added into the mixed solution with stirring at 350 rpm, the colour of solution changed from red to bottle green or black in 5 seconds. The mixed solution was purified by centrifugation with DI water at 5000 rpm for 2 times, then the branched Au nanoparticles were successfully obtained.

Synthesis of Au seeds nanoparticles for photothermal. The synthesis process of seed nanoparticles was slightly changed, extra 180 μL 0.1 M NaOH was dropped into bottle before oil bath, other processes remained unchanged, the diameter of the obtained gold seed nanoparticles was about 40 nm.

The controlled variable experiments. According to the part of synthesis of branched Au superparticles, replacing 3-aminophenol with other equal amounts of reducing agents. The transitional times of their solution color are more than 5 seconds.

The morphological regulation of branched Au superparticles. Based on the synthetic process of Au superparticles, an amount of HCl or CTAC was added to the solution before the reaction begins, keeping the total volume at 5 mL.

The measurement of SERS. The SERS substrateswere obtained by dropping the Au superparticles solution on a silicon wafer several times. After natural drying, the substrates were purified by a plasma cleaner in 5 min. Then, the substrates were incubated in the 4-Aminothiophenol solution (10^{-6} M) for 6 h before the measurement.

The measurement of photothermal conversion. In a 3.5 mL quartz cuvettes,1 mL branched Au superparticles solution was dropped into it, turning on the laser to irradiate the solution, the temperature of the solution was collected per 1 min until reaching the maximum.Then, turning off the laser, the solution was cooled in the nature, the temperature of the solution was collected per 30 second until it matched the room temperature.

Cell Cultures. According to the recommended procedure, EMT-6 cells were cultured in DMEM medium supplemented with 10% FBS and 1% penicillin/streptomycin under humidified normoxic (95% air, 5% CO_2) conditions at 37 °C.

Cellular uptake *in vitro.* EMT-6 cells were seeded in 24-well plates at a density of 3×10^4 cells per well and cultured overnight. Then the cells were washed with PBS and treated with Au superparticles at a different concentration (3.1, 6.3, 12.5, 25, 50 μg/mL). Then the cells were washed with 1×PBS buffer, collected, counted and analyzed by ICP-MS(ELAN DRC II with Axial Field Technology, PerkinElmer, Waltham, MA).

***In Vitro* PTT.** EMT-6 cells were seeded at 2×10^3 cells per well in 96-well plates and further cultured for 24 h. The PBS and Au superparticles(3.1, 6.3, 12.5, 25, 50 μg/mL) were added to the DMEM medium for another 4 h and irradiated by 1064 nm laser for

5 min. After incubation for 24 h, 25μL of MTT stock solution (5 mg/mL) was introduced into the wells for another 4 h. Subsequently, culture medium was replaced by 100 μL of DMSO. The absorbance was measured at 490 nm on Microplate reader (Bio-tek). Cell viabilities were evaluated according to the cells cultured in medium.

Apoptosis and necrosis. The apoptosis and necrosis induced by PTT of Au superparticles were evaluated by flow cytometry. EMT-6 cells were seeded at 1×10^6 cells per well in 6-well plates and further cultured for 24 h. The culture media were replaced by 2 mL of fresh culture media containing 10% FBS. Au superparticles (50 μg/mL) were added to the cells. Cells incubated with PBS served as control. After 24 h incubation, the cells were irradiated with 1064 nm laser at 1 W/cm^2 for 5 min. Following further incubation of 12 h, the floating and adherent cells were collected and stained with Alexa Fluor 488 Annexin V/dead cell apoptosis kit according to manufacturer's instructions. The apoptosis and necrosis was examined on a flow cytometer.

