Electronic Supplementary Information (ESI)

Mesoporous gold nanospheres *via* thiolate-Au(I) intermediates

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1. Chemicals and Materials

Chloroauric acid ($HAuCl_4$), silver nitrate ($AgNO_3$), hexadecyltrimethylammonium Chloride (CTAC), dioctadecyldimethylammonium chloride (DODAC), and thiourea was purchased from Alfa Aesar. Hydrochloric acid, isopropanol, methanol, acetonitrile, hydrazine hydrate (N_2H_4, 50%), and diethyl ether were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai). 3-chloro-1-propanethiol was obtained from Sigma-Aldrich. N,N-dimethyldocosylamine was purchased from Heowns Opde Technologies (Tianjin). Behenyltrimethylammonium chloride (C_{22}TAC) and N-(carboxymethyl)-N,N-dimethylheptadecan-1-aminium chloride (C_{22}TACOOH) were synthesized according to our previously reported procedures.(S*1*) All the reagents were of analytical reagent grade and used without further purification.

2. Synthesis of C_{22}N-SH

In a typical synthesis of C_{22}N-SH, 7.5 g of N,N-dimethyldocosylamine (10 mM) and 2.2 g of 3-Chloro-1-propanethiol were totally mixed in 120 ml of acetonitrile and then refluxed under 95 ^oC for 24 h. After the removal of solvent by reduced pressure distillation, the crude product was washed with diethyl ether several times and dried in a vacuum oven overnight. The product of C_{22}N-SH was verified by ^1H NMR (500 MHz, CD_3OD): δ 3.15-3.04 (m, 1H), 2.97-2.84 (m, 2H), 2.71 (s, 6H), 1.64-1.67 (m, 2H), 1.27-1.39 (m, 44H), 0.89 (t, J = 7.1 Hz, 3H), and ^{13}C NMR (500 MHz, CD_3OD): δ 59.46, 43.84 (2C), 33.10, 30.90 (15C), 30.69, 30.58, 30.51, 30.34, 27.73, 26.31, 23.77, 14.48.

3. Au-4 and Au-70 nanoparticles: solid Au-4 and Au-70 nanoparticles were synthesized according to previous reports.(S*2, S3*)

Supporting References

S1. D. Xu, X. Liu, H. Lv, Y. Liu, S. Zhao, M. Han, J. Bao, J. He, B. Liu, Ultrathin Palladium Nanosheets with Selectively Controlled Surface Facets. *Chem. Sci.* **9**, 4451-4455 (2018).

S2. S. Pedireddy, H. K. Lee, W. W. Tjiu, I. Y. Phang, H. R. Tan, S. Q. Chua, C. Troadec, X. Y. Ling, One-Step Synthesis of Zero-Dimensional Hollow Nanoporous Gold Nanoparticles with Enhanced Methanol Electrooxidation Performance. *Nat. Commun.* **5**, 4947 (2014).

S3. J. Fang, L. Zhang, J. Li, L. Lu, C. Ma, S. Cheng, Z. Li, Q. Xiong, H. You, A General Soft-Enveloping Strategy in the Templating Synthesis of Mesoporous Metal Nanostructures. *Nat. Commun.* **9**, 521 (2018).

