Supporting Information

A General Method for Precise Chain Assembly of Noble Metal Nanoparticles

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Contents

Section S1. Experimental

1. Chemicals

All chemical reagents were used as purchased without further purification. Hydrogen tetrachloroaurate(III) hydrate (HAuCl$_4$·3H$_2$O, 99.9%, metal basis Au 49%) and 2-mercaptobenzo-imidazole-5-carboxylic acid (MBIA, 97.21%) were purchased from Alfa Aesar; Sodium citrate dehydrate (CA, 99%) was purchased from Innochem; Citric acid (99%), hexadecyl trimethyl ammonium bromide (CTAB, 98%), *L*-ascorbic acid (AA, 99%), silver nitrate (AgNO$_3$, 99.9999% trace metals basis), chloroplantinic acid hexahydrate (H$_2$PtCl$_6$·6H$_2$O, > 37.5% Pt basis), tetraethoxysilane (TEOS, 99%), 4-mercaptobenzoic acid (MBA, technical grade 90%), and 6-mercaptonicotinic acid (6-MNA, technical grade 90%) were purchased from Sigma-Aldrich; Mercaptoacetic acid (MAA, 90%), 3-mercaptopropionic acid (3-MPA, 99%), 3-mercaptobenzoic acid (3-MBA, 96%), *N*-acetyl-*L*-cysteine (99%), 3-mercapto-1-propanol (97%), 4-ethynylbenzoic acid (4-EBA, 95%), 2,2'-Dithiosalicylic acid (DTSA, 96%) and ammonia solution (AR, 25-28%) were purchased from Aladdin; 4-Mercaptophenylacetic acid (4-MPAA, 97%) was purchased from Picasso; 2-mercaptonicotinic acid (2-MNA, 99.93%) was purchased from Leyan. Ethanol (EtOH), and 2-naphthalenethiol (99%) were purchased from Rhawn; Isopropanol (IPA), and tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent. Ultrapure deionized water (18.2 MΩ/cm) was used for all solution preparations.

2. Measurements and characterizations

Transmission electron microscopy (TEM) images were collected on a Hitachi HT7800 operated at 80 kV. UV–Vis-NIR spectra were collected on a Mettler Toledo UV7. Dynamic Light Scattering (DLS) and Zeta potential were collected on a Brookhaven

BI-200SM. Raman spectra and SERS were collected from colloidal samples in a quartz cuvette (path length = 1.00 cm) on a portable Raman analyzer (Accuman SR-510 Pro) equipped with 785 nm laser (350 mW). The integration times are 3 or 10s for different samples.

3. Preparation of Au-chains@silica

The citrate-stabilized AuNPs (d = 15, 40, 60 and 80 nm) were synthesized according to the literatures[1-3]. The concentration of AuNPs (d = 15, 40, 60 and 80 nm) were about 1.47×10^{12}, 1.41×10^{11}, 4.76×10^{10}, 1.96×10^{10} NP/mL, respectively. The synthesis of Au-chains@silica was as follows: the pre-synthesized AuNPs (d = 40 nm, 1 mL) was concentrated to 6 µL via centrifugation and dispersed into the mixture containing 92 µL EtOH and 8 µL water. After adding the ligand MBA (1.2 mM in EtOH, 10 µL), the mixture solution (V_{EtOH}: V_{water} = 7.3: 1) was incubated at room temperature. After 2 h, the Au chains were formed and trapped by silica encapsulation. In detail, the obtained Au-chain solution was mixed with 0.31 mL H_2O, 0.554 mL IPA (containing 1.6 µL TEOS/1 mL IPA), and 20 µL ammonium. Then, the mixture solution was incubated at room temperature for 6 h.

The same method was used to prepare Au-chains@silica of other sizes (d = 15, 60 and 80 nm). There are slight differences in the MBA concentration, the EtOH/water ratio, and the amount of TEOS: For 60 nm AuNPs, [MBA] = 2 mM; For 80 nm AuNPs, [MBA] = 2.25 mM; For 15 nm AuNPs, [MBA] = 0.6 mM, V_{EtOH}/V_{water} = 9.5: 1, and 0.554 mL IPA (containing 0.9 µL TEOS/1 mL IPA) were used instead.

Scale-up synthesis of Au-chains@silica: The same method was used to prepare 100 mL Au-chains@silica, all volumes are expanded by 100 times.

4. Preparation of salt-induced Au-aggregates.

Method 1: The salt-induced aggregation of AuNPs (d = 40 nm) in the DMF-water solution was modified from our previously reported methods[4]. In a typical process, the 1 mL synthesized AuNPs were purified and concentrated via centrifugation. The concentrated AuNPs (6 µL) were mixed with 90 µL DMF, 6.67 µL 2-naphthalenethiol (3 mg/ mL in DMF), and 3.33 µL NaOH aqueous solution (2.5 mM). Then, the mixture was incubated at 60 °C for 2 h. After that, NaCl (10 mM, 10 µL) was added into the

mixture, to induce the aggregation of AuNPs. Finally, the mixture ($[NaCl]_{final}$ = 0.862 mM) was incubated at room temperature for another 2 h.

Method 2: The aggregation occurred in the ethanol-water solution. The 3 mL synthesized AuNPs (*d* = 40 nm) were purified via centrifugation, and the concentrated AuNP solution (6 μL) was dispersed into the solution containing 209 μL EtOH, 4 μL MBA (4 mM in EtOH), 91 μL water. Then, the mixture ($[MBA]_{final}$ = 0.05 mM) was incubated at room temperature. After 2 h, 10 μL 20 mM NaCl aqueous solution was added into the mixture to induce the aggregation of AuNPs. Such mixture ($[NaCl]_{final}$ = 0.625 mM) was incubated at room temperature for another 2 h. Finally, the mixture was mixed with 0.93 mL H_2O, 1.662 mL IPA (containing 1.6 μL TEOS/1 mL IPA), and 60 μL ammonium solution. After incubation at room temperature for 6 h, the Au-chains@silica nanostructures were obtained.

5. Preparation of Au-chains@silica with different solvent.

Similar procedure described in Section 2.3 was used for preparing Au-chains@silica with different solvents. The solvent IPA and THF were used to instead EtOH. In IPA system, the volume of IPA and water are 88 and 12 μL, respectively. In THF system, the volume of THF and water are 85 and 15 μL, respectively.

6. Preparation of Au-chains@silica with different ligands

Similar procedure described in Section 2.3 was used, where different ligands were employed to modified Au-chains. For clarification, the synthetic conditions for each ligand were listed in Table 2. It should be noted that the degree of aggregation was determined by the color change (red to dark purple), and the incubation time differed a bit.

7. Preparation of Ag-chains@silica

The citrate-stabilized AgNPs (*d* = 25 and 45 nm) were synthesized according to the literature method[5]. The concentration of AgNPs (*d* = 25 and 45 nm) were about 3.78 × 10^{12} and 3.78 × 10^{11} NP/mL, respectively. The synthesized AgNPs (0.5 mL, *d* = 25 nm) were purified and concentrated via centrifugation. The concentrated AgNP solution (20 μL) was dispersed into 86 μL EtOH. In the presence of vortexing, 10 μL MBA (16 mM in EtOH) was added into the AgNP solution in five times, to slow down the aggregation

rate of AgNPs. Then, the mixture (V_{EtOH}: V_{water} = 4.8: 1) was incubated at room temperature. The colour changed from light yellow to red, brick-red, and finally green. After 2 h, the Ag chain was formed and mixed with 0.31 mL H_2O, 0.554 mL IPA (containing 1.6 μL TEOS/1 mL IPA), and 20 μL ammonium. Finally, the mixture was further incubated at room temperature for 6 h. The similar method was used to synthesize the Ag-chains@silica in other size, where 45 nm AgNPs (1 mL) and 10 μL MBA (3 mM in EtOH) were used instead.