The Calculation of photothermal conversion efficiency. Generally, the total energy balance of system could be expressed by the equation 1 as follow:[2]

$$\Sigma_{\mathrm{i}} m_i C_{p,i} \frac{dT}{dt} = Q_{NC} + Q_{Dis} - Q_{surr} \quad (1)$$

The m and C_p are the mass and heat capacity of water, respectively, and T is the solutiontemperature.Q_{Dis} is the baseline energy inputted by thesample cell, which expressed that heat dissipated from light absorbed by thequartz sample cell itself, it is a constant (5.39 mW) according to the literature. Q_{surr} is the energy outputted by convection from the system surface to air, and it is linear with the temperature, the formula as shown in equation 2.

$$Q_{\mathrm{surr}} = hS(T - T_{surr}) \quad (2)$$

Theh is the heat transfer coefficient, the S is the surface area of quartz container, and the T_{surr} is the atmosphere temperature.

Q_{NC} is the energy inputted by NCs, it is related to the heat dissipation caused by the electron-phonon relaxation of plasmonic resonance of Au superparticles surface under 1064 nm laser irradiation, the formula is shown in equation 3.

$$Q_{NC} = I(1 - A^{-1064})\eta \quad (3)$$

Where the I is the power density of laser, it is 1.0 W/cm^2 in this work. η is the conversion efficiency from laser energy to heat energy, A^{-1064} is the extinction coefficient of superparticles solution at 1064 nm wavelength.

Because the Q_{surr} isincreased as the temperature increased according to the equation 2, the system temperature will be risen to a maximum when the heat input is equal to the heat output, thereby the relationship of Q_{NC}, Q_{Dis},and Q_{surr} could be expressed as follow:

$$Q_{NC} + Q_{Dis} = Q_{Surr-Max} = hS(T_{Max} - T_{Surr}) \quad (4)$$

The $Q_{surr\text{-}Max}$ is the heat conduction away from the system surface by air when the sample cell reaches the equilibrium temperature, the T_{max} is the equilibrium temperature. Therefore, the heat conversion efficiency under 1064 nm laser irradiation could be determined by substituting equation 3 for Q_{NC} into equation 4 and rearranging to get

$$\eta = \frac{\mathrm{h}S(T_{\max} - T_{surr}) - Q_{Dis}}{I(1 - 10^{-A_{1064}})} \quad (5)$$

The T_{max}-T_{surr} is the difference value between the equilibrium temperature and the surrounding temperature, and others variables have been explained except the hS. In order to get the hS, a dimensionless driving force temperature, θ is introduced to express the maximum system temperature, and the θ could be expressed as follow:

$$\theta = \frac{T - T_{surr}}{T_{\max} - T_{surr}} \quad (6)$$

According to the equation 1, a sample system time constant τ_s can be transformed as follow:

$$\tau_s = \frac{\Sigma_i m_i C_{p,i}}{hS} \quad (7)$$

which is substituted into equation 1 and rearranged to yield

$$\frac{d\theta}{dt} = \frac{1}{\tau_s}[\frac{Q_{NC} + Q_{Dis}}{hS(T_{\max} - T_{surr})} - \theta] \quad (8)$$

Because the laser was shut off when the branched Au superparticles solution in the cooling stage, thereby the $Q_{NC}+Q_{Dis}=0$, the equation 8 can be simplified as follow:

$$\mathrm{d}t = -\tau_s \frac{d\theta}{\theta} \quad (9)$$

The equation 9 can be further express as follow:

$$\tau = -\tau_s \ln\theta \quad (10)$$

Therefore, the hS could be expressed as follow:

