COMMUNICATION

Supporting information for

Uniform Colloidal Synthesis of Highly Branched Chiral Gold Nanoparticles

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S1. Experimental procedures

S1.1 Chemicals and materials

L-ascorbic acid (L-AA, 99%), hexadecyltrimethylammonium bromide (CTAB, ≥ 99%), citric acid trisodium salt (TSC, 98%) were purchased from Sigma Aldrich. Tetrachloroauric (III) acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$) was obtained from Sinopharm Chemical Reagent. Cetyltrimethylammonium chloride (CTAC, 99%) and aminoacetic acid (99.5%) were obtained from J&K. Sodium hydroxide (NaOH, 99%), potassium iodide (KI, 99%) and 3-mercaptopropionic acid (99%) were obtained from Innochem. L-cysteine hydrochloride monohydrate (L-Cys, > 99%) was obtained from TCI. Hydrochloric acid (HCl, ≈ 36.0-38.0 wt%) was obtained from Xilong Chemical Reagent. Sodium borohydride ($NaBH_4$, ≥ 96%) was obtained from Guangzhou Huada Chemical Reagent.

S1.2 Nanoparticle synthesis

Synthesis of gold nanospheres (GNSs). GNSs were prepared using a seed-mediated growth and oxidation method, as described in previous work.[1]

Step 1: GNS seeds. For the preparation of small GNSs, a $HAuCl_4$ solution (0.01 M, 0.25 mL) was first mixed with a CTAB solution (0.1 M, 9.75 mL), followed by the rapid injection of a freshly prepared, ice-cold $NaBH_4$ solution (0.01 M, 0.60 mL) under vigorous stirring. The resulting solution was used as the seed after gentle stirring for 3 h at 30 °C. The as-prepared seed solution (0.12 mL) was injected into the as-grown solution containing CTAB (0.1 M, 9.75 mL), water (190 mL), $HAuCl_4$ (0.01 M, 4 mL) and AA (0.1 M, 15 mL). The reaction mixture was gently shaken and then left undisturbed overnight at 30 °C. The resultant small GNS sample was centrifuged and redispersed in water with an optical density (OD) of around 3.0 at 521 nm for further use.

Step2: Gold nanopolyhedrons. The gold nanopolyhedrons were grown by the seed-mediated method using the small GNSs as seeds. 3 mL of small GNSs was first added into a CTAC solution (0.025 M, 30 mL). After the sequential addition of AA (0.1 M, 0.75 mL) and $HAuCl_4$ (0.01 M, 1.5 mL), the mixed solution was placed in a water-bath shaker (45 °C and 160 revolutions per minute) and left for 3 h. The obtained gold nanopolyhedrons were centrifuged and redispersed in a CTAB solution (0.02 M, 30 mL).

Step3: GNSs. The gold nanopolyhedrons were oxidized into large GNSs by $HAuCl_4$ (0.01 M, 0.2 mL) in a water-bath shaker (45 °C and 160 revolutions per minute) for 2 h. The obtained large GNSs were centrifuged and redispersed in water for use.

Synthesis of long gold nanorods (GNRs). The long GNRs were grown using a seed-mediated growth method, as described previously with slight modifications.[2] Specifically, the seed solution was made by the addition of a fresh prepared, ice-cold $NaBH_4$ solution (0.1 M, 1 mL) to a mixture solution composed of TSC (0.01 M, 1 mL), $HAuCl_4$ (0.01 M, 1 mL), and water (37 mL) under vigorous stirring. The seed solution immediately became ruby red in color and kept under stirring for 5 min. The resultant solution was kept at 30 °C for 2 h before use. The growth solution

was prepared by the sequential addition of CTAB (0.1 M, 50 mL), $HAuCl_4$ (0.01 M, 2.5 mL), water (47.5 mL), and AA (0.1 M, 0.55 mL) in a 250 mL conical flask under stirring. The pH value of the mixture solution was adjusted to 4.0 using HCl solution (0.1 M, 3.3 mL). To initiate the growth of long GNRs, the seed solution (0.1 mL) was injected into the growth solution under stirring for 2 min. The resultant solution was kept undisturbed at 30 °C overnight.

Synthesis of hexagonal gold nanoplatelets (GNPLs). The hexagonal GNPLs were prepared through the overgrowth on the rounded triangular GNPLs, as described in previous works.[3]

Step 1: Triangular GNPLs. The triangular GNPLs were obtained by a seed-mediated growth method. Briefly, the mixture of $HAuCl_4$ (0.01 M, 1 mL) and TSC (0.01 M, 1 mL) solutions was added to water (36 mL), followed by adding ice-cold and freshly prepared $NaBH_4$ solution (0.1 M, 1 mL) under vigorous stirring. The gold seeds solution was stirred for 2 min and then left undisturbed for 4 h at 30 °C. For the triangular GNPLs growth solution, two vials labelled A and B containing the same composition were first prepared. Solution A and B: CTAB (0.05 M, 9 mL), $HAuCl_4$ (0.01 M, 0.25 mL), NaOH (0.1 M, 0.05 mL), KI (0.01 M, 0.05 mL), and AA (0.1 M, 0.05 mL). Then, solution C was also prepared. Solution C: CTAB (0.05 M, 90 mL), $HAuCl_4$ (0.01 M, 2.5 mL), NaOH (0.1 M, 0.5 mL), KI (0.01 M, 0.5 mL), and AA (0.1 M, 0.5 mL). For the synthesis of triangular GNPLs, 1 mL of the gold seeds solution was first added to solution A, then 1 mL of solution A was transferred to solution B for the dilution of gold seeds. Finally, all of solution B was added to solution C for the overgrowth. The obtained mixture solution was mixed by gentle shaking and then left undisturbed at 30 °C for 24 h.

Step 2: Circular GNPLs. In the triangular GNPLs synthesis period, the triangular GNPLs were precipitated at the bottom of the reaction vessel and the supernatant was gently removed. The purified triangular GNPLs were then redispersed in water overnight. During storage, the sharp corners of the GNPLs gradually became rounded, eventually leading to the formation of circular GNPLs.

Step3: Hexagonal GNPLs. The hexagonal GNPLs were produced by performing overgrowth on circular GNPLs. Briefly, one overgrowth solution was prepared by mixing together CTAB (0.1 M, 2.5 mL), $HAuCl_4$ (0.01 M, 0.2 mL), AA (0.1 M, 0.1 mL), and water in sequence, and the total volume was adjusted to 20 mL. To initiate the overgrowth, the circular gold NPLs solution (5 mL) whose optical density (OD) at the major plasmon peak pre-adjusted to 3.0 was added. The resultant solution was kept in a water-bath at 30 °C for 10 h.

Synthesis of highly branched gold nanoparticles (GNPs). Highly branched GNPs were prepared through the overgrowth of different gold nanocrystals in the presence of $HAuCl_4$, CTAB, CTAC, AA, and cysteine. In a typical procedure, the growth solution was prepared by sequentially adding CTAC (0.2 M, 0.32 mL), CTAB (0.2 M, 0.32 mL), $HAuCl_4$ (0.01 M, 0.2 mL), AA (0.1 M, 0.475 mL), and L-Cys (5 mM, 5 μL) into water (4.11 mL). To initiate the overgrowth, the different gold nanocrystals solution (50 μL) whose optical density (OD) at the major plasmon peak pre-adjusted to 2.0 was added. The resultant solution was kept in a water-bath at 30 °C for 7 min. The product was collected by centrifugation and redispersed in 1 mL water for further characterization.

S1.3 Characterization

The optical extinction spectra of the NPs were measured using aqueous colloidal suspensions at room temperature with a TU-1901 spectrophotometer. Ensemble circular dichroism (CD) spectra were obtained using a JASCO J-1700 spectrometer at room temperature. The branched GNPs were placed in a 10 mm diameter quartz sample cell and scanned between 400 and 800 nm at a bandwidth of 3 nm with a rate of 50 nm/min. Transmission electron microscopy (TEM) images were obtained with a JOEL JEM-2200FS transmission electron microscope operated at an accelerating voltage of 200 kV. High-resolution TEM (HRTEM) images were obtained with a JEOL JEM-2100F transmission electron microscope operated at an accelerating voltage of 200 kV. All samples for TEM and HRTEM measurements were dispersed in water and drop-dried on 300 mesh Formvar/carbon-coated Cu grids. Atomic force microscopy (AFM) images were obtained using a Bruker Dimension Icon atomic force microscope. Dynamic light scattering (DLS) measurements were performed by using Malvern Zetasizer Nano ZS. The X-ray diffraction (XRD) pattern was recorded by a PANalytical Empyrean diffractometer.