8. Preparation of Pt-chains@silica

The citrate-stabilized PtNPs (d = 29 and 42 nm) were synthesized according to the literature method[6]. The concentration of AgNPs (d = 25 and 45 nm) were about 4.32 × 10^{11} NP/mL. To obtain Pt-chains@silica nanostructures, the synthesized PtNPs (0.5 mL, d = 29 nm) were purified and concentrated via centrifugation. The concentrated PtNP (6 μL) was dispersed into the mixture containing 92 μL EtOH and 8 μL water, After introducing 10 μL MBA (1.8 mM in EtOH), the mixture (V_{EtOH}: V_{water} = 7.3: 1) was incubated at room temperature. The colour becomes slightly lighter and there is no precipitate at the bottom of the samples. After 2 h, the Pt chain was formed and further mixed with 0.31 mL H_2O, 0.554 mL IPA (containing 2.3 μL TEOS/1 mL IPA), and 20 μL ammonium. Finally, the mixture was incubated at room temperature for another 6 h. The similar method was used to synthesize Pt-chains@silica of other size, where 42 nm PtNPs and 10 μL MBA (5.3 mM in EtOH) were used instead.

Section S2. The calculation of SERS enhancement factor:

We employed the peak 1586 cm^{-1} of MBA to calculate the SERS enhancement factor (EF) of Au-chains@silica nanostructures. The calculation is based on the following Equation 1:

$$EF = (I_{SERS} \times C_{bulk})/ (I_{bulk} \times C_{SERS}) \qquad \text{Equation (1)}$$

Where I_{SERS} and I_{bulk} are the Raman intensities of the 1586 cm^{-1} peak for Au-chains@silica and pure MBA. C_{SERS} and C_{bulk} are the concentrations of MBA on/in Au-chains@silica and in pure solution. For the selection of I_{bulk}, we made a 0.15 M MBA aqueous solution in 1.25 M NaOH. By stepwise diluting, we got titration plots of SERS intensities vs [MBA] (Figure S1). Within this titration plots, the I_{bulk} should be in the range with fine linear ship between Raman intensity and [MBA]. Thus, we selected Raman intensity corresponding to 0.12 M as I_{bulk}.
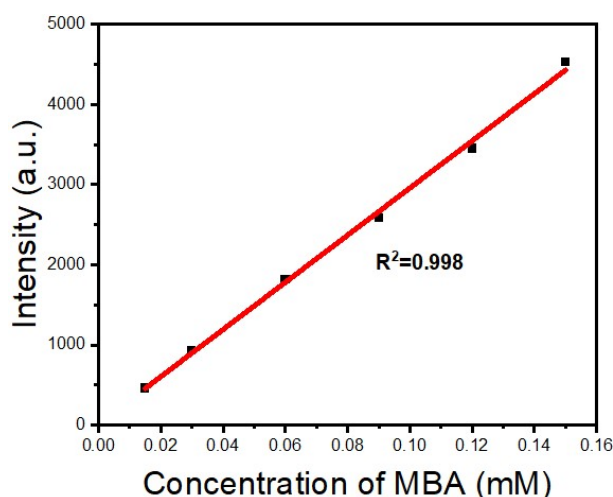
Figure S1. Linear fit for Raman intensity of MBA.

Calculation:

The concentration of the as-synthesized 40 nm AuNP solution can be estimated from the total amount of Au used in the synthesis, the density of Au, and the volume of each AuNP. Here, we assume that the as-synthesized 40 nm AuNPs are ideally uniform in size and shape.

The density of AuNPs is 19.32 g/cm^3, and the volume of 40 nm AuNP is

$$V_{Au} = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi (20 \times 10^{-9})^3 \, m^3 = 3.35 \times 10^{-23} \, m^3$$

Weight of Au (including Au seeds and hydrogen tetrachloroaurate(III) hydrate) in the as-synthesized 40 nm AuNP solution = 5 mg

Weight of each 40 nm AuNP = $\rho_{Au} \times V_{Au}$ = 6.47 × 10⁻¹⁹ kg = 6.47× 10⁻¹³ mg

Total number of 40 nm AuNPs = 5 mg/6.47 × 10⁻¹³ mg = 7.73 × 10¹² particles = 1.28 × 10⁻¹¹ mol

Total volume of the synthesis solution = 55 mL

Concentration of the as-synthesized 40 nm AuNP solution = 1.28 × 10⁻¹¹ mol/0.055 L = 23.27 × 10⁻¹¹ M = 232.7 pM

According to the literature[7], surface area of one ligand binding site on Au surface: S = 0.2155 nm²

The Surface area of 40 nm AuNP is:

$$S_{Au} = 4\pi r^2 = 5026.5\ nm^2$$

Total number of ligand binding sites on the surface of NP = C × S_{Au}/0.2155 = 5.4 × 10³ nM

I_{SERS} = 15623 counts, I_{bulk} = 3449 counts, C_{bulk} = 120 mM

EF_{MBA} = ($I_{SERS} \times C_{bulk}$)/($I_{bulk} \times C_{SERS}$) = 1.01 × 10⁵.
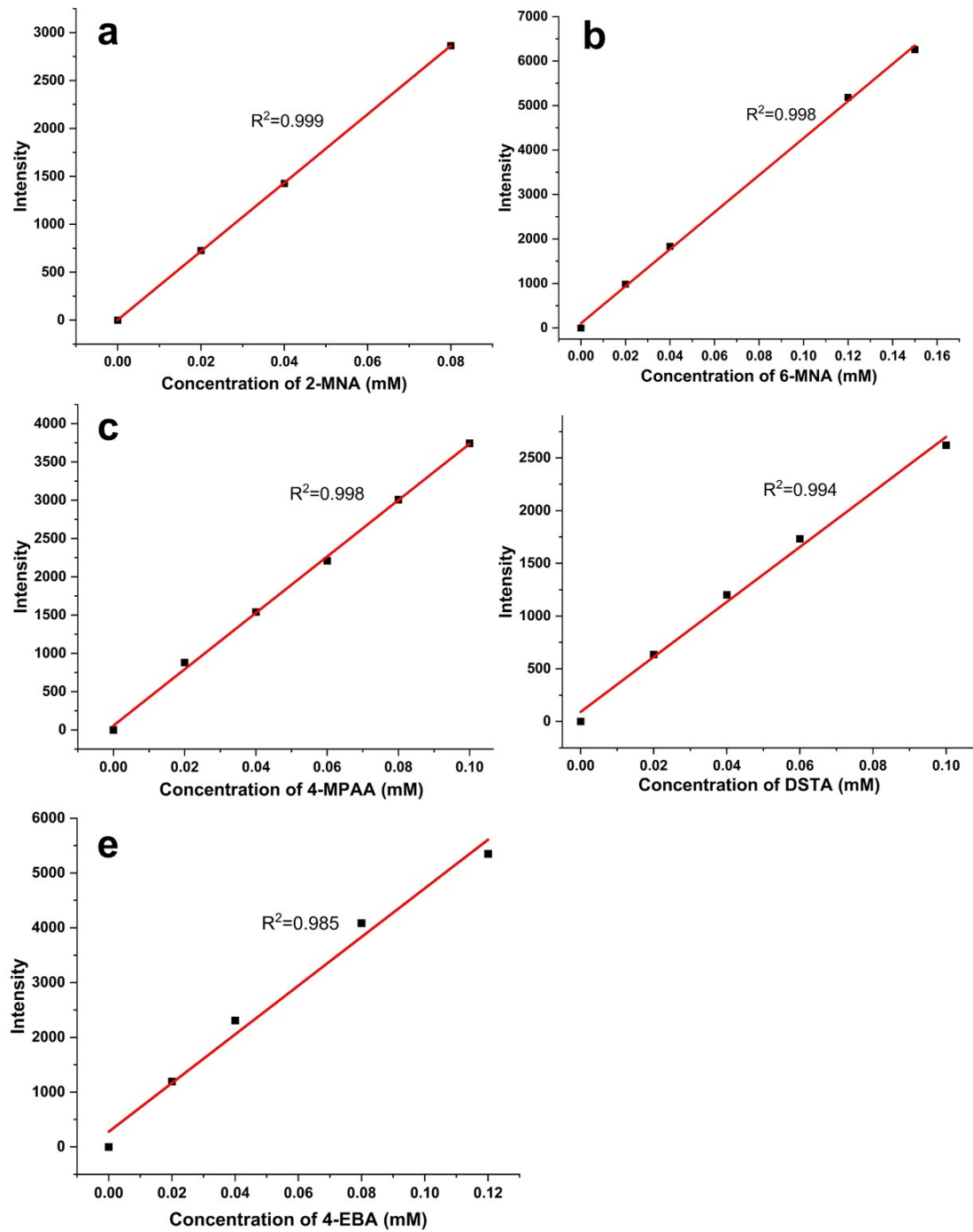
Figure S2. Linear fit for Raman intensity of (a) 2-MNA, (b) 6-MNA, (c) 4-MPAA, (d) DSTA, and (e) 4-EBA.