$$hS = -\frac{\ln\theta * \Sigma_i m_i C_{p,i}}{\tau} \quad (11)$$

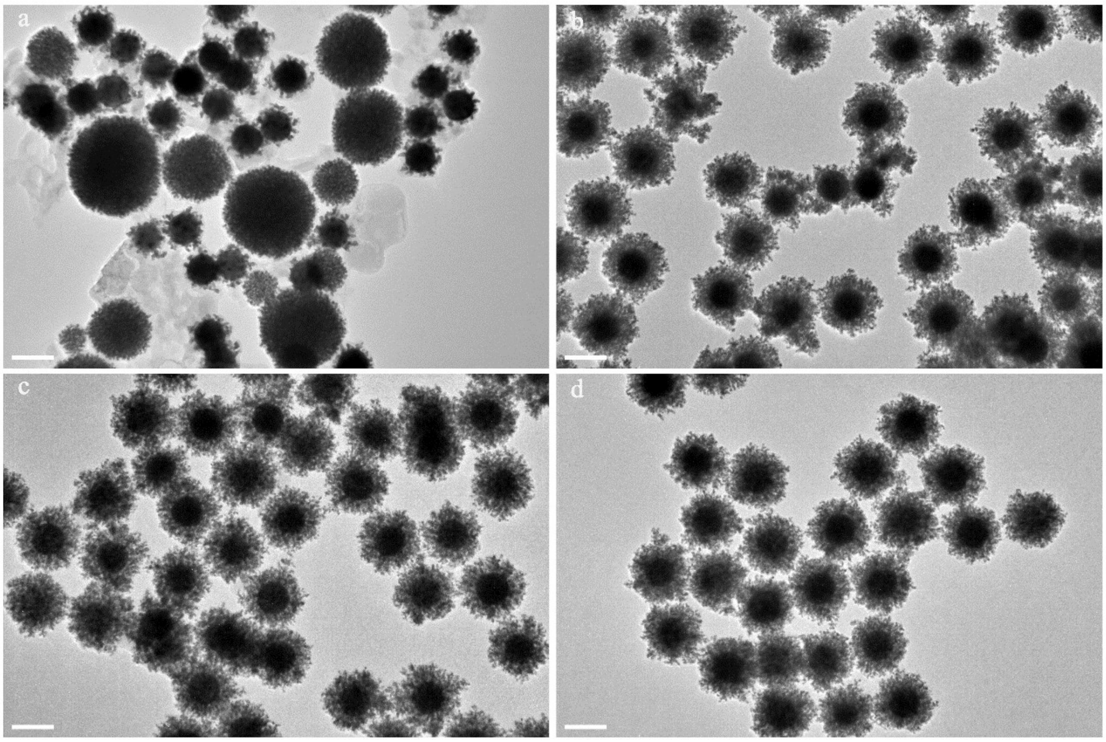

Figure S1. The TEM images of branched Au superparticles with different PDDA content. a) 0 μL. b) 5 μL. c) 10 μL. d) 15 μL. The scar bars are 100 nm.

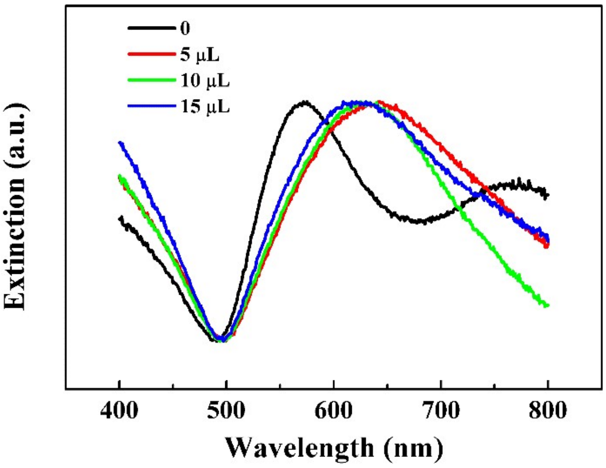

Figure S2. The extinction spectra of Au superparticles fabricated by different amount of PDDA.