S1.4 Photothermal performance of samples

To explore the photothermal effect of the GNPs, the NP dispersions with a given concentration were irradiated by an 808 nm laser (Changchun New Industries Optoelectronics Tech. Co., Ltd, China) with a given power density for 10 min. When the power density was changed, the concentration of NP dispersions was fixed to be 20 μg mL^{-1}. When the concentrations of NP dispersions were changed, the power density of the laser was fixed to be 2 W cm^{-2}. For the repeated heating/cooling cycles, the NP concentration was 20 μg mL^{-1} and the power density was 2 W cm^{-2}. The temperatures were analysed by an IR-thermal camera (FOTRIC, China).

S1.5 Calculation of anisotropy factor (g-factor) values

The g-factor was calculated based on the following equation:

$$g\text{-}factor = \frac{CD\ (mdeg)}{32980 \times Extinction}$$

S1.6 Calculation of photothermal conversion efficiency

The photothermal conversion efficiency of GNP dispersion was calculated according to previous reports.[4] Detailed calculation was given below:

The total energy balance of the system as following equation:

$$\sum_i m_i C_{p,i} \frac{dT}{dt} = Q_{NPs} + Q_s - Q_{loss} \qquad (1)$$

where m and C_p are the mass and heat capacity, respectively. The suffix "i" of m and C_p refers to solvent or dispersed matter. T is the solution temperature. Q_{NPs} is the photothermal energy absorbed by GNPs per second:

$$Q_{NPs} = I\,(1\text{-}10^{-A_\lambda})\eta \qquad (2)$$

where I is the laser power, A_λ is the absorbance of gold NPs at the wavelength of 808 nm in aqueous solution, and η is the photothermal conversion efficiency of GNPs.

Q_{loss} is thermal energy lost to the surroundings:

$$Q_{loss} = hA\Delta T \qquad (3)$$

Where h is the heat transfer coefficient, A is the surface area of the container, and ΔT is the difference between the solution temperature and ambient temperature of the surrounding.

Q_s is the heat associated with the light absorbance of the solvent per second. The heat input is equal to the heat output at the maximum steady-statue temperature when heating pure water, so the equation can be:

$$Q_s = Q_{loss,H_2O} = hA\Delta T_{max,H_2O} \qquad (4)$$

Where $\Delta T_{max,H_2O}$ is the temperature change of water at the maximum steady-state temperature.

As it to the experiment of GNP dispersions, the heat inputs are the heat generated by NPs and the heat generated by water, which is equal to the heat output at the maximum steady-statue temperature, so the equation can be:

$$Q_{NPs}+Q_s = Q_{loss} = hA\Delta T_{max,mix} \qquad (5)$$

Where $\Delta T_{max,mix}$ is the temperature change of GNP dispersion at the maximum steady-statue temperature. According to the equation (2), (4) and (5), the photothermal conversion efficiency (η) can be expressed as following:

$$\eta = \frac{hA\Delta T_{max,mix}\text{-}hA\Delta T_{max,H_2O}}{I(1\text{-}10^{-A_\lambda})} \qquad (6)$$

In this equation, only hA is unknown. In order to get the hA, we introduce θ, which is defined as the ratio of ΔT to ΔT_{max}:

$$t = -\frac{\sum_i m_i C_{p,i}}{hA}\ln\theta \qquad (7)$$

Where $\frac{\sum_i m_i C_{p,i}}{hA}$ can be calculated by linear relationship of time versus-lnθ. Substituting hA value into equation (6), the photothermal conversion efficiency (η) of GNPs can be calculated.

S2. Supplementary figures

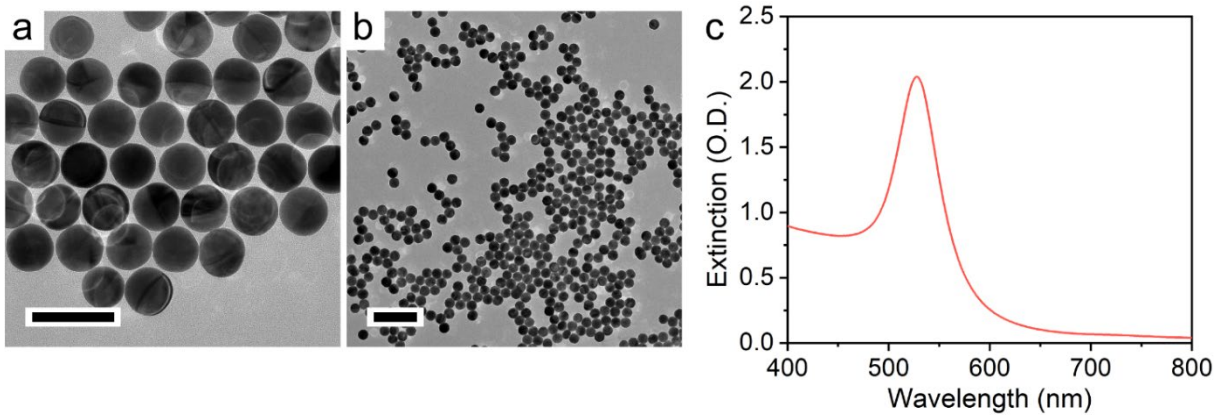

Fig. S1 (a, b) TEM images and (c) UV-Vis spectrum of GNSs. Scale bars: 50 nm (a), 200 nm (b).

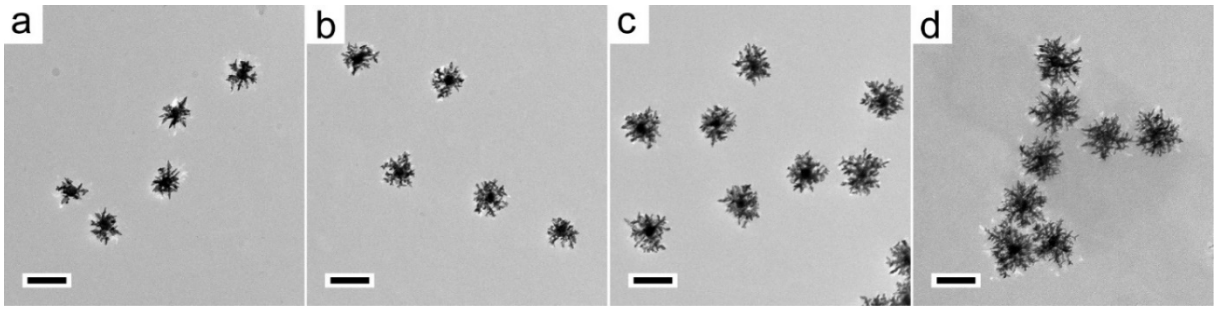

Fig. S2 TEM images of the branched GNPs obtained at (a) 30 s, (b) 2 min, (c) 4 min and (d) 7 min. Scale bar: 200 nm.

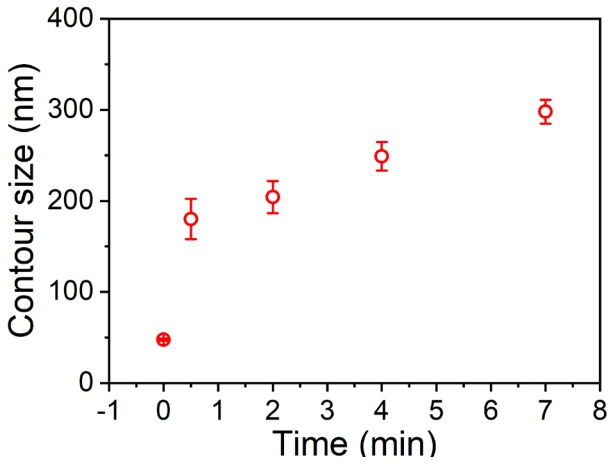

Fig. S3 The contour size of the branched GNPs as a function of time at 30 °C.