Table S1. The enhancement factor (EF) of 40 nm Au-chains@silica prepared with different SERS-active ligands.

Ligand	Raman Shift (cm^{-1})	Ligand Concentration[1] (M)	SERS Intensity[2]	Ligand Concentration[3] (nM)	SERS Intensity of Monomer AuNPs	SERS Intensity of Au Chains[4]	$I_{chains}/I_{monomer}$	Enhancement Factor[5]
2-MNA	1038	0.1	3578	5.4×10^3	210	10168	48.4	5.26×10^4
6-MNA	1078	0.15	6348	5.4×10^3	659	23979	36.4	1.05×10^5
4-MPAA	1062	0.1	3737	5.4×10^3	283	12144	42.9	6.02×10^4
DSTA	1017	0.1	2699	5.4×10^3	443	11584	26.1	7.95×10^4
4-EBA	1592	0.1	4789	5.4×10^3	411	11829	28.8	4.57×10^4

Table S2. The enhancement factor of 42 nm Ag-chains@silica prepared with different SERS-active ligands.

Ligand	Ligand Concentration[3] (mM)	Raman Shift (cm^{-1})	SERS Intensity of Monomer AgNPs	SERS Intensity of Ag Chains[4]	$I_{chains}/I_{monomer}$
3-MBA	0.431	983	121	2790	23.1
MBIA	0.323	1267	100	4418	44.2
2-MNA	0.517	1041	319	4959	15.5
6-MNA	0.302	1087	339	7711	22.7
MBA	0.259	1065	1176	10142	8.6

Annotation:

1. The concentration of free ligands dispersed in 1.25 M NaOH aqueous solution.

2. SERS intensity of free ligands dispersed in 1.25 M NaOH aqueous solution.

3. The concentration of ligands presented in the solution was enough to fully cover the AuNP and AgNP surface.

4. SERS intensity of Au-chains@silica and Ag-chains@silica were measured in the colloidal solution.

5. EF of ligands was calculated by the method in **Section S2**.
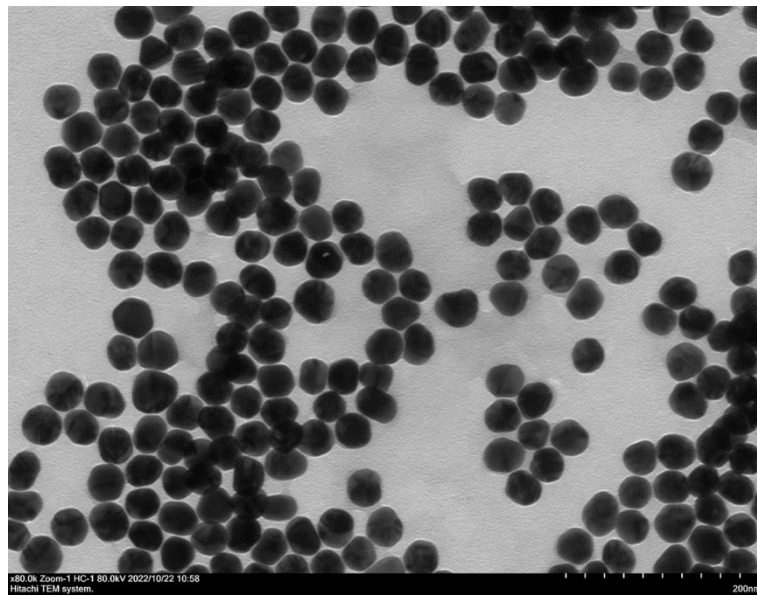
Section S3. Figure S3-S17.

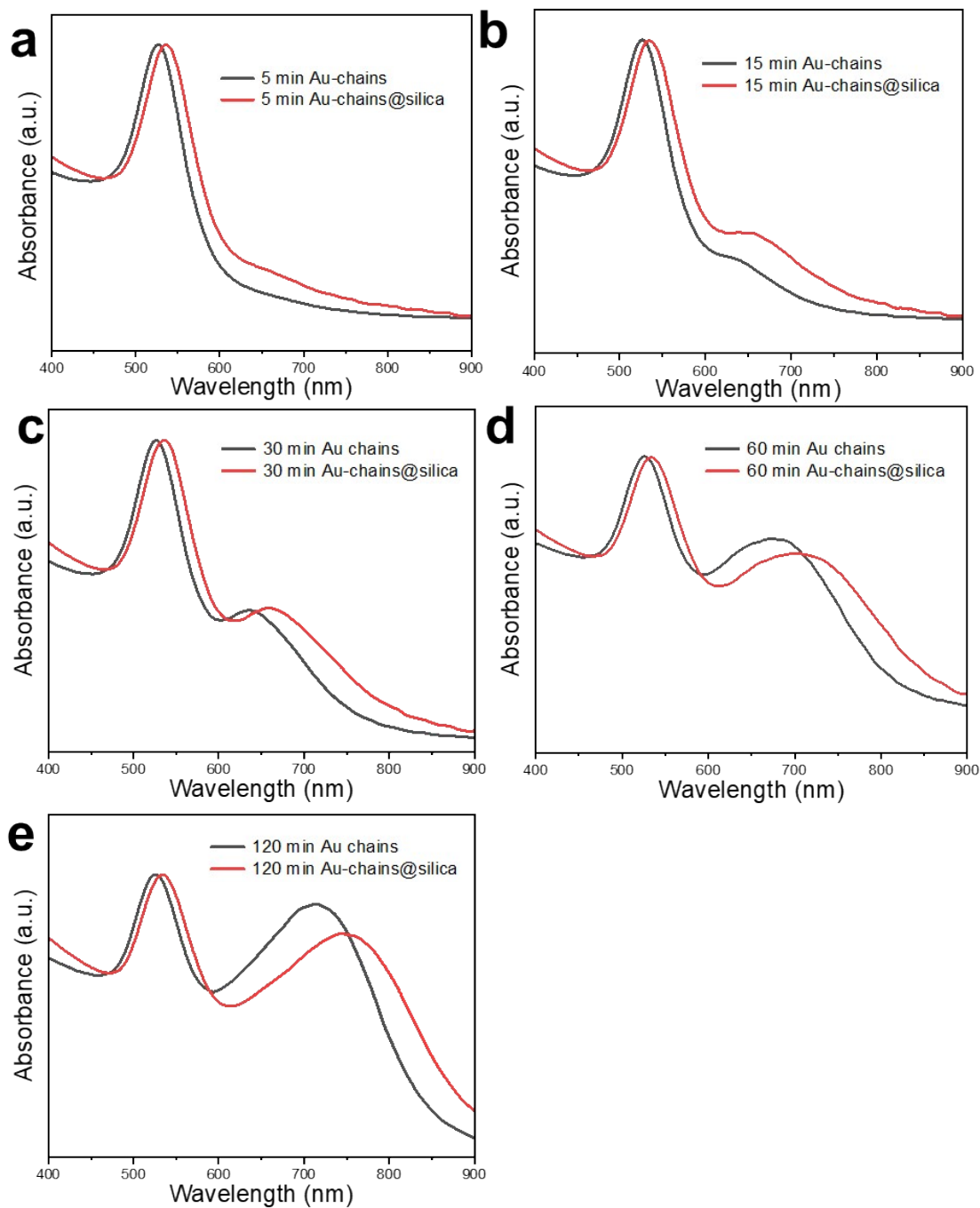**Figure S3.** TEM image of the citrate-stabilized 40 nm AuNPs.