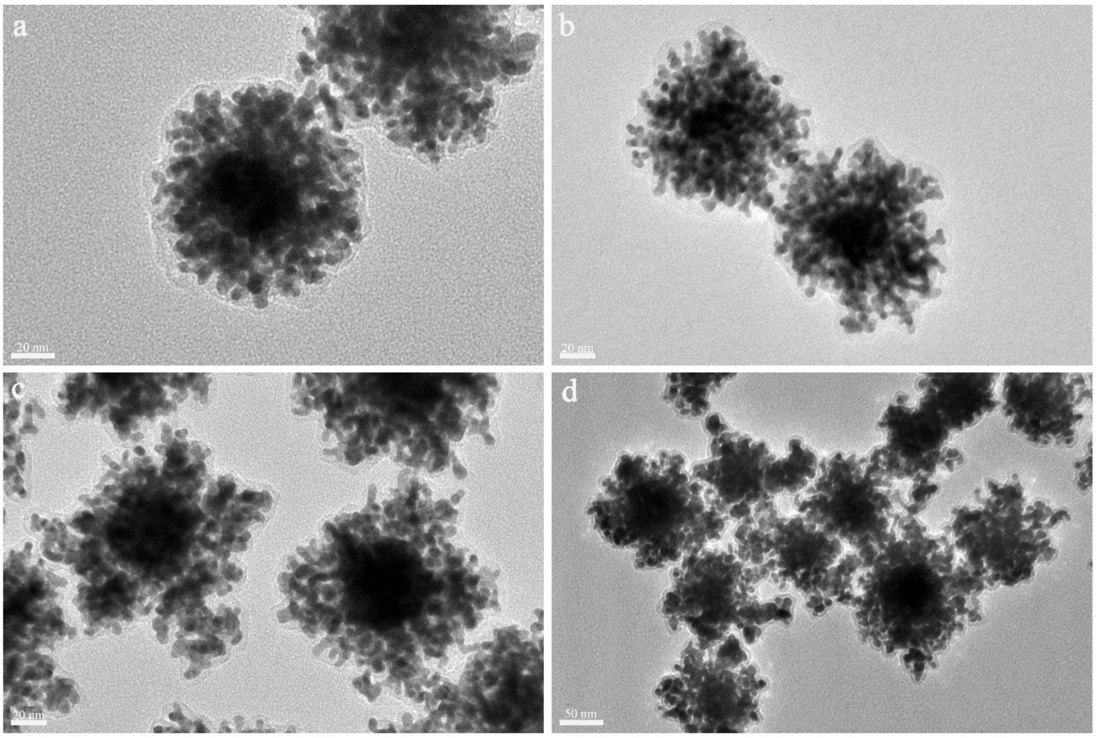

Figure S3. The TEM images of branched Au spuerparticles with different 3-aminophenol contents. a) 140 μL. b) 105 μL. c) 70 μL. d) 35 μL.

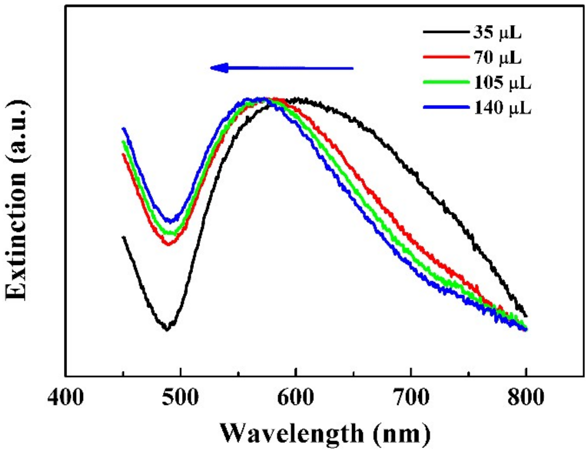

Figure S4. The extinction spectra of Au superparticles with different 3-aminophenol contents.

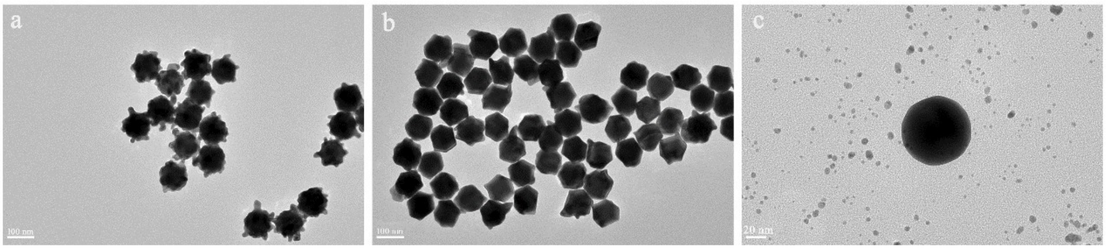

Figure S5. The TEM images of Au nanoparticles fabricated by different reducers. a) ascorbic acid. b) dopamine. c) sodium borohydride.