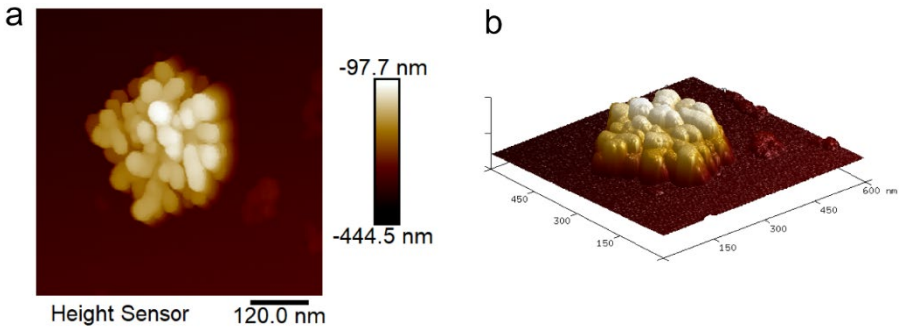

Fig. S4 AFM images of a branched GNP. (a) Height image and (b) the reconstructed three-dimensional image.

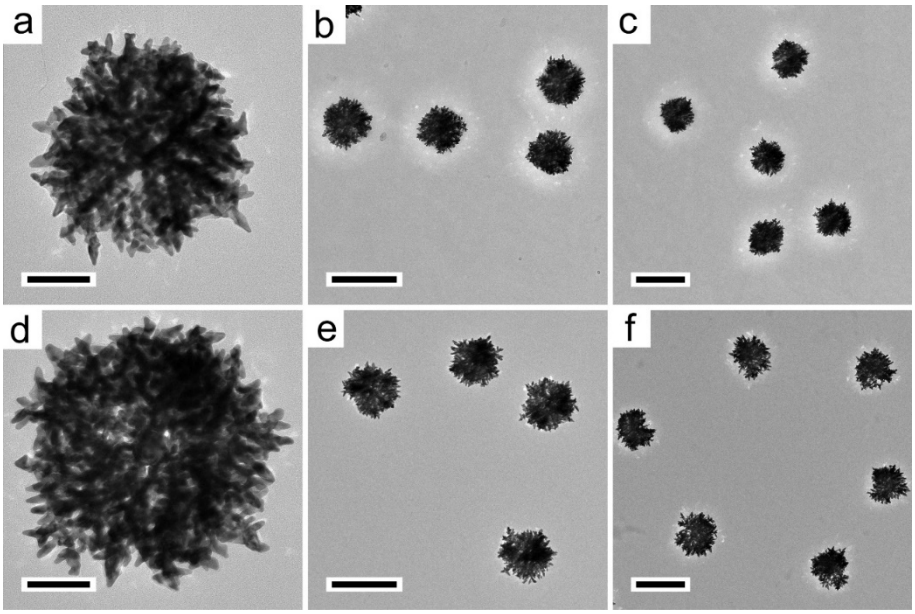

Fig. S5 TEM images of the branched GNPs obtained at (a-c) 15 min and (d-f) 20 min. Scale bars: 100 nm (a, d), 500 nm (b, c, e and f).

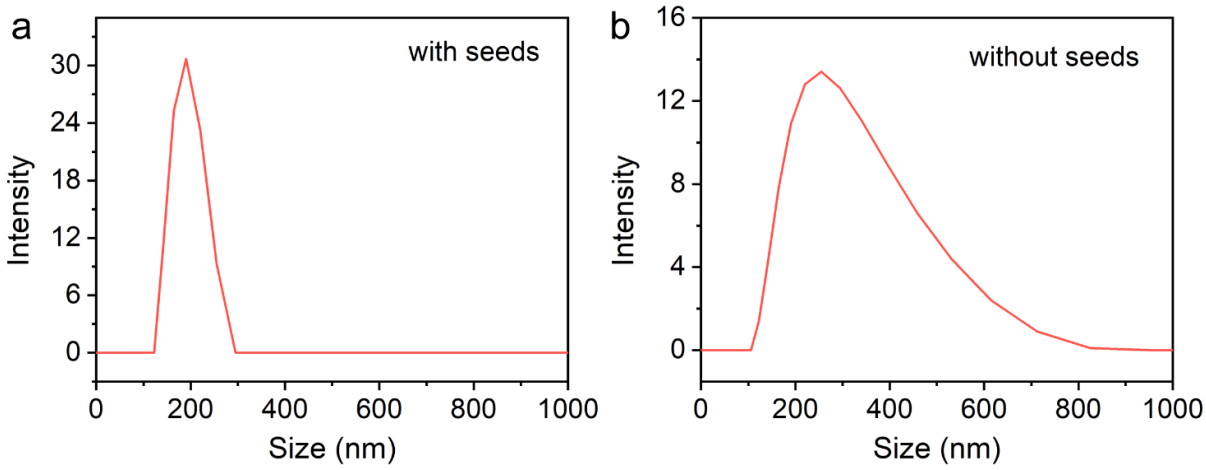

Fig. S6 Hydrodynamic sizes of the branched GNPs synthesized (a) with and (b) without seeds.

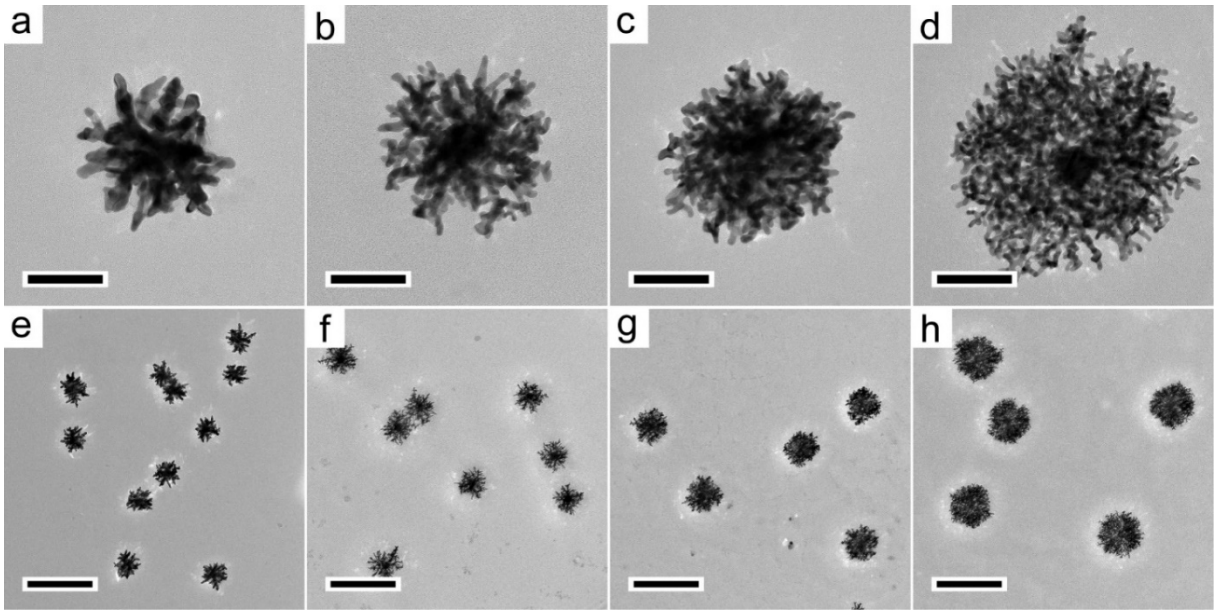

Fig. S7 TEM images of the branched GNPs obtained at different cysteine concentrations: (a, e) 2.7 μM, (b, f) 4.6 μM, (c, g) 6.4 μM and (d, h) 9.1 μM. Scale bars: 100 nm (a-d), 500 nm (e-h).

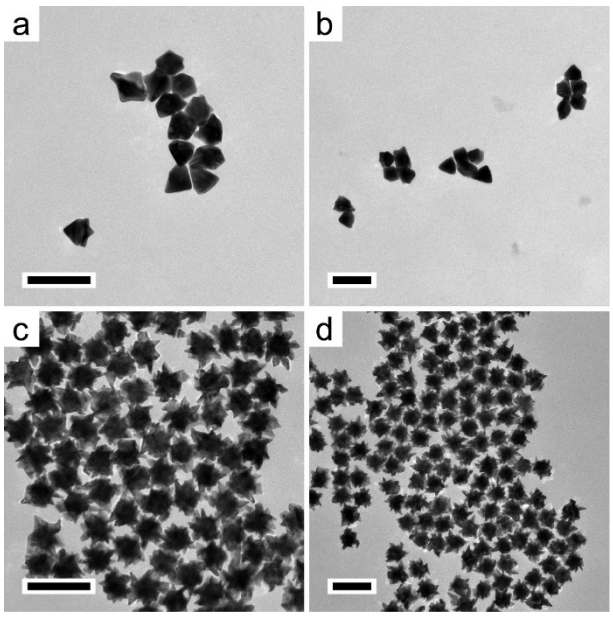

Fig. S8 (a, b) TEM images of GNPs synthesized without cysteine. (c-d) TEM images of GNPs synthesized with a concentration of cysteine of 0.9 μM. Scale bar: 200 nm.