6. Figures and Table

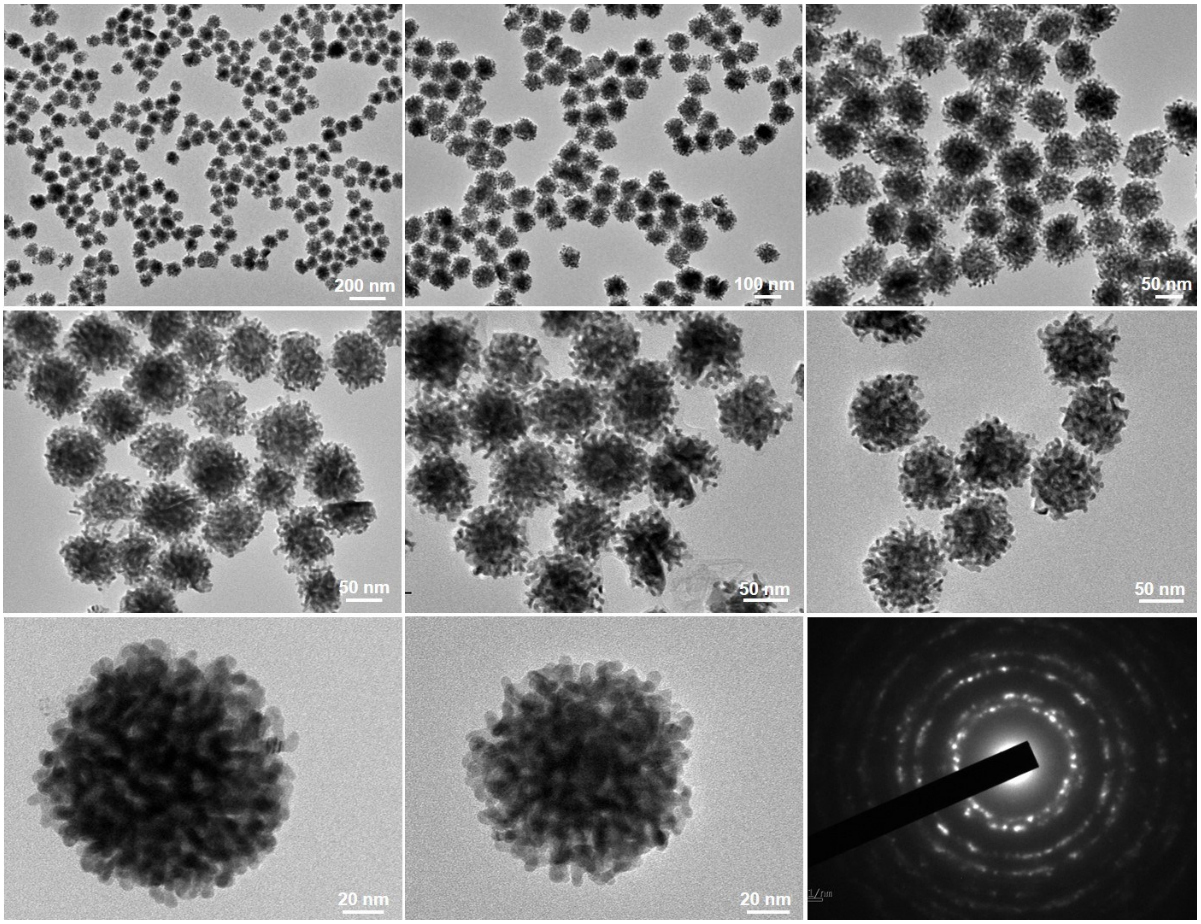

Figure S1. More TEM images of mesoAu-74 nanospheres with different magnifications. The results definitely exhibited the spherical shape with 3D interconnected mesochannels.