Figure S4. The UV-Vis extinction spectra of Au-chains before and after the silica encapsulation measured at (a) 5, (b) 15, (c) 30, (d) 60, and (e) 120 min, respectively.
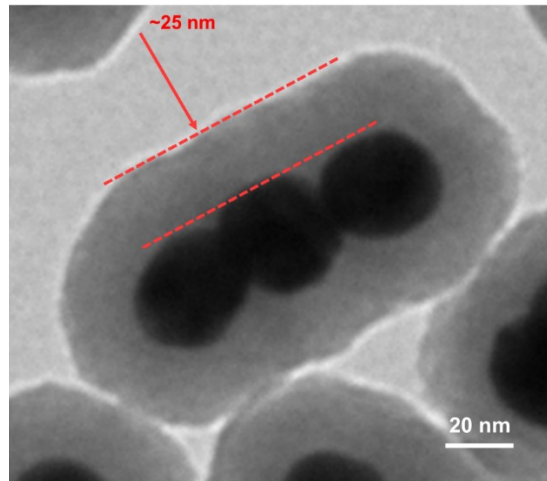
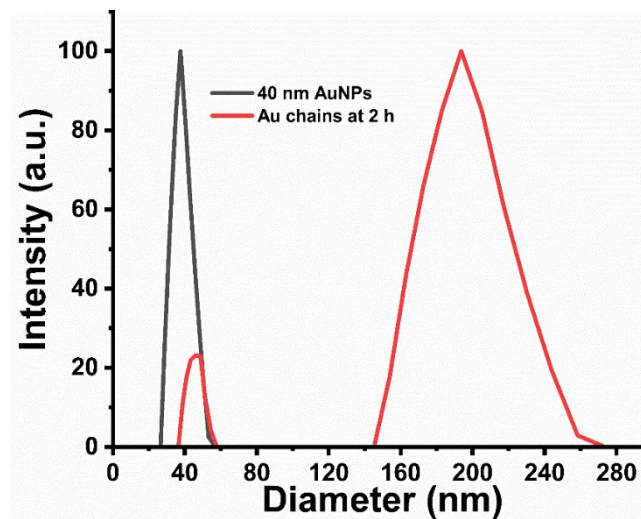**Figure S5.** High magnification TEM image of Au-chain@silica nanostructure and the thickness of the silica shell.