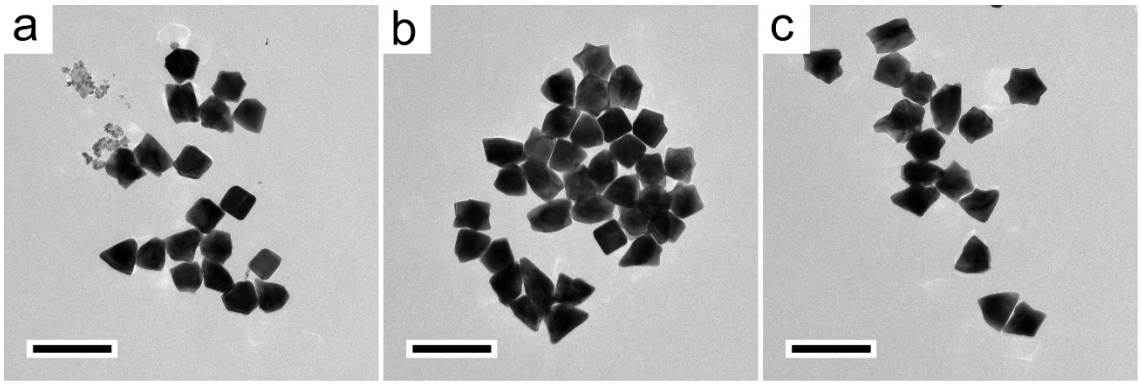

Fig. S9 TEM images of GNPs. (a) Using 3-mercaptopropionic acid instead of cysteine. (b) Using aminoacetic acid instead of cysteine. (c) Using a combination of 3-mercaptopropionic acid and aminoacetic acid instead of cysteine. Scale bar: 200 nm.

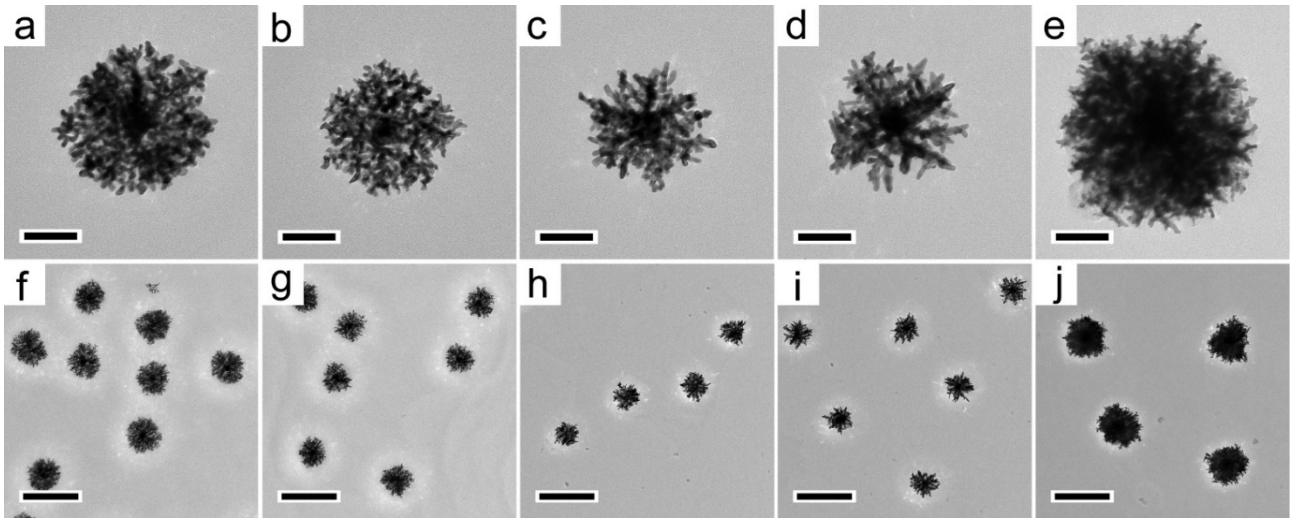

Fig. S10 TEM images of the branched GNPs synthesized at different CTAC/CTAB ratio: (a, f) 0:4, (b, g) 1:3, (c, h) 2:2, (d, i) 3:1 and (e, j) 4:0. Scale bars: 100 nm (a-e), 500 nm (f-j).

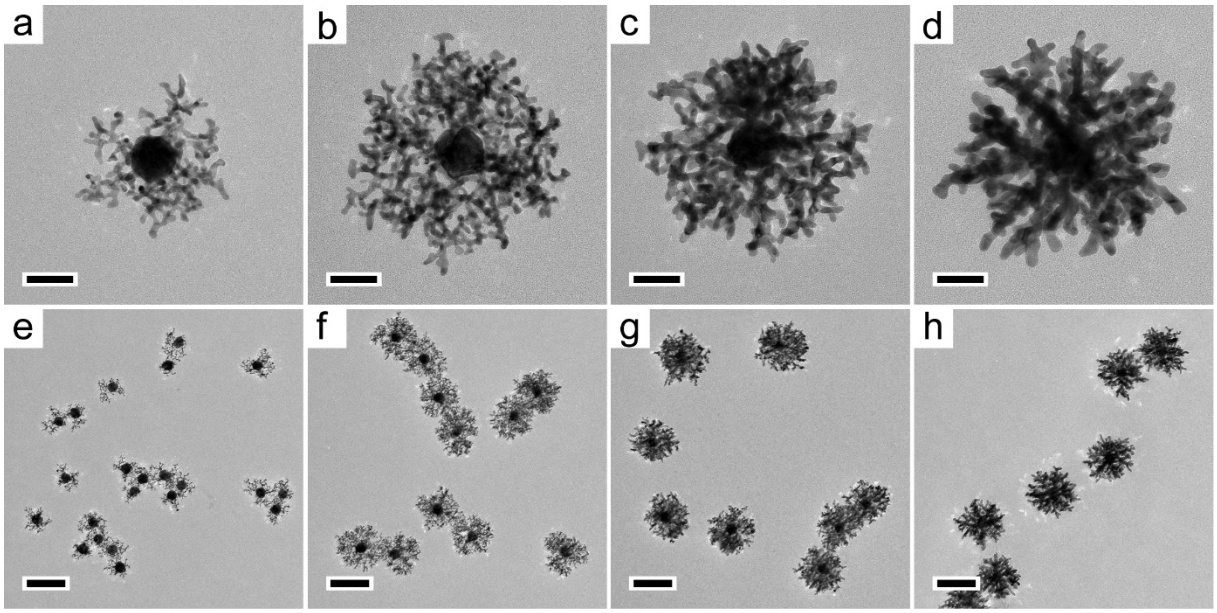

Fig. S11 TEM images of the branched GNPs synthesized at different $HAuCl_4$ concentrations: (a,e) 91 μM, (b,f) 182 μM, (c,g) 274 μM and (d,h) 365 μM. Scale bars: 50 nm (a-d), 200 nm (e-h).