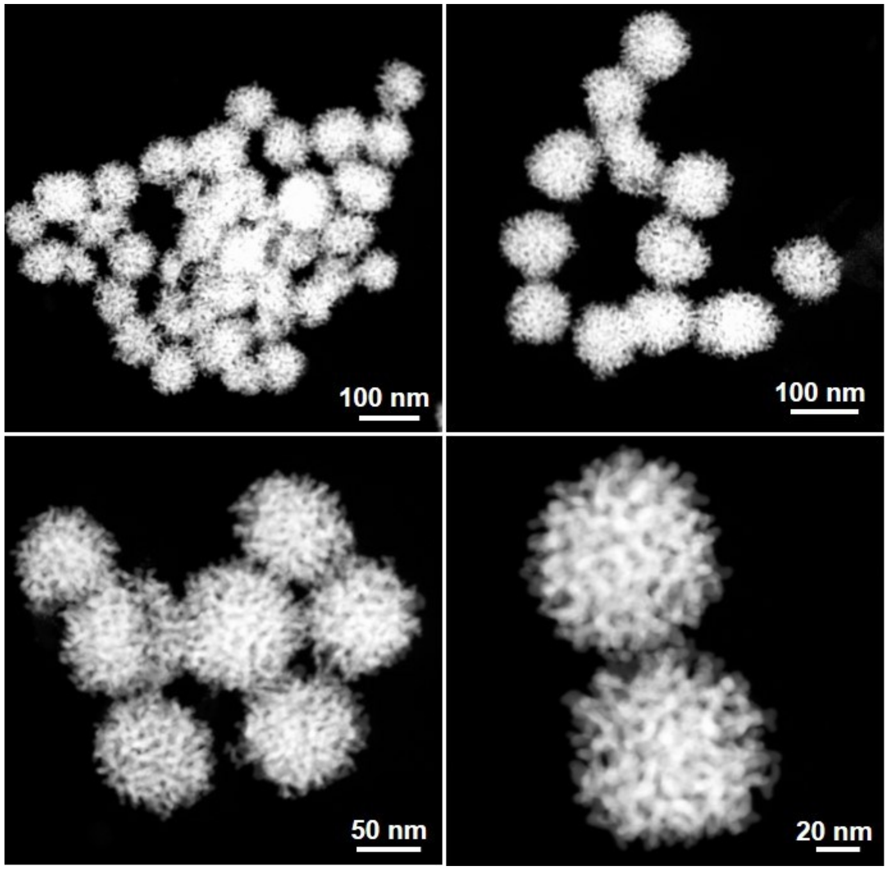

Figure S2. More HAADF-STEM images of mesoAu-74 nanospheres.

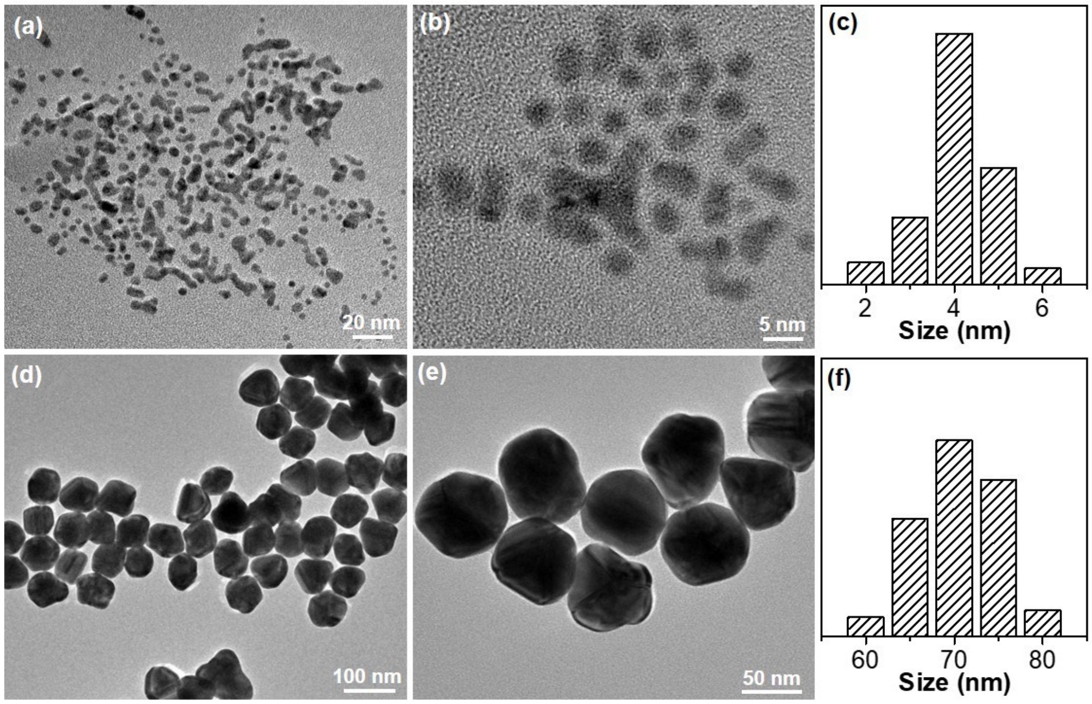

Figure S3. Structural characterizations of Au-4 and Au-70 bulk nanoparticles. TEM images and corresponding size distributions of (a-c) Au-4 and (d-f) Au-70 nanoparticles.