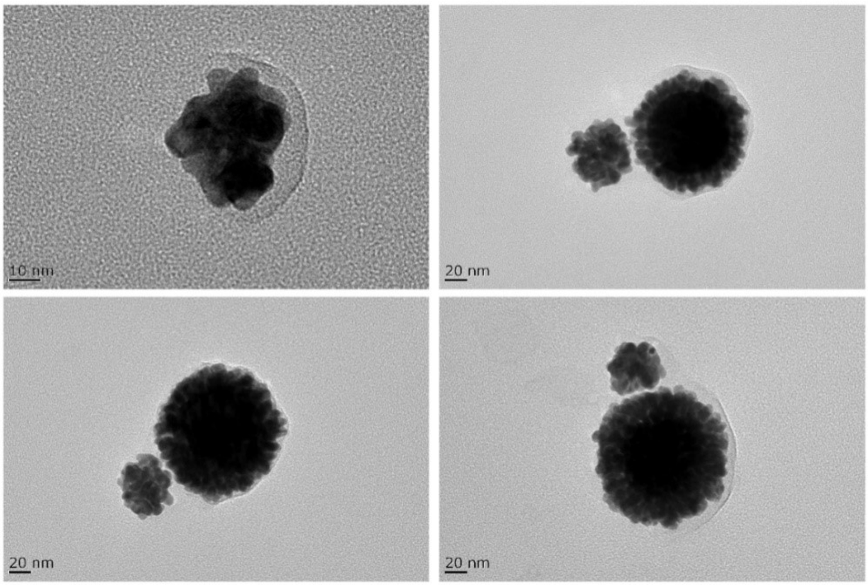

Figure S6. The TEM images of the self-nucleation phenomenon of Au nanoparticles synthesized by p-Phenylenediamine.

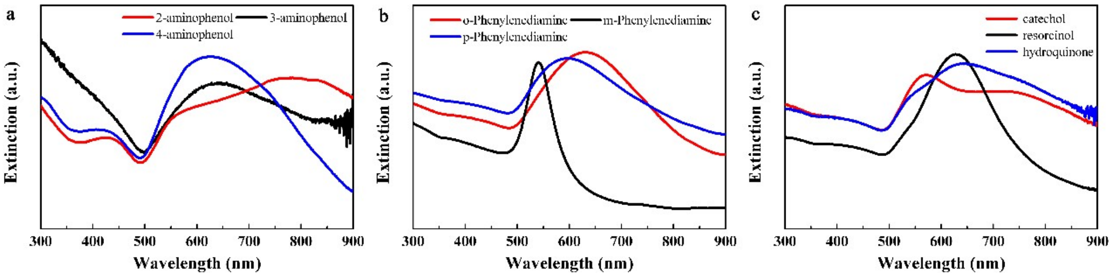

Figure S7. The extinction spectra of Au nanoparticles fabricated by different reducing agents. a) aminophenol. b) Phenylenediamine. c) catechol, resorcinol and hydroquinone.