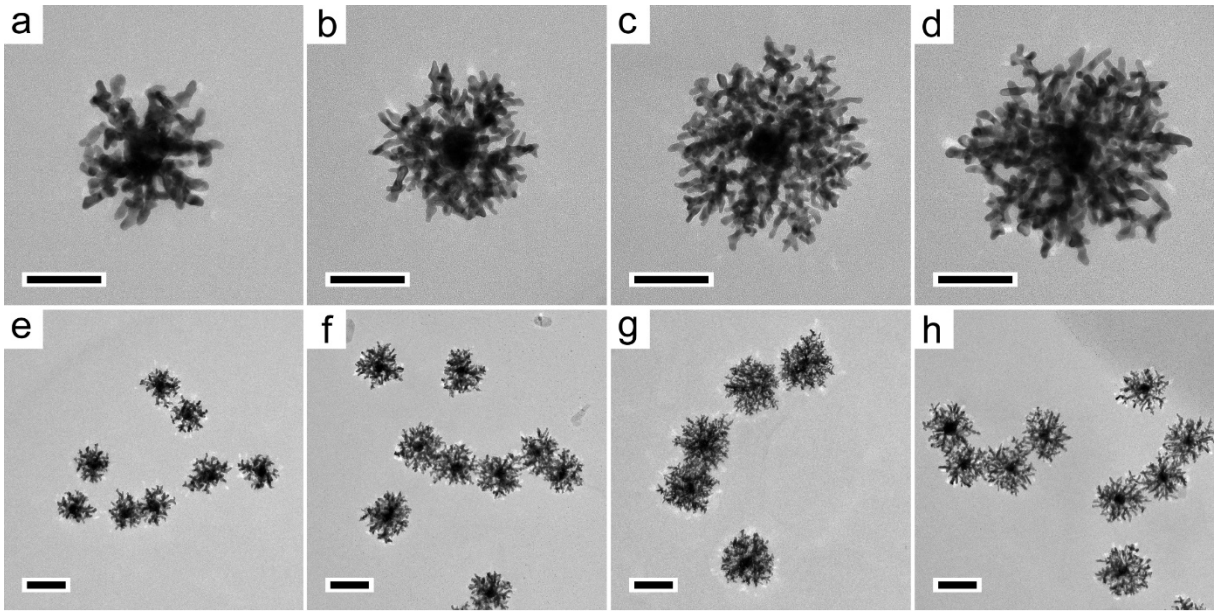

Fig. S12 TEM images of the branched GNPs synthesized at different AA concentrations: (a,e) 0.4 mM, (b,f) 2.6 mM, (c,g) 5.2 mM and (d,h) 8.7 mM. Scale bars: 100 nm (a-d), 200 nm (e-h).

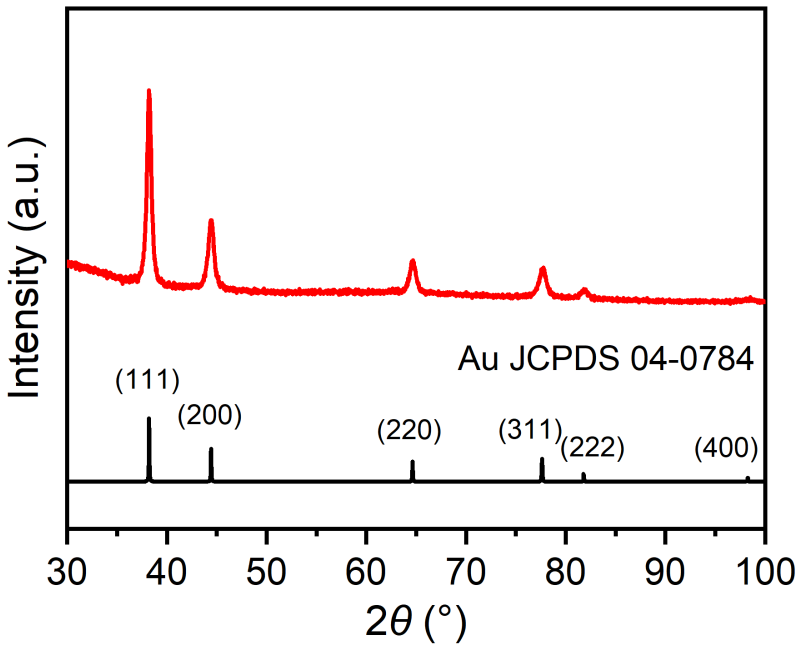

Fig. S13 XRD patterns of branched GNPs. The bottom black line represents a standard XRD pattern of gold.

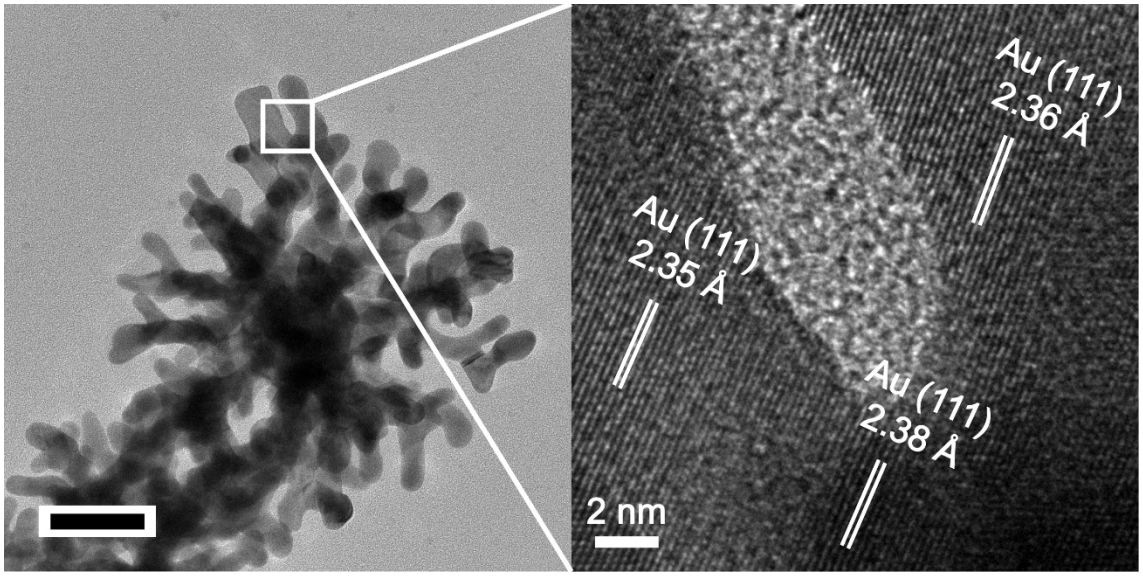

Fig. S14 TEM (left) and HRTEM (right) images of the branches on the GNS seed. Scale bar: 50 nm.

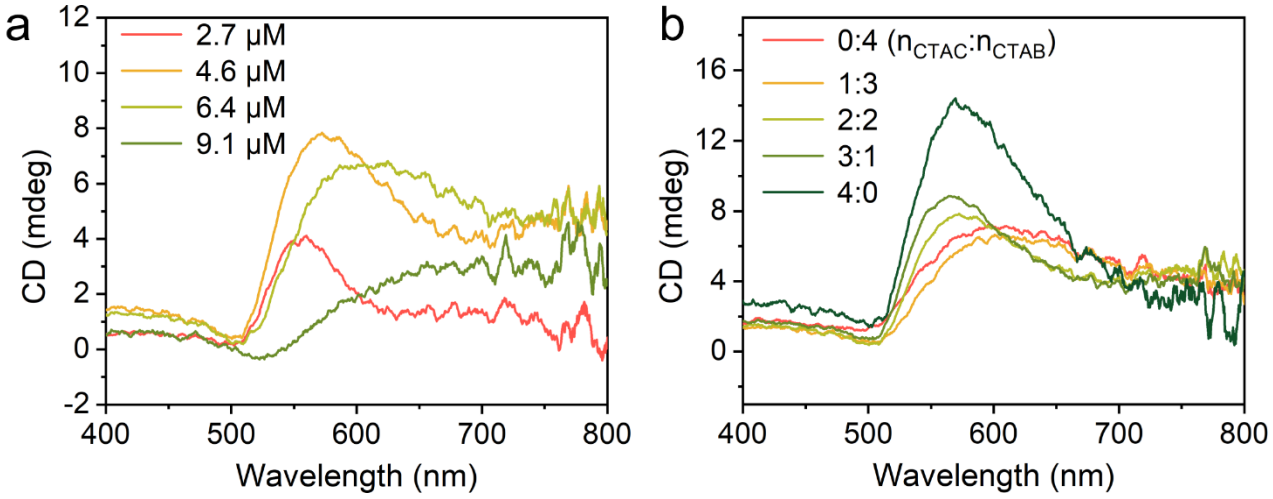

Fig. S15 CD spectra of the branched GNPs obtained for different (a) cysteine concentrations and (b) molar ratios of CTAC/CTAB.