Figure S6. DLS of the AuNPs and Au chains (without silica encapsulation) formed under the standard condition (2 h incubation time).
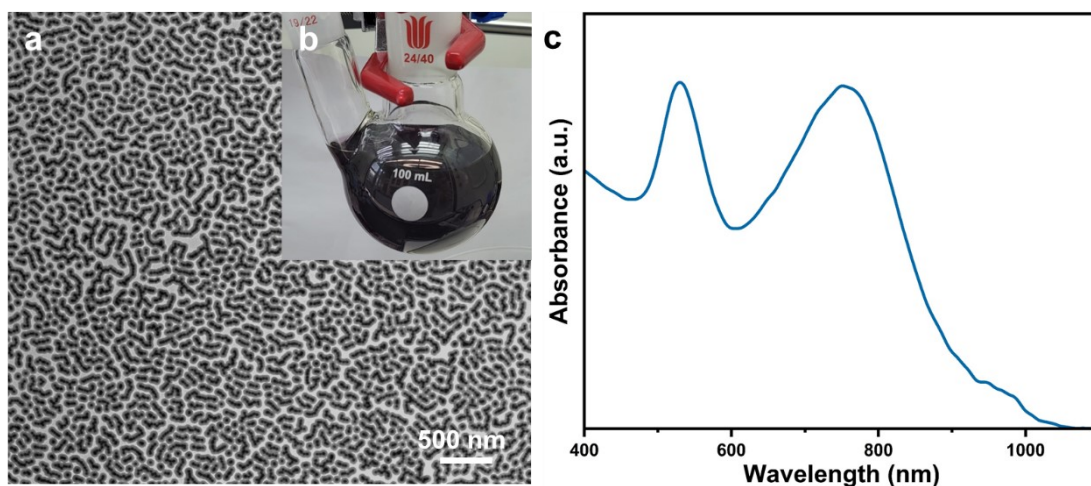
Figure S7. (a) The TEM image of Au-chains@silica at low magnification; inset, a photograph showing the product of a scaled-up synthesis (100 mL); (b) The UV-Vis extinction spectrum of the Au-chains@silica.
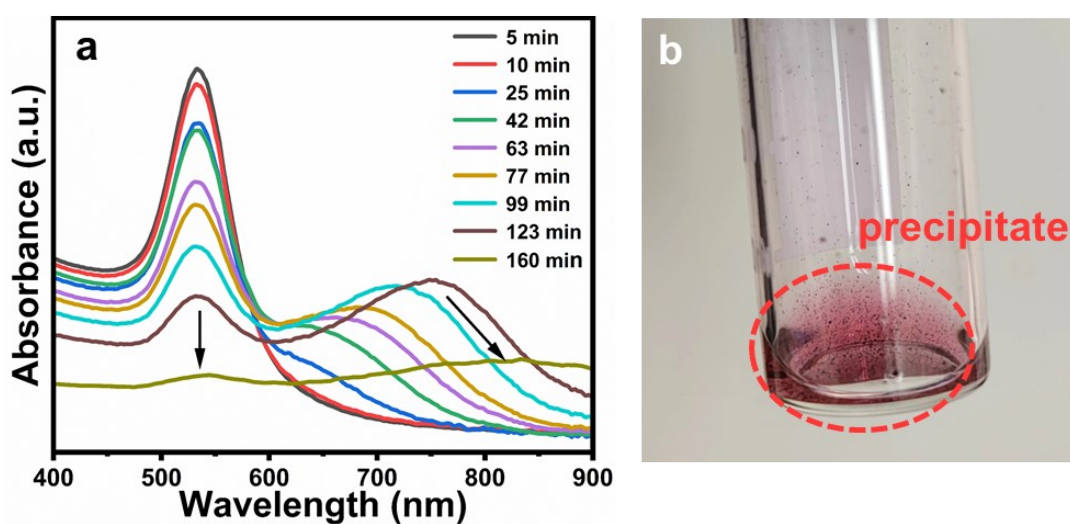
Figure S8. (a) UV-Vis spectra of Au aggregates formed in 2-naphthalentiol/DMF solution with the varied incubation time: 5-160 min; (b) The photograph showing the precipitate appeared at 63 min.
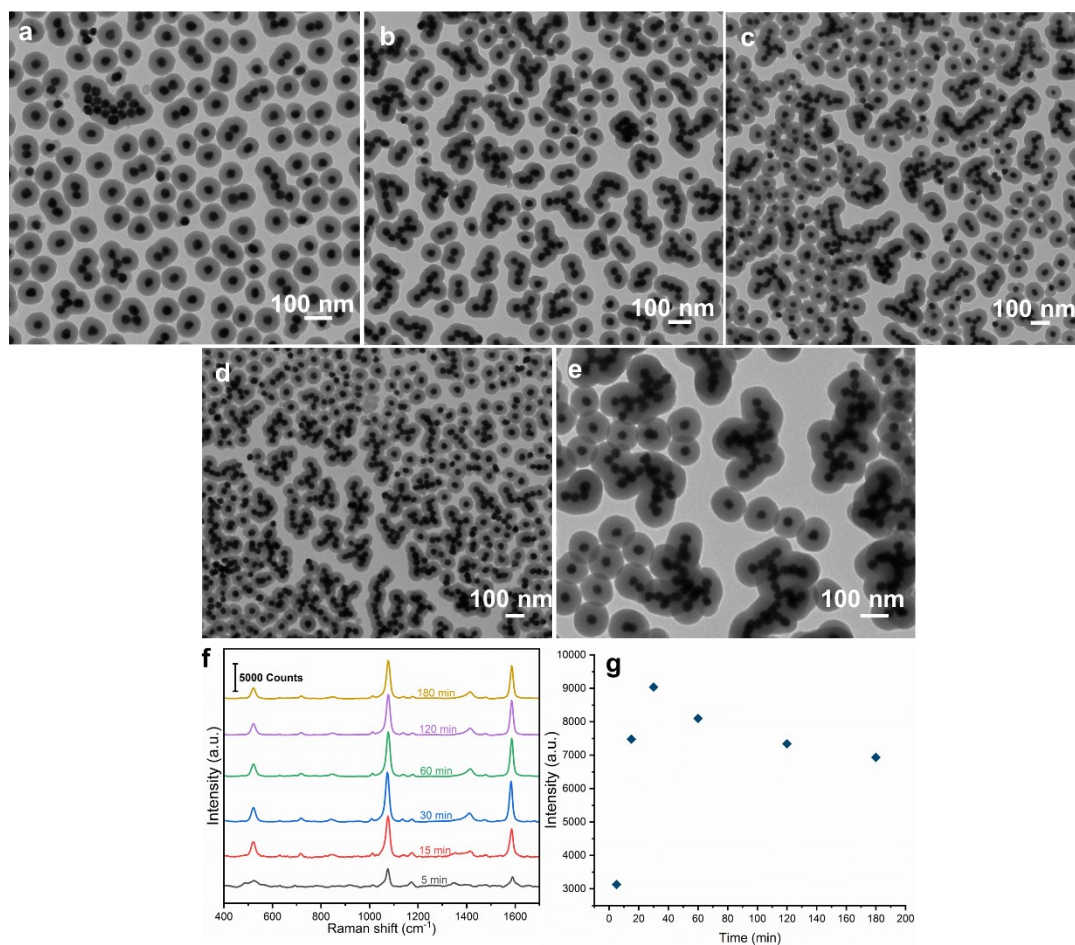
Figure S9. Large-area TEM images of Au-aggregrates@silica nanostructures trapped at different time: (a) 5 min, (b) 30 min, (c) 60 min, (d) 120 min, and (e) 180 min; (f) SERS of the corresponding Au-aggregrates@silica nanostructures; (h) SERS trace of the 1073 cm^{-1} peak for the Au-aggregrates@silica nanostructures against the incubation time.