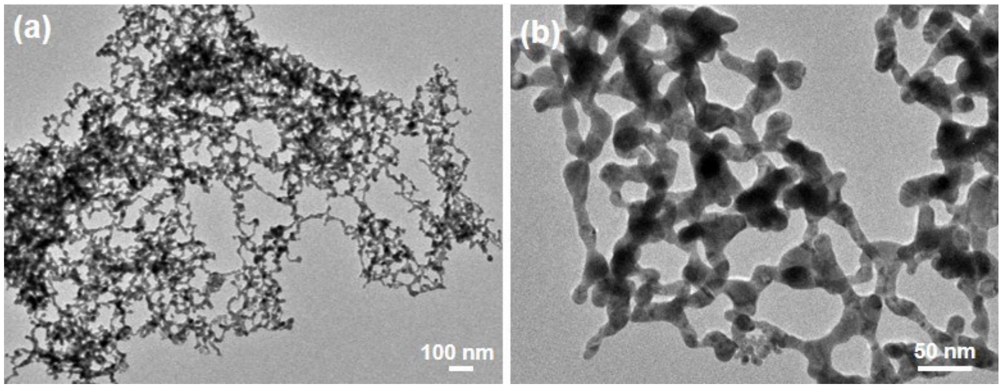

Figure S4. TEM of Au nanostructures synthesized in the absence of the surfactant.

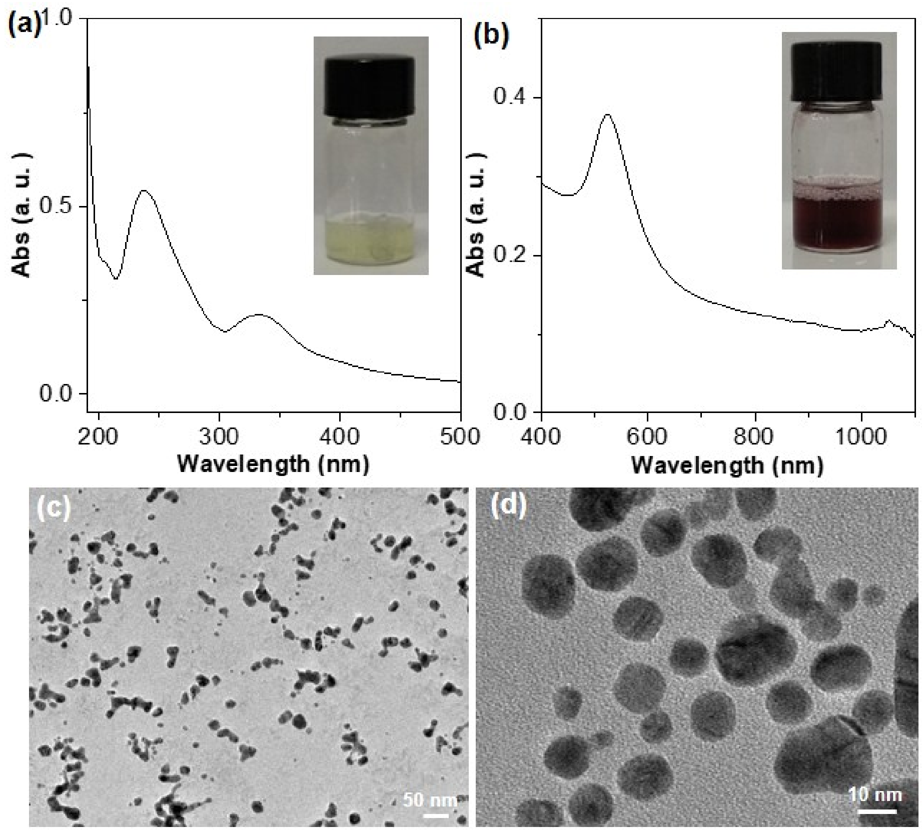

Figure S5. Au nanostructures synthesized with the surfactant of CTAC. UV-vis spectra of (a) solution of CTAC/$HAuCl_4$ and (b) resultant nanostructure, and (c, d) corresponding TEM images.