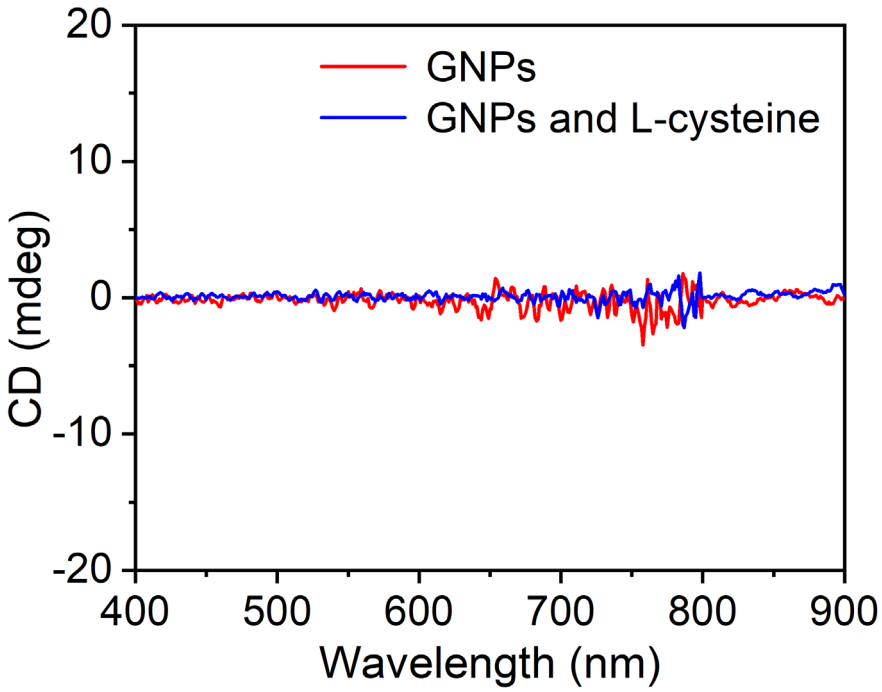

Fig. S16 CD spectra of GNS dispersion. (a) GNP dispersion where GNPs were stabilized by CTAB/CTAC. (b) GNP dispersion after adding L-cysteine solution for adsorption for 24 h.

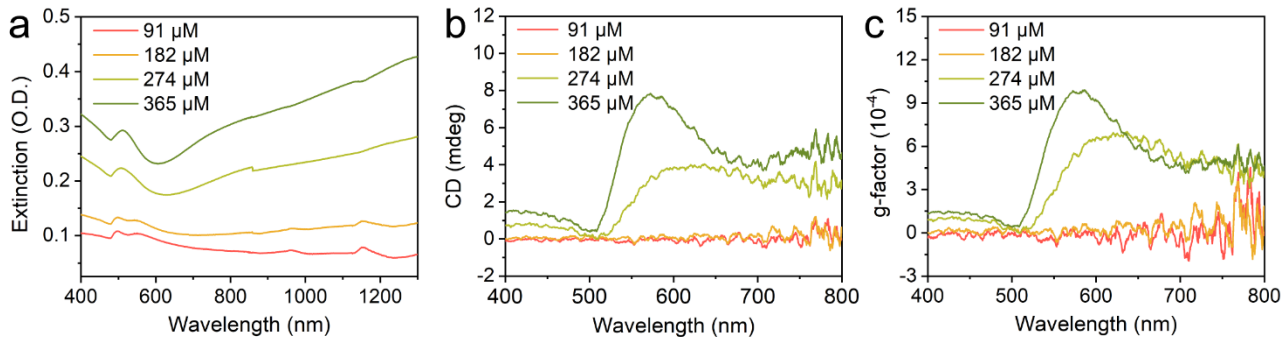

Fig. S17 (a) UV-Vis-NIR spectra, (b) CD spectra and (c) calculated g-factor spectra of branched GNPs obtained at different $HAuCl_4$ concentrations.

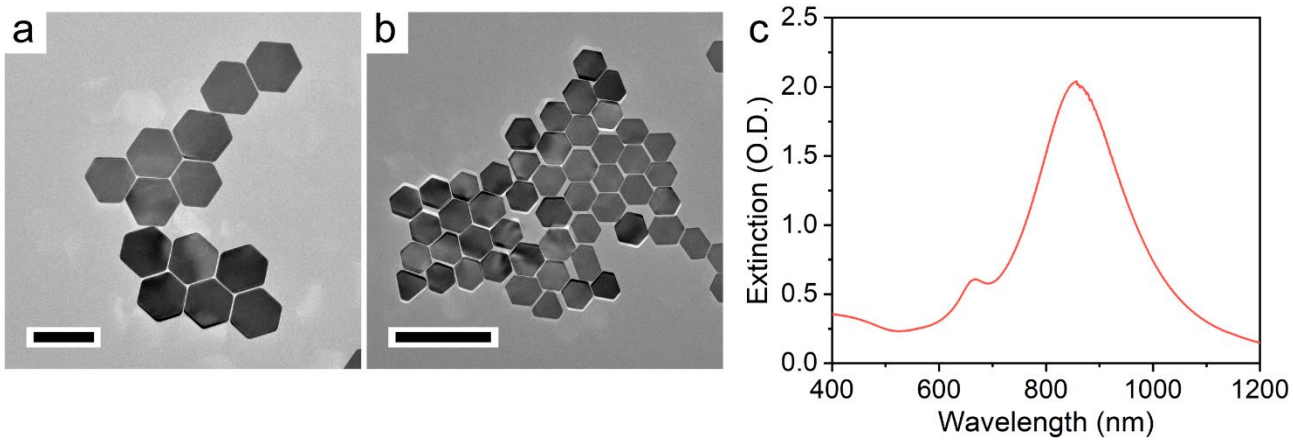

Fig. S18 (a, b) TEM images and (c) UV–Vis–NIR spectra of GNPLs. Scale bars: 200 nm (a), 500 nm (b).

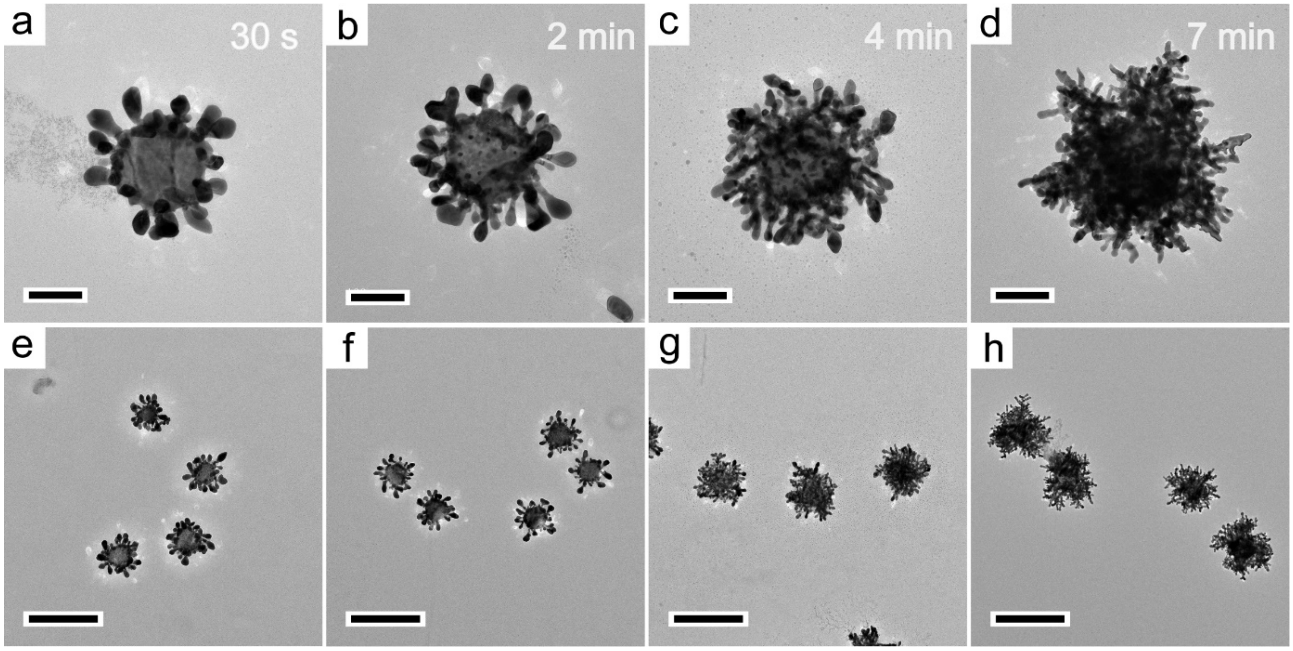

Fig. S19 TEM images of branched GNPLs obtained at (a, e) 30 s, (b, f) 2 min, (c, g) 4 min and (d, h) 7 min. Scale bars: 100 nm (a-d), 500 nm (e-h).