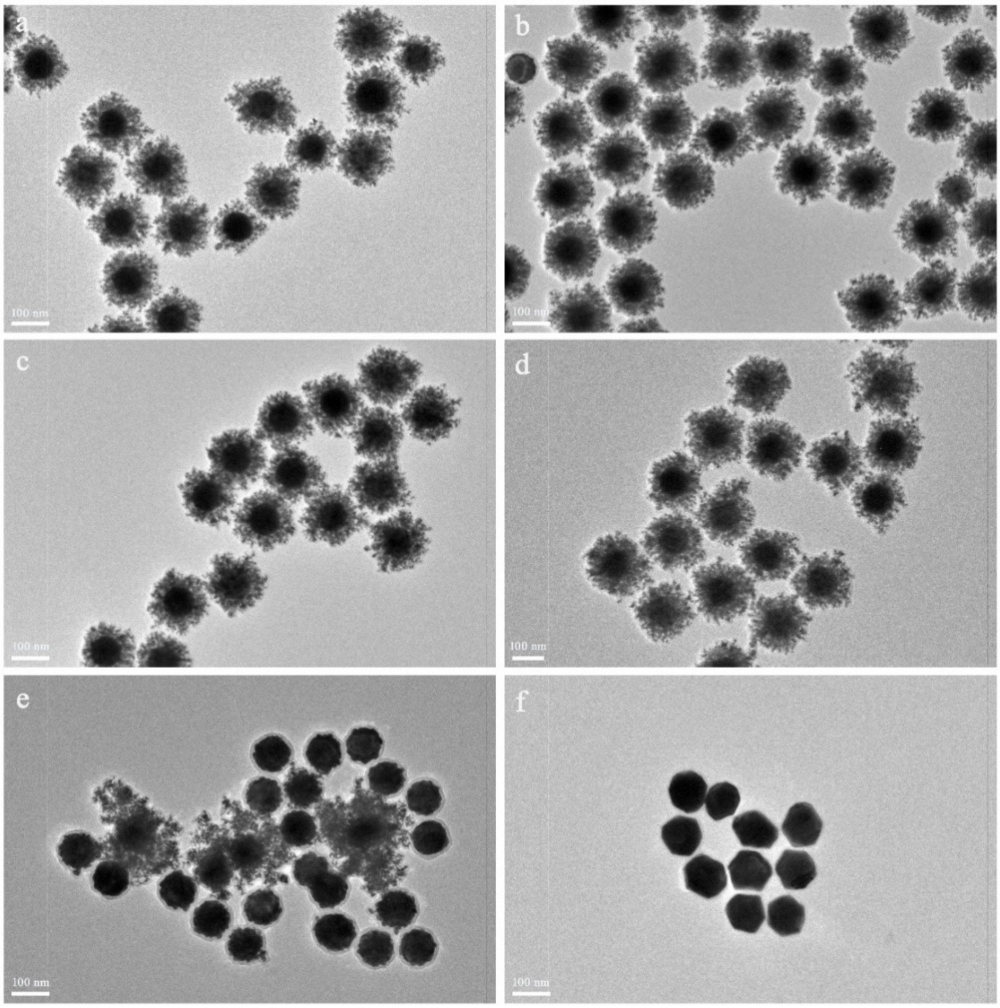

Figure S8. The TEM images of branched Au nanoparticles under different HCl concentrations. a) $2*10^{-7}$ M. b) $2*10^{-6}$ M. c) $2*10^{-5}$ M. d) $2*10^{-4}$ M. e) $2*10^{-3}$ M. f) $2*10^{-2}$ M.

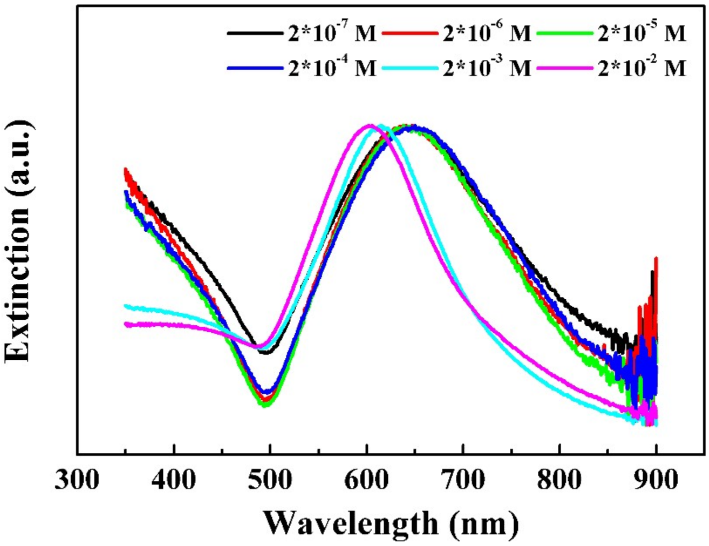

Figure S9. The extinction spectra of branched Au superparticles with different concentrations of HCl