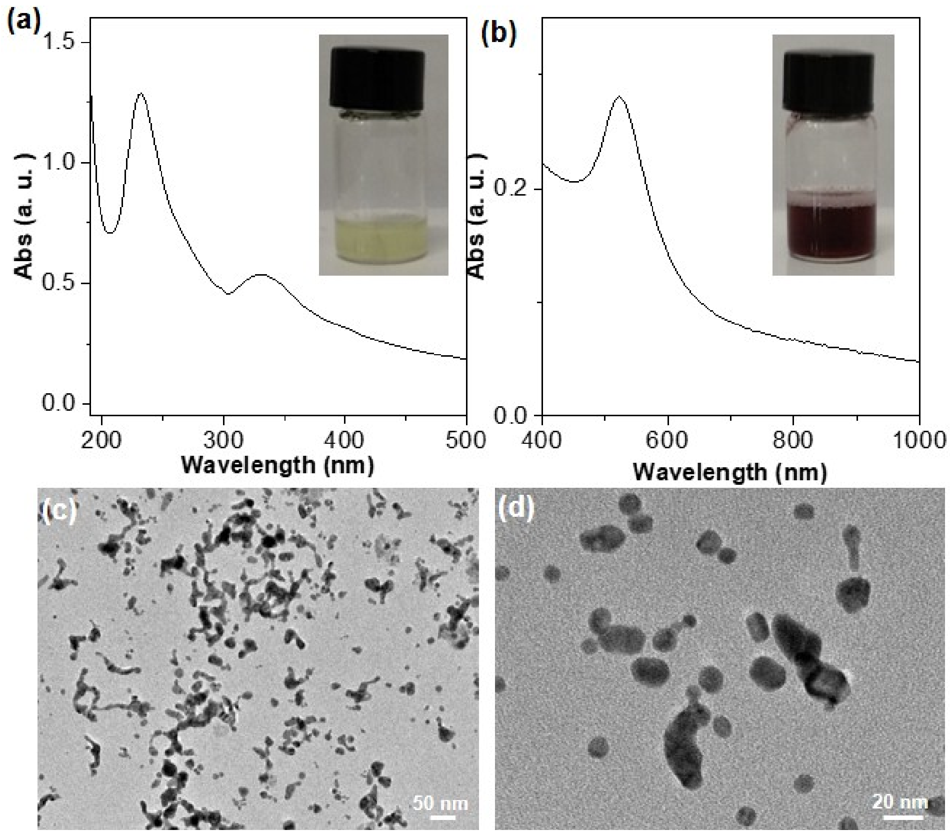

Figure S6. Au nanostructures synthesized with the surfactant of C_{22}TAC. UV-vis spectra of (a) solution of C_{22}TAC/$HAuCl_4$ and (b) resultant nanostructure, and (c, d) corresponding TEM images.