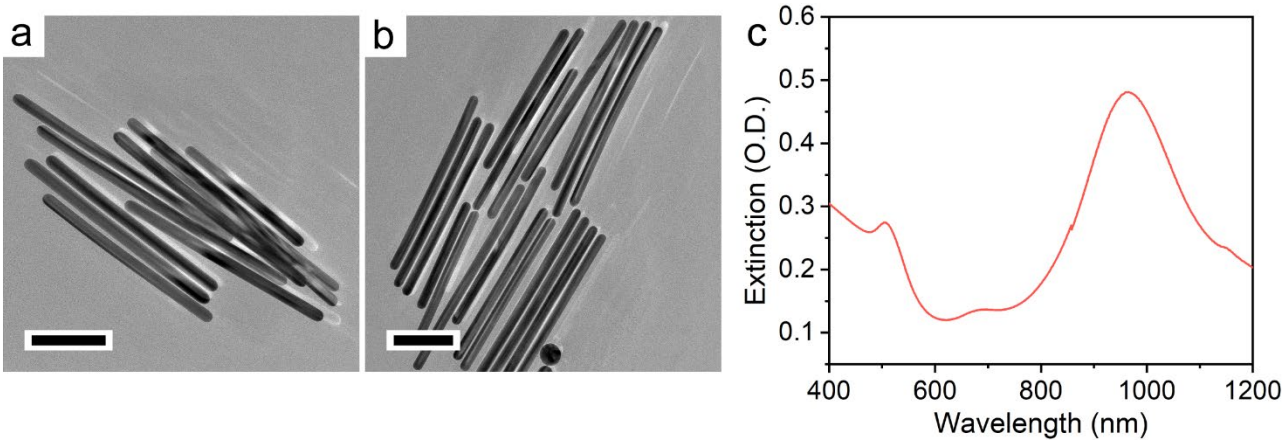

Fig. S20 (a, b) TEM images and (c) UV–Vis–NIR spectrum of GNRs. Scale bar: 100 nm.

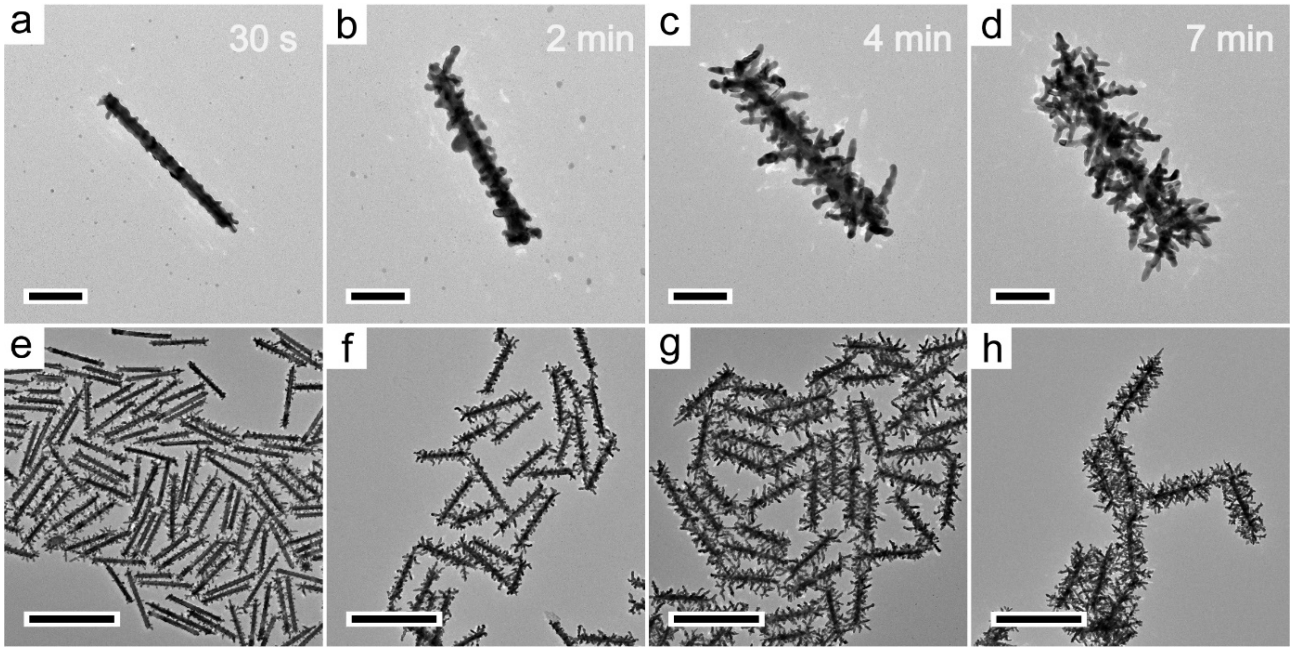

Fig. S21 TEM images of branched GNRs obtained at (a, e) 30 s, (b, f) 2 min, (c, g) 4 min and (d, h) 7 min. Scale bars: 100 nm (a-d), 500 nm (e-h).

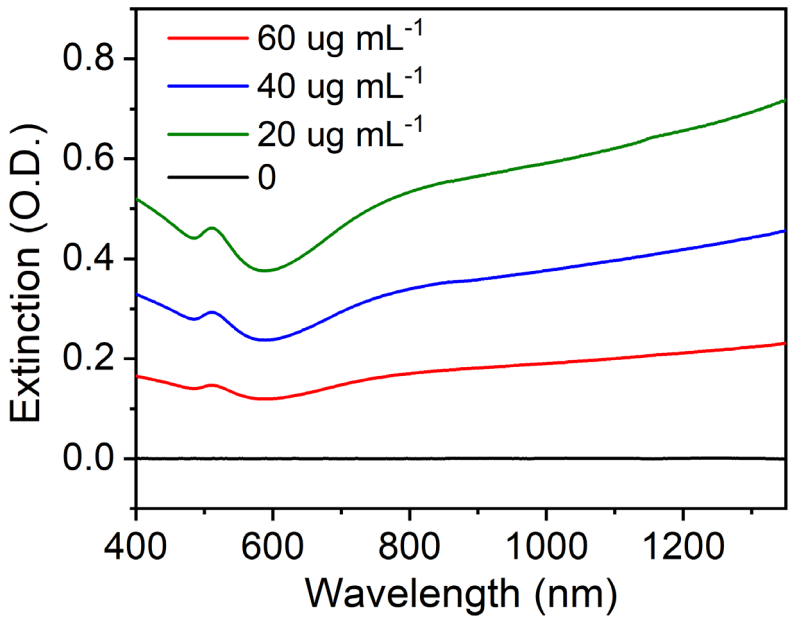

Fig. S22 UV–Vis–NIR spectra of branched GNSs at different concentrations of 0, 20, 40 and 60 μg mL^{-1}.

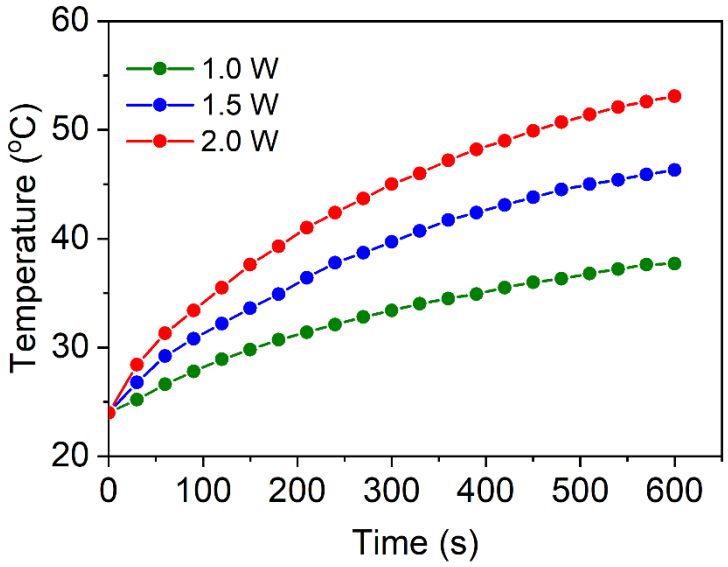

Fig. S23 Temperature curves of branched GNS dispersions (20 μg mL^{-1}) under different laser power density.