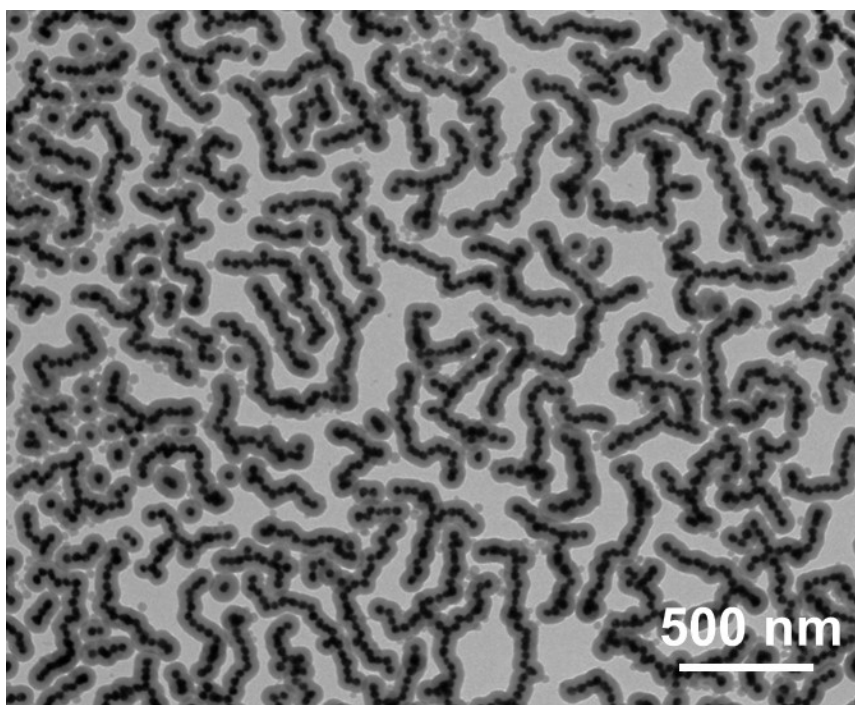
Figure S10. TEM image of Au-chains@silica prepared using [MBA] of 0.207 mM (200% of the standard condition).
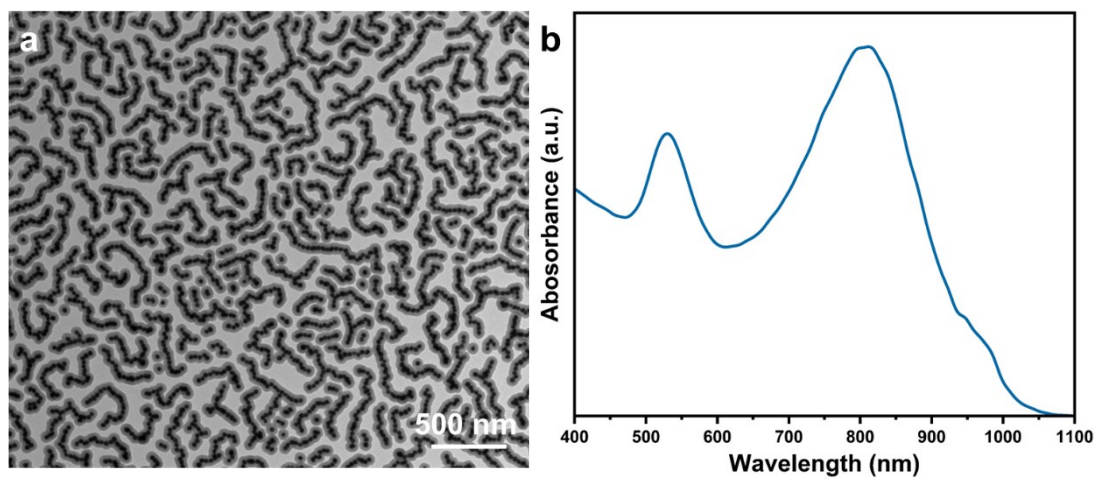
Figure S11. (a) TEM image and (b) UV-Vis spectrum of Au-chains@silica prepared with the 0.138 mM of [MBA] (134% of the standard condition) and the incubation time of 6 h (300% of the standard condition).
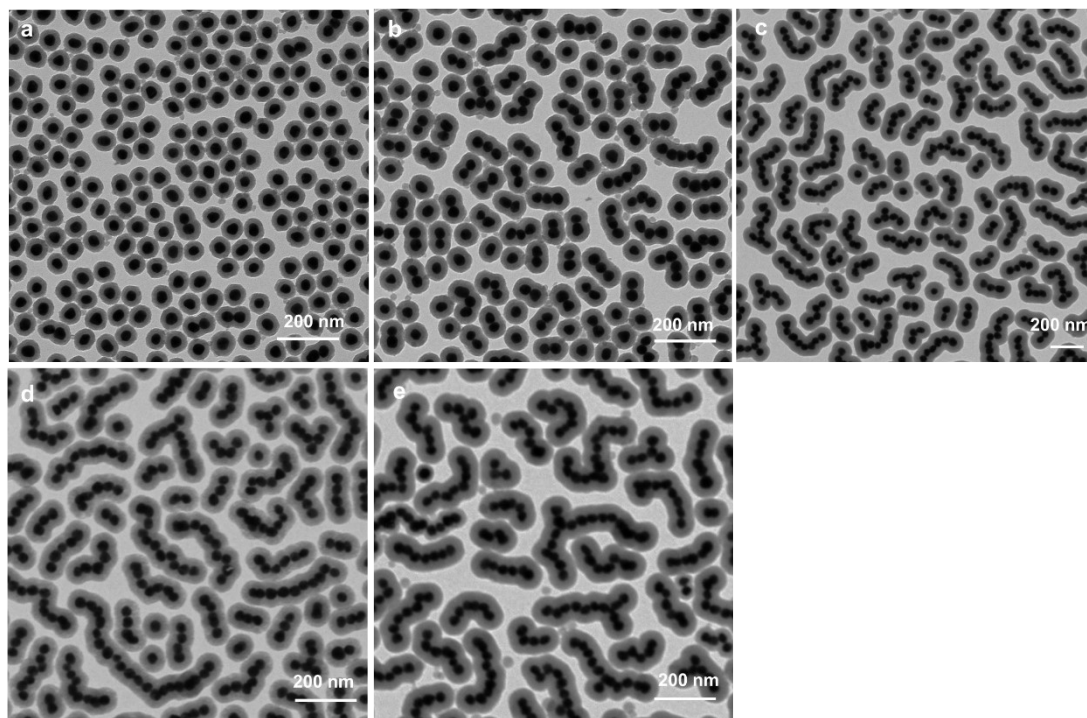
Figure S12. TEM images of Au-chains@silica prepared with different ethanol to water ratio: (a) 1.5: 1, (b) 3.5: 1, (c) 4.8: 1, (d) 7.3: 1, and (e) 13.5: 1.
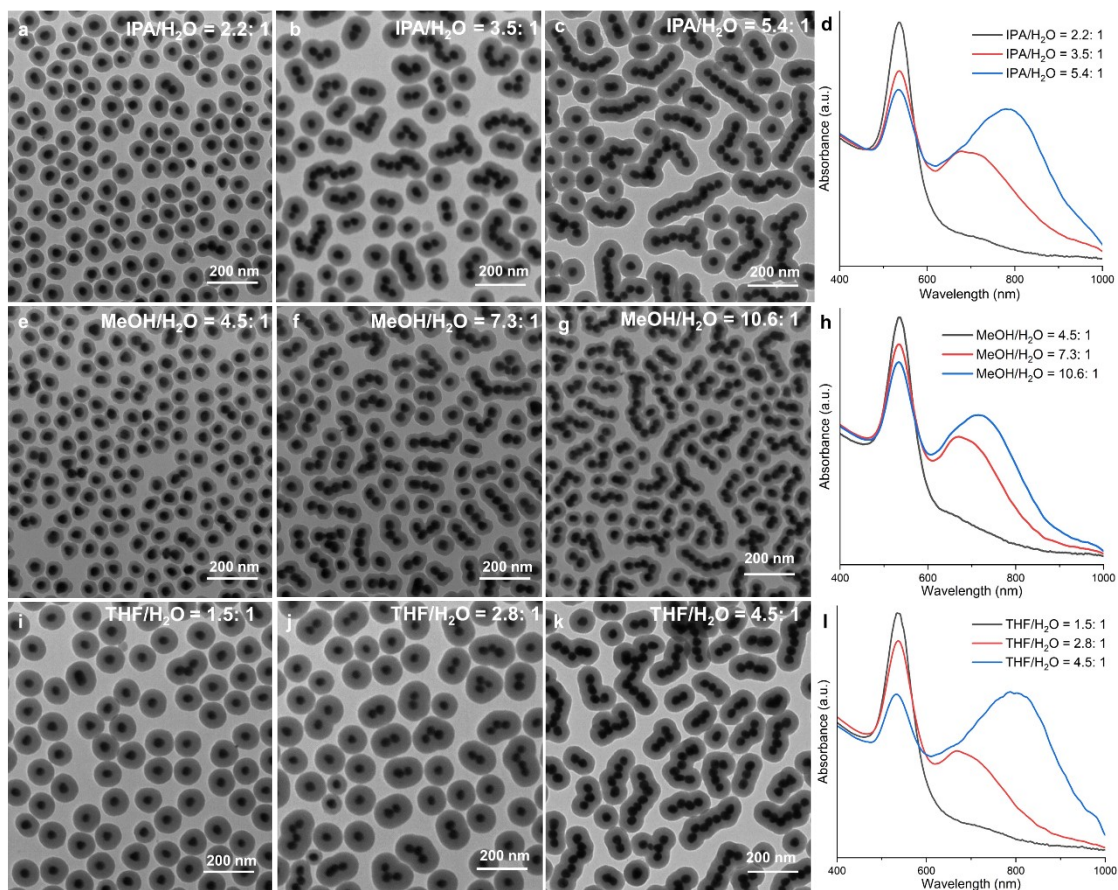
Figure S13. TEM images of Au-chains@silica prepared with different non-polar solvent to water ratio: IPA to water ratio (a) 2.2: 1, (b) 3.5:1, (c) 5.4: 1, and (d) their UV-Vis spectra; MeOH to water ratio (e) 4.5: 1, (f)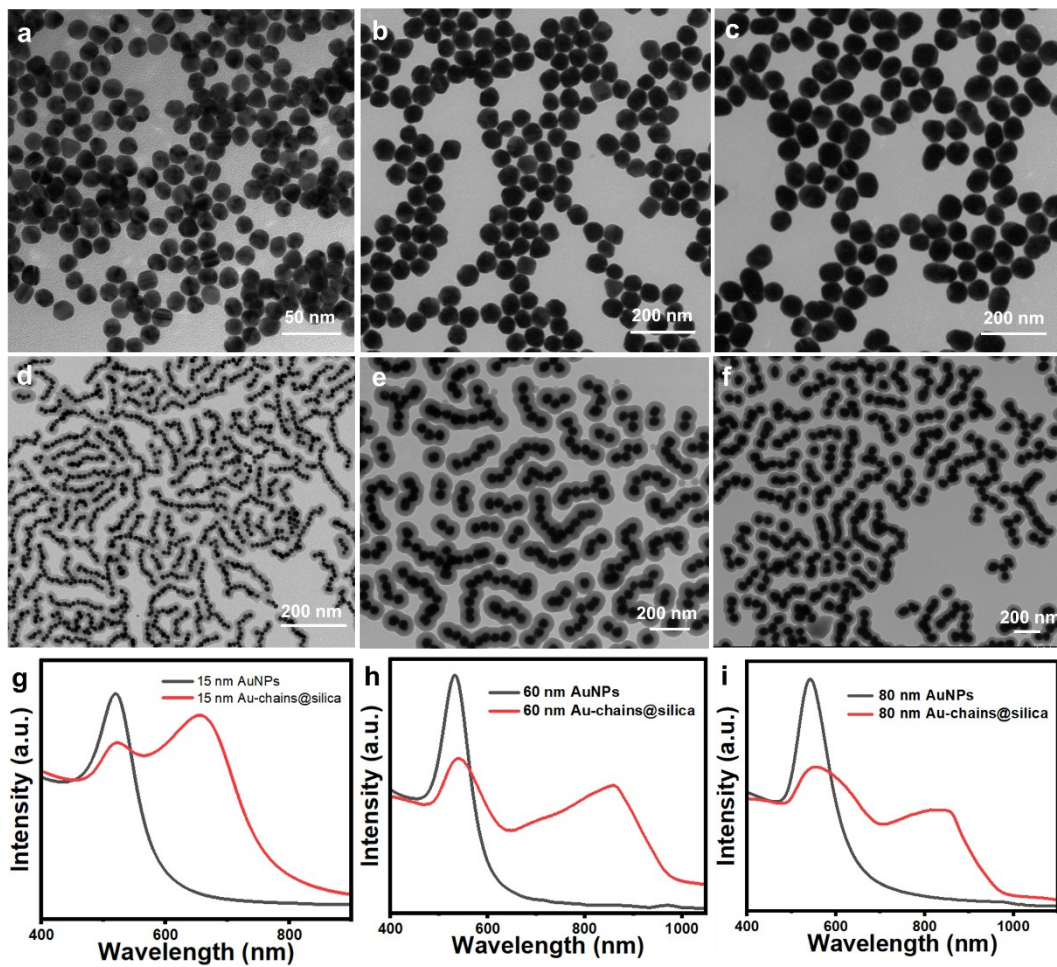 7.3:1, (g) 10.6: 1, and (h) their UV-Vis spectra; THF to water ratio (e) 1.5: 1, (f) 2.8:1, (g) 4.5: 1, and (l) their UV-Vis spectra.