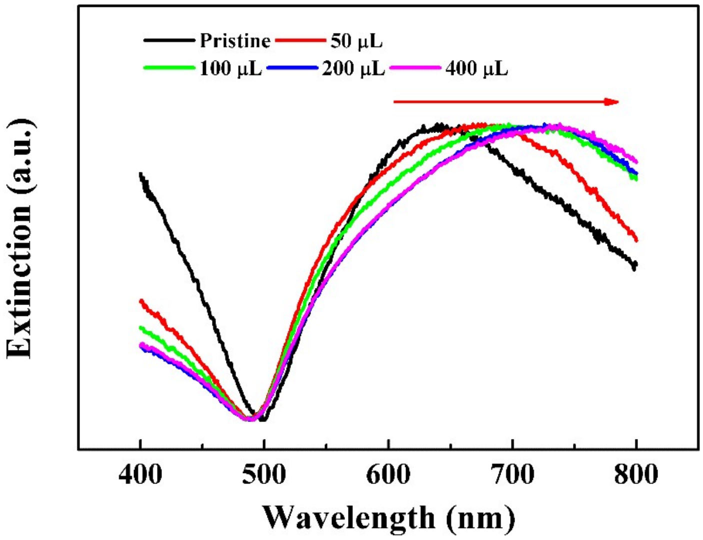

Figure S10. The extinction spectra of branched Au superparticles with different CTAC contents.

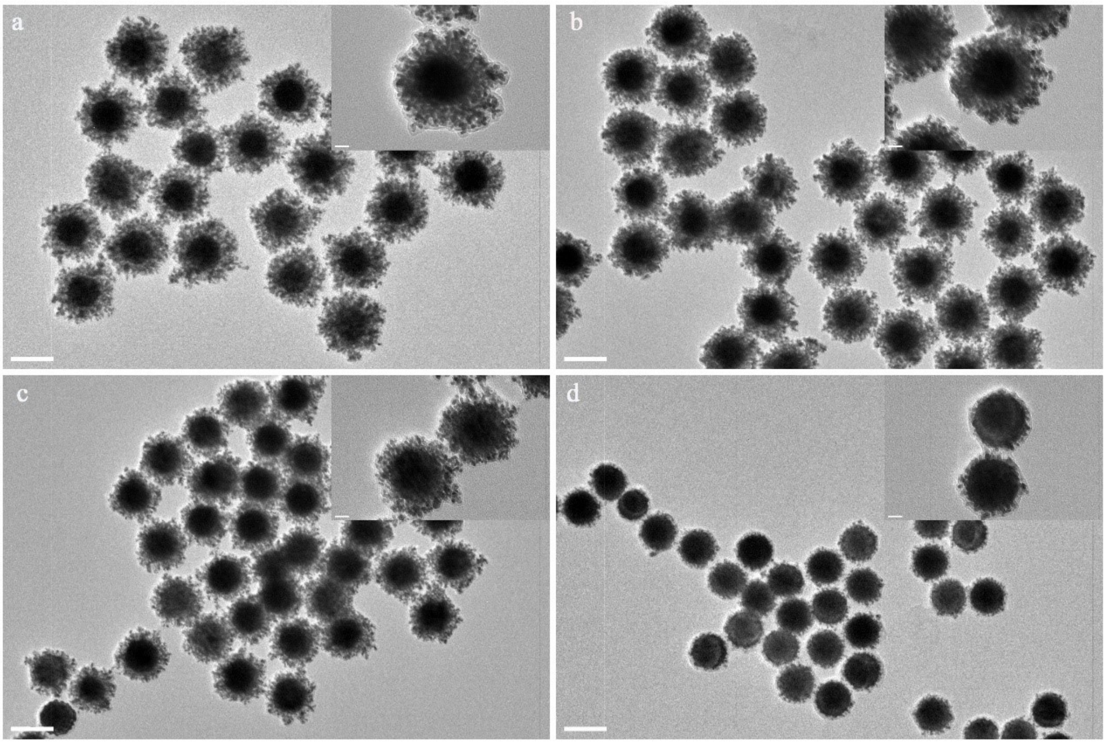

Figure S11. The TEM images of branched Au superparticles with different chloroauric acid contents. a) 100 μL. b) 75 μL. c) 50 μL. d) 25 μL. The scale bar is 100 nm, and the scale bar in the insert is 20 nm.