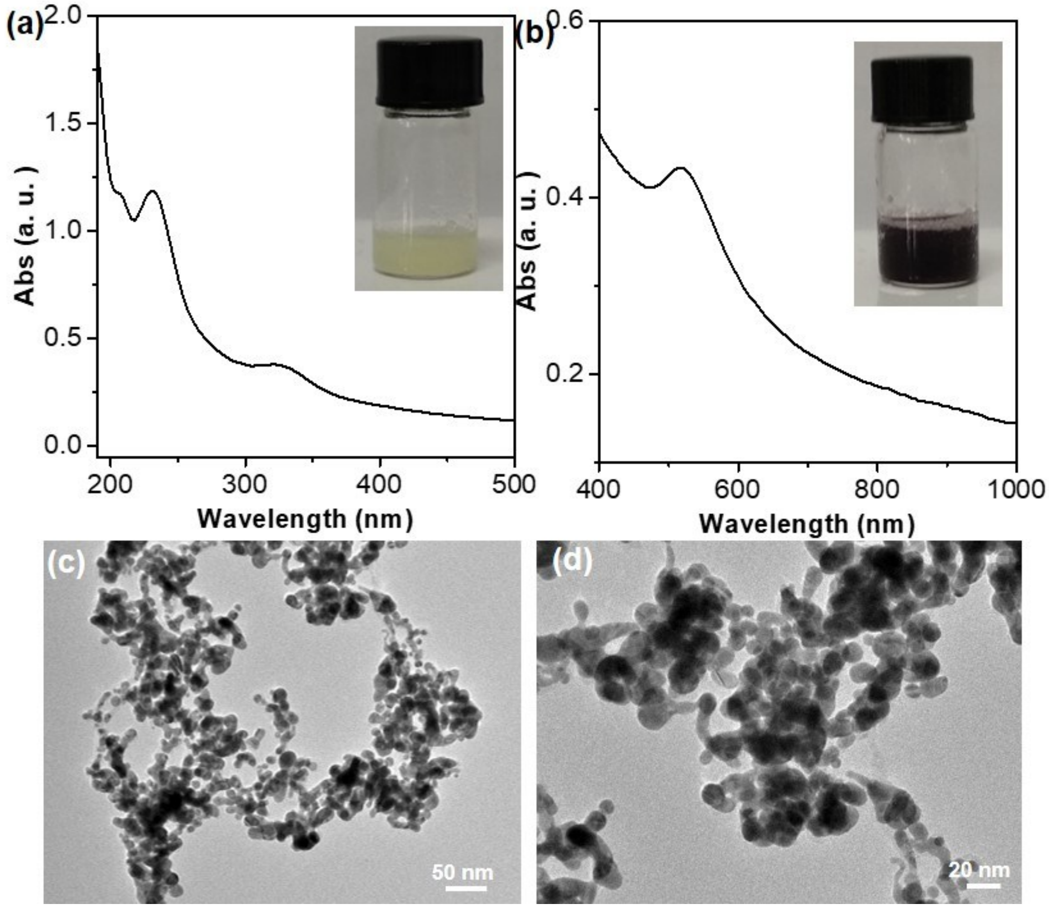

Figure S7. Au nanostructures synthesized with the surfactant of DODAC. UV-vis spectra of (a) solution of DODAC/$HAuCl_4$ and (b) resultant nanostructure, and (c, d) corresponding TEM images.