Figure S14. TEM images of the synthesized Au nanoparticles and the corresponding Au-chains@silica: (a, d) 15 nm, (b, e) 60 nm, and (c, f) 80 nm; and (g-i) UV-Vis extinction spectra of the samples a-f.
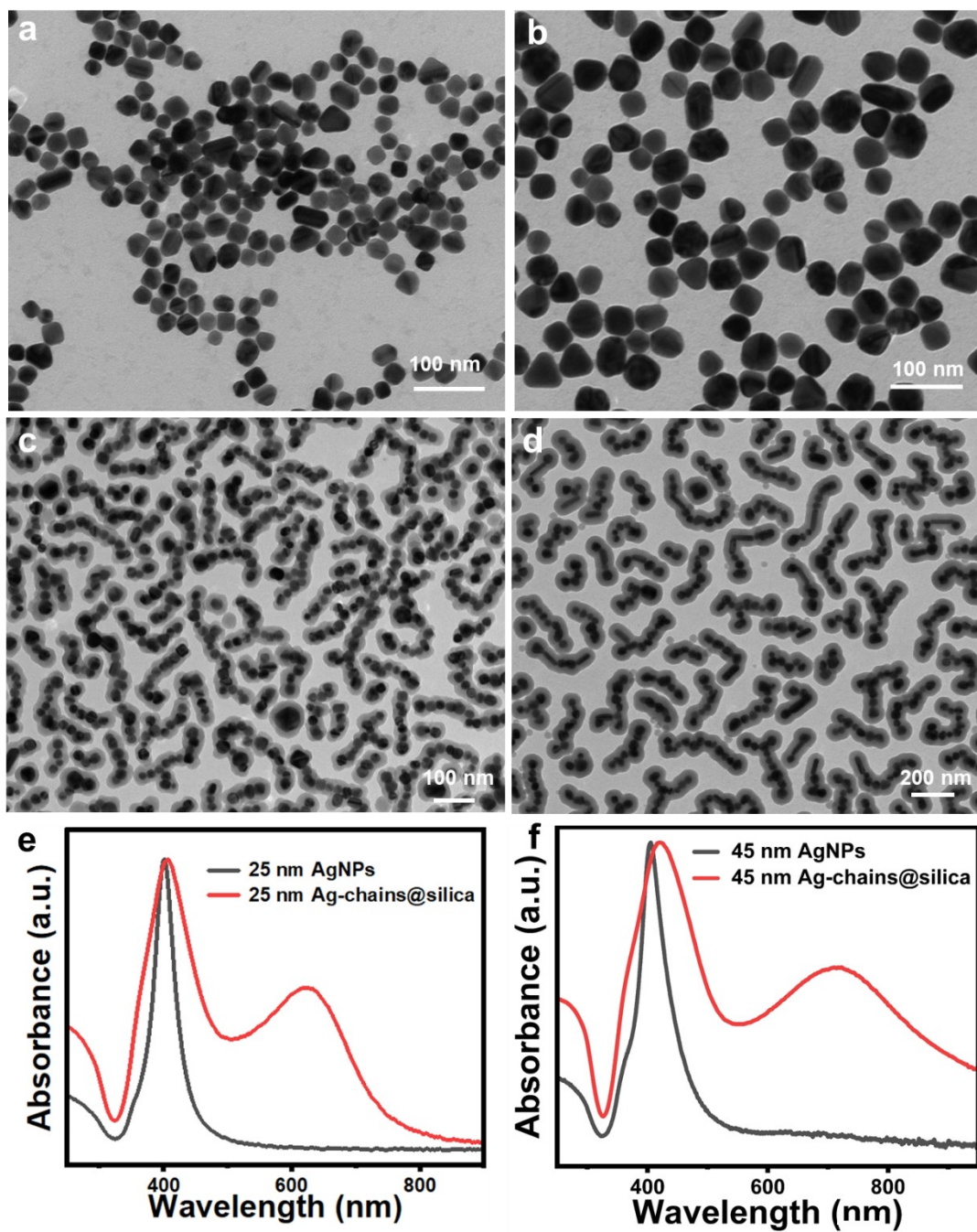
Figure S15. TEM images of the synthesized AgNPs and the corresponding Ag-chains@silica: (a, c) 25 nm, and (b, d) 45 nm; (e, f) UV-Vis extinction spectra of samples a-d.
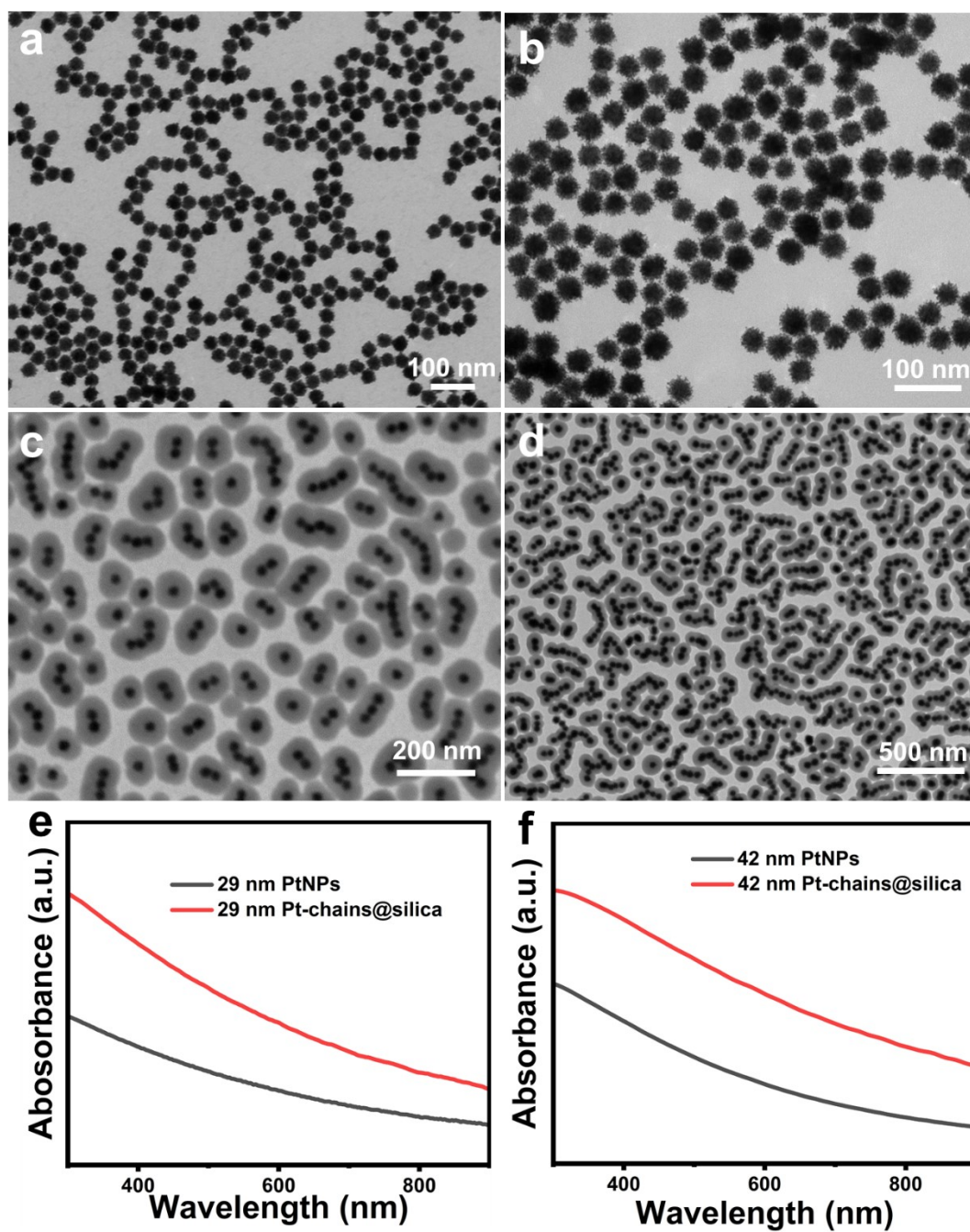
Figure S16. TEM images of synthesized PtNPs and the corresponding Pt-chains@silica: (a, c) 29, and (b, d) 42 nm; (e, f) the UV-Vis spectra of the samples a-d.
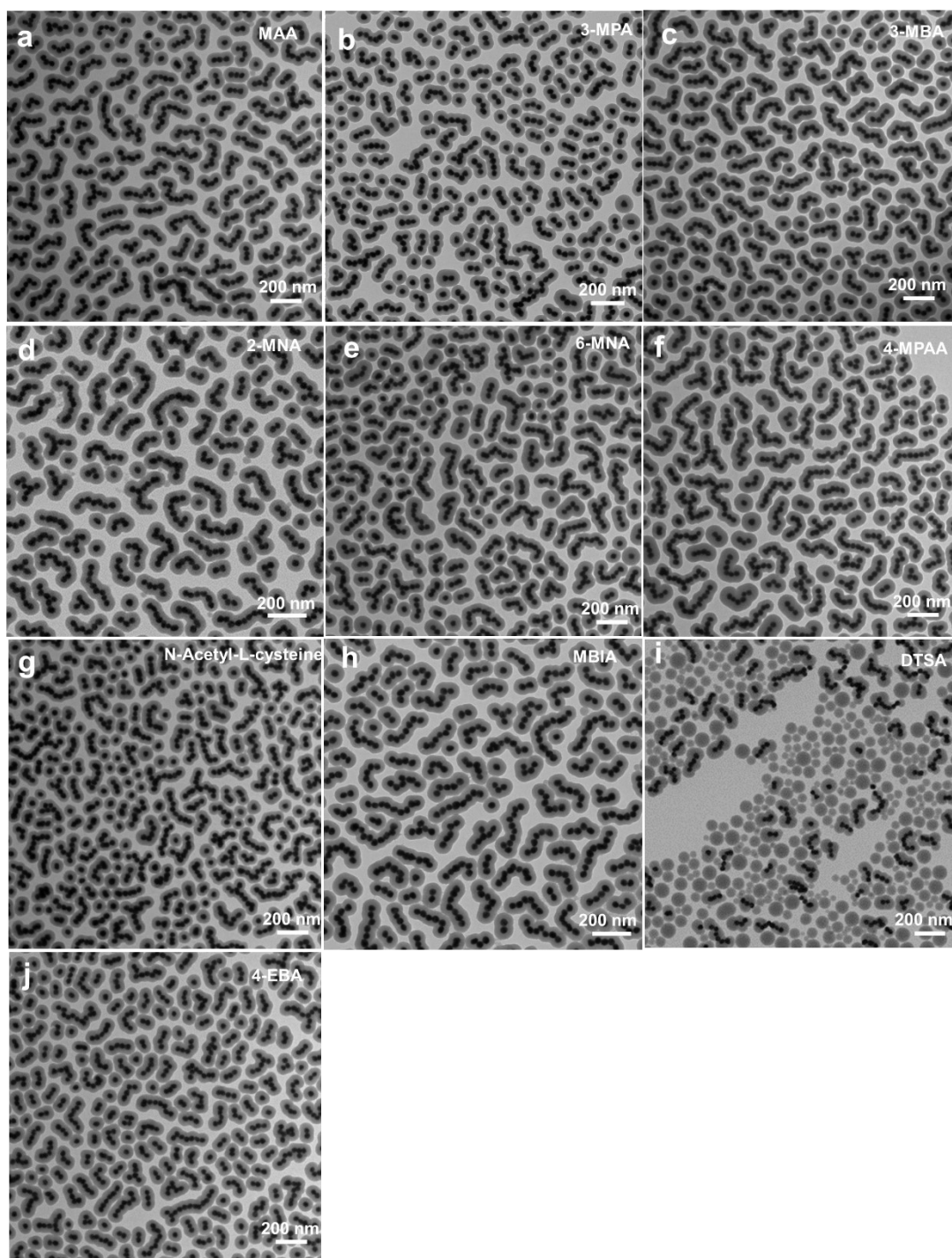
Figure S17. TEM images of Au-chains@silica prepared with different ligands as shown in Table 2.
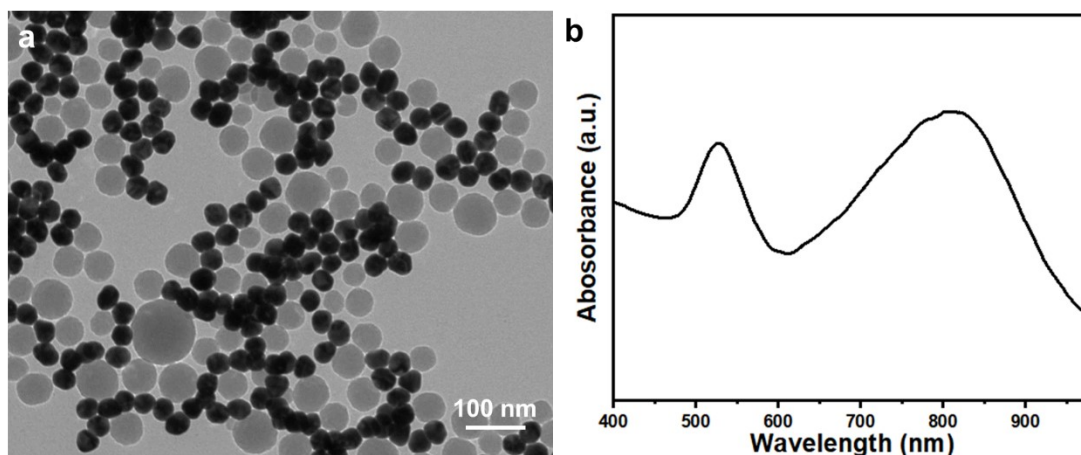
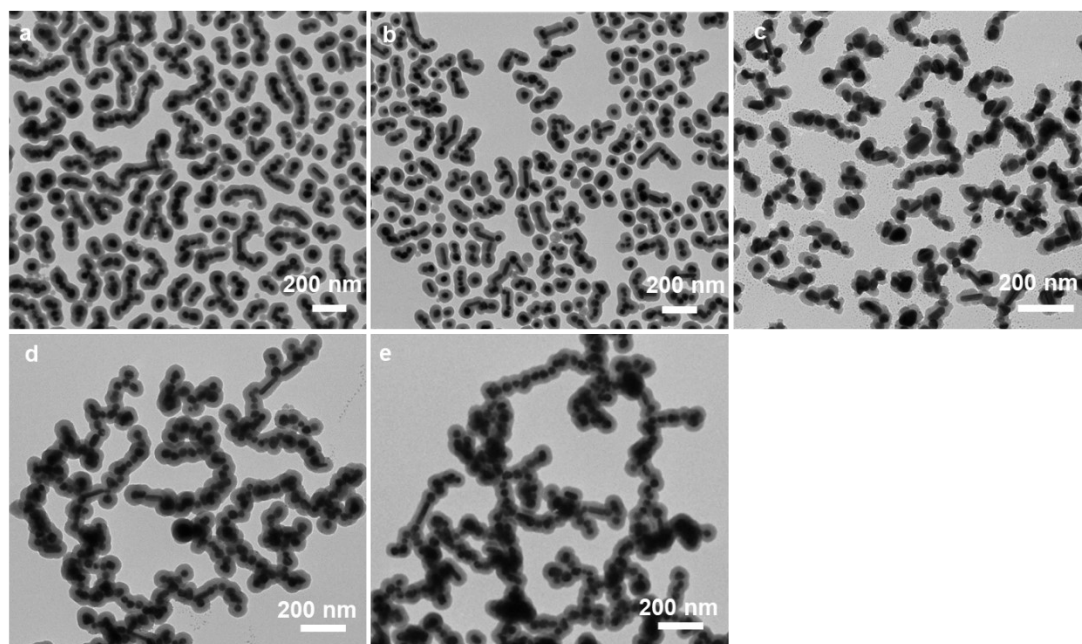**Fig. S18.** (a) TEM image and (b) UV-Vis spectra of Au-chains@silica prepared with ligand 3-mercapto-1-propanol.