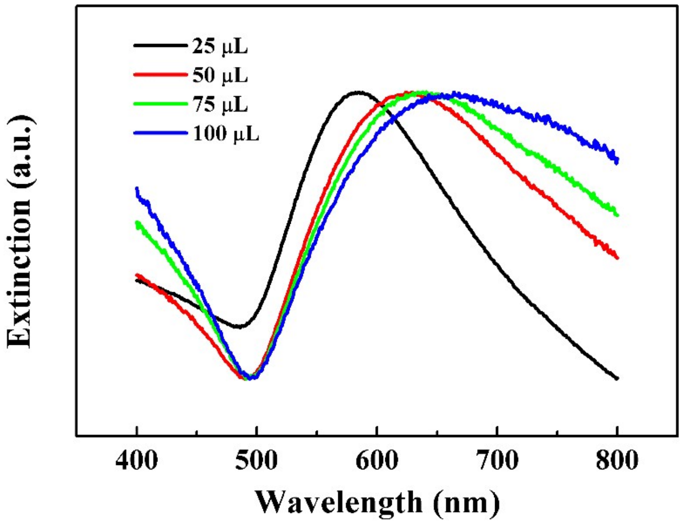

Figure S12. The extinction spectra of Au superparticles fabricated by different chloroauric acid contents.

Table S1. The comparison of the Au superparticles synthesized by different wet-chemical method.

Time consumption	**Morphology**	**Regulation**	**Reference**
Unclear	Uniform	No	*Chem. Mater.*, 2015, **27**, 5678-5684.
30 min	Uniform	No	*Biomaterials*, 2016, **104**, 138-144.
8 h	Uniform	No	*Chem. Eng. J.*, 2023, **455**, 140586.
6 h	Uniform	No	*J. Am. Chem. Soc.*, 2021, **143**, 20513–20523.
6 h	Uniform	No	*ACS Nano*, 2018, **12**, 2643-2651.
5 s	Ultra-uniform	Yes	*This work*

Table S2. Photothermal performance of recently reported photothermal agents employed in NIR-II window (1064 nm).

Photothermal agents	**Photothermal conversion efficiency**	**Reference**
Au nanobipyramids	44.2%	*Biomaterials*, 2020, **257**, 120235.
Au nanorods@PPy@Fe_xO nanocomposites	46%	*Nano Res., 2016, 9, 787-799.*
Au@Cu_9S_5 nanoparticles	37%	*J Am Chem Soc*, 2014, **136**, 15684-15693.
Au@Ti_3C_2	39%	*ACS Nano, 2019, 13, 284-294.*
Au@Cu_xS	43.3%	*ACS Appl. Mater. Interfaces* **2020,***12* (2), 2152-2161.
Au superparticles (nanorods as the seeds)	67.2%	*Angew. Chem. Int. Ed.*, 2020, **132**, 14551-14556.
Au superparticles (nanospheres as the seeds)	62.6%	*This work*

1. Zhang, T.; Li, X.; Li, C.; Cai, W.; Li, Y., One-Pot Synthesis of Ultrasmooth, Precisely Shaped Gold Nanospheres via Surface Self-Polishing Etching and Regrowth. *Chem. Mater.* **2021,***33* (7), 2593–2603.
2. Zhang, C.; Men, D.; Zhang, T.; Yu, Y.; Xiang, J.; Jiang, G.; Hang, L., Nanoplatforms with Remarkably Enhanced Absorption in the Second Biological Window for Effective Tumor Thermoradiotherapy. *ACS Appl. Mater. Interfaces* **2020,***12* (2), 2152-2161.