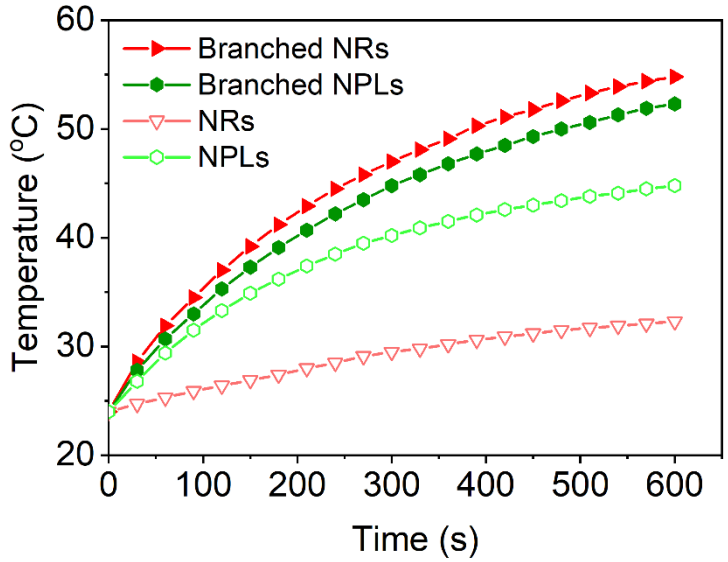

Fig. S24 Temperature curves of GNR, GNPL, branched GNR and branched GNPL aqueous dispersions (20 μg mL^{-1}) under 808 nm laser irradiation (2.0 W cm^{-2}).

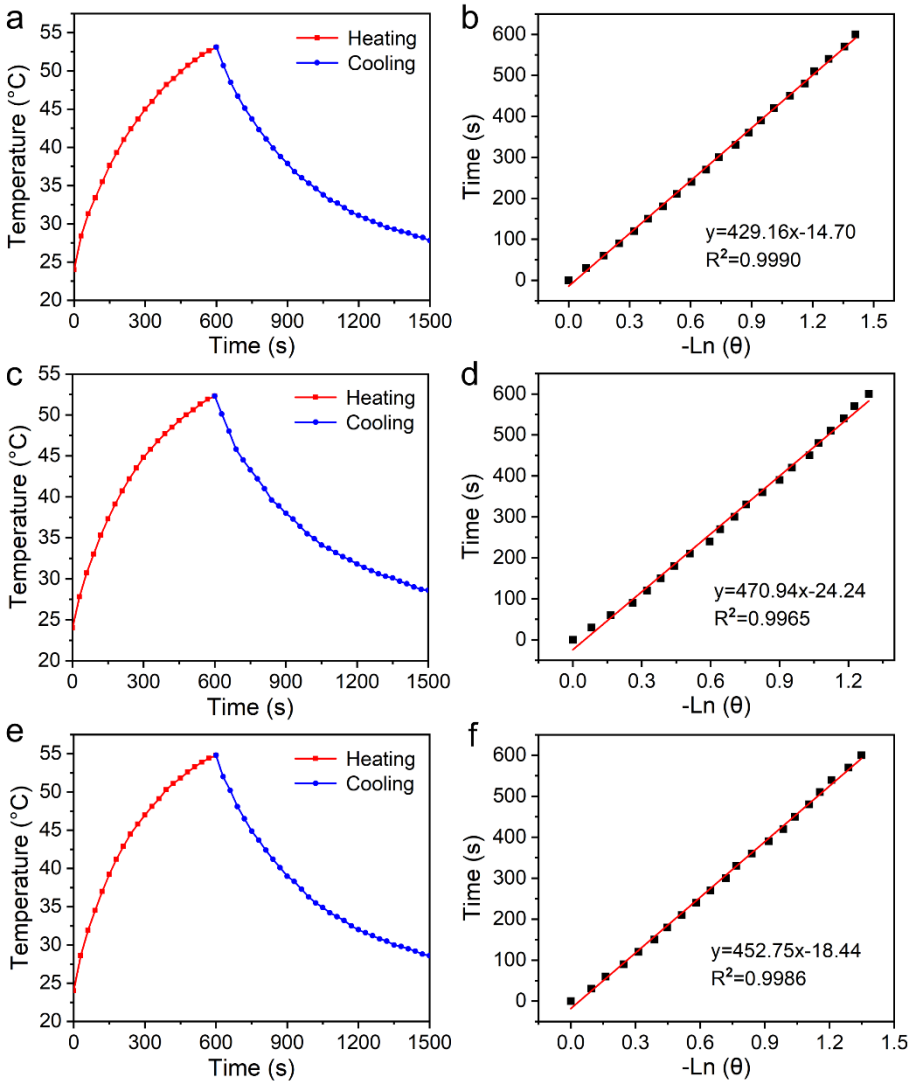

Fig. S25 The heating and cooling curves of branched (a) GNS, (c) GNPL and (e) GNR dispersions. The right column represents the time constant (τ_s) for the heat transfer, obtained by regression analysis of the linear time data from the cooling curve.

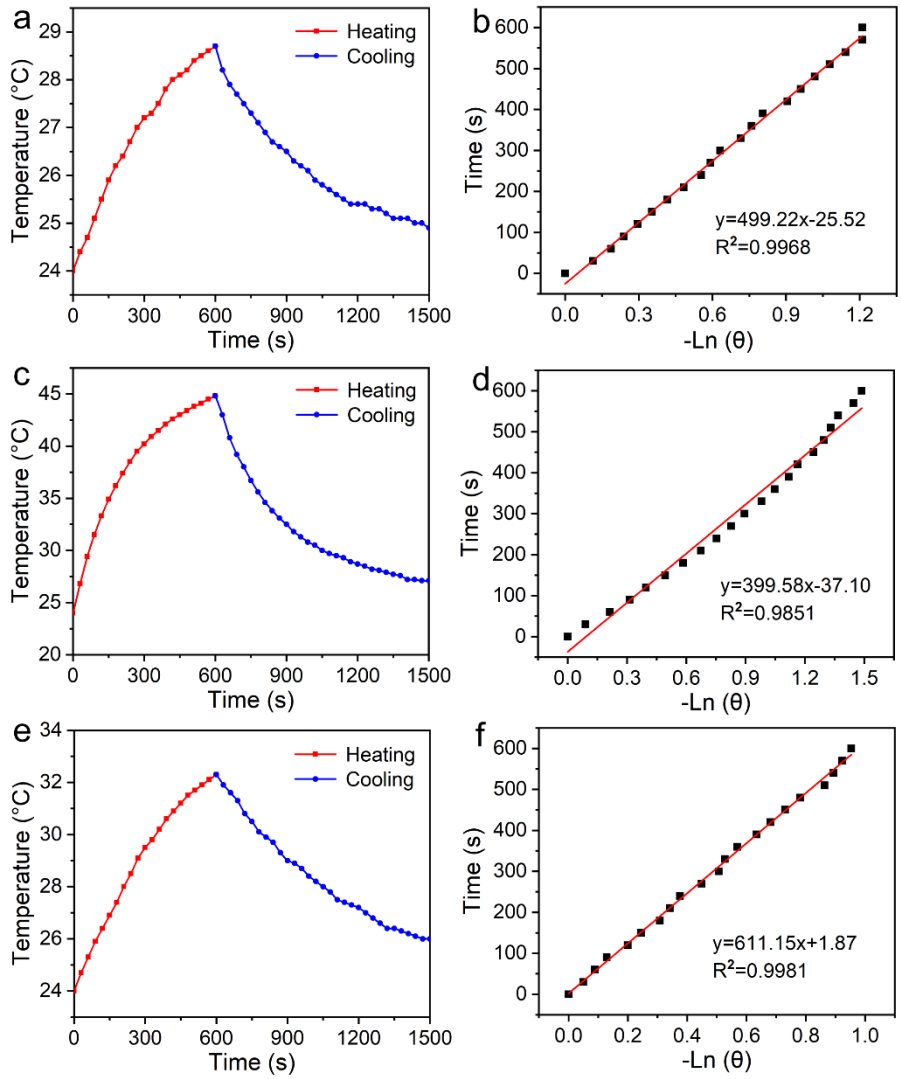

Fig. S26 The heating and cooling curves of (a) GNS, (c) GNPL and (e) GNR dispersions. The right column represents the time constant (τ_s) for the heat transfer, obtained by regression analysis of the linear time data from the cooling curve.

References

1. Q. Ruan , L. Shao , Y. Shu , J. Wang and H. Wu , *Adv. Opt. Mater.* **2014**, *2*, 65-73.
2. J. S. DuChene, W. X. Niu, J. M. Abendroth, Q. Sun, W. B. Zhao, F. W. Huo, W. D. Wei, *Chem. Mater.* **2013**, *25*, 1392.
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