Figure S19. TEM images of Ag-chains@silica prepared with (a) MBA; (b) 3-MBA; (c) 2-MNA; (d) 6-MNA; and (e) MBIA.

References

1. Y. Feng, J. He, H. Wang, Y. Y. Tay, H. Sun, L. Zhu and H. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 2004-2007.

2. Y. Feng, Y. Wang, J. He, X. Song, Y. Y. Tay, H. H. Hng, X. Y. Ling and H. Chen, *J. Am. Chem. Soc.*, 2015, **137**, 7624-7627.

3. G. Frens, *Nat. Phys. Sci.*, 1973, **241**, 20-22.

4. M. Yang, G. Chen, Y. Zhao, G. Silber, Y. Wang, S. Xing, Y. Han and H. Chen, *Phys. Chem. Chem. Phys.*, 2010, **12**, 11850-111860.

5. Y. Wan, Z. Guo, X. Jiang, K. Fang, X. Lu, Y. Zhang and N. Gu, *J. Colloid. Interface. Sci.*, 2013, **394**, 263-268.

6. R. Dasari, D. A. Robinson and K. J. Stevenson, *J. Am. Chem. Soc.*, 2013, **135**, 570-

573.

7.   G. Chen;, Y. Wang;, M. Yang;, J. Xu;, S. J. Goh;, M. Pan; and H. Chen., *J. Am. Chem. Soc.*, 2010, **132**, 3644-3645.