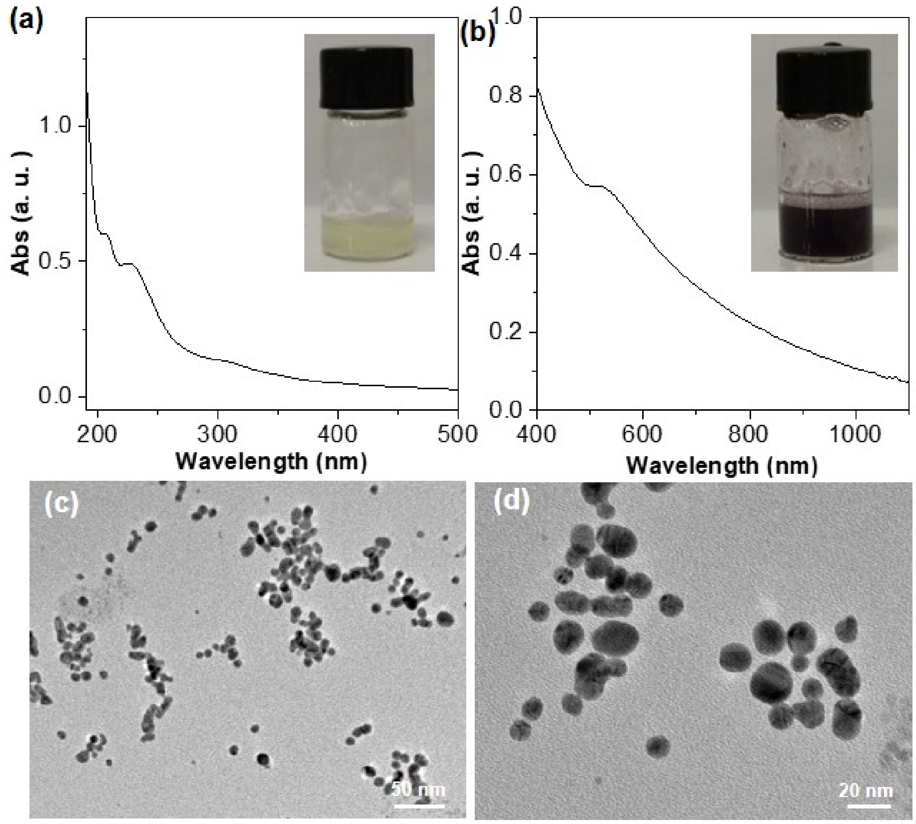

Figure S8. Au nanostructures synthesized with the surfactant of C_{22}TACOOH. UV-vis spectra of (a) solution of C_{22}TACOOH/$HAuCl_4$ and (b) resultant nanostructure, and (c, d) corresponding TEM images.

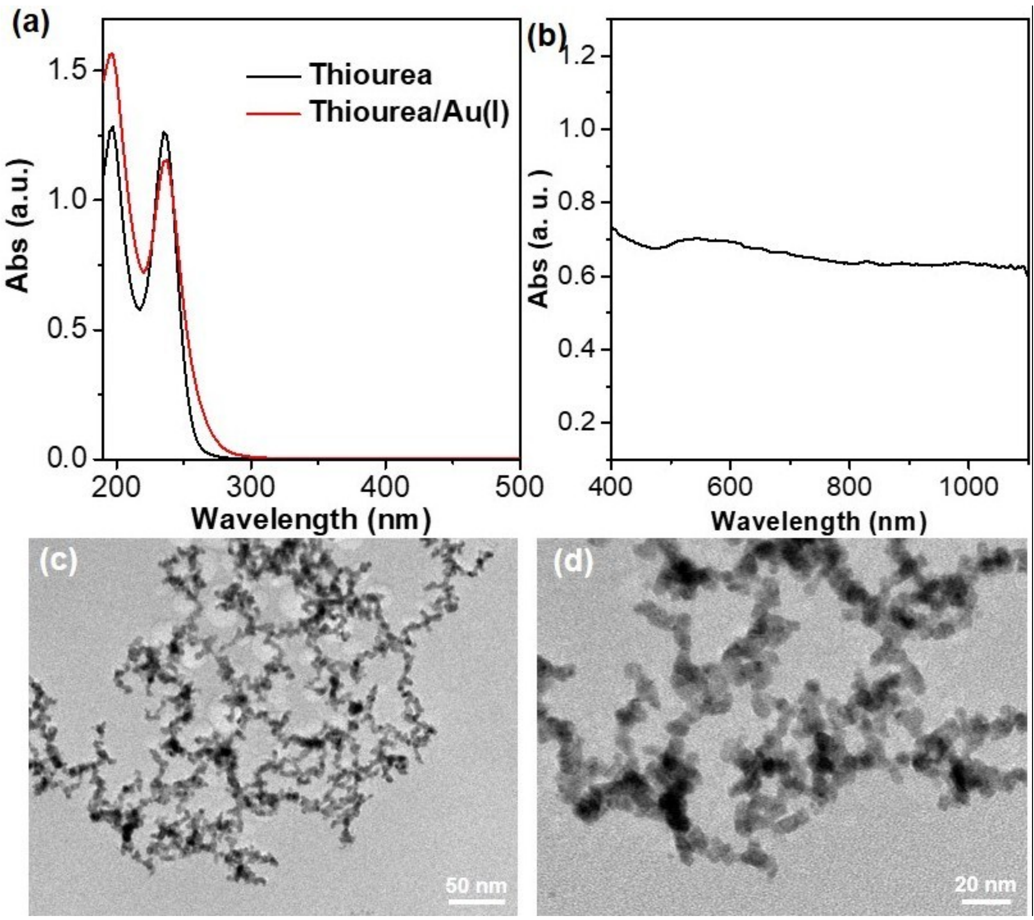

Figure S9. Au nanostructures synthesized with thiourea. UV-vis spectra of (a) the solution of thiourea/$HAuCl_4$ and (b) resultant nanostructure, and (c, d) corresponding TEM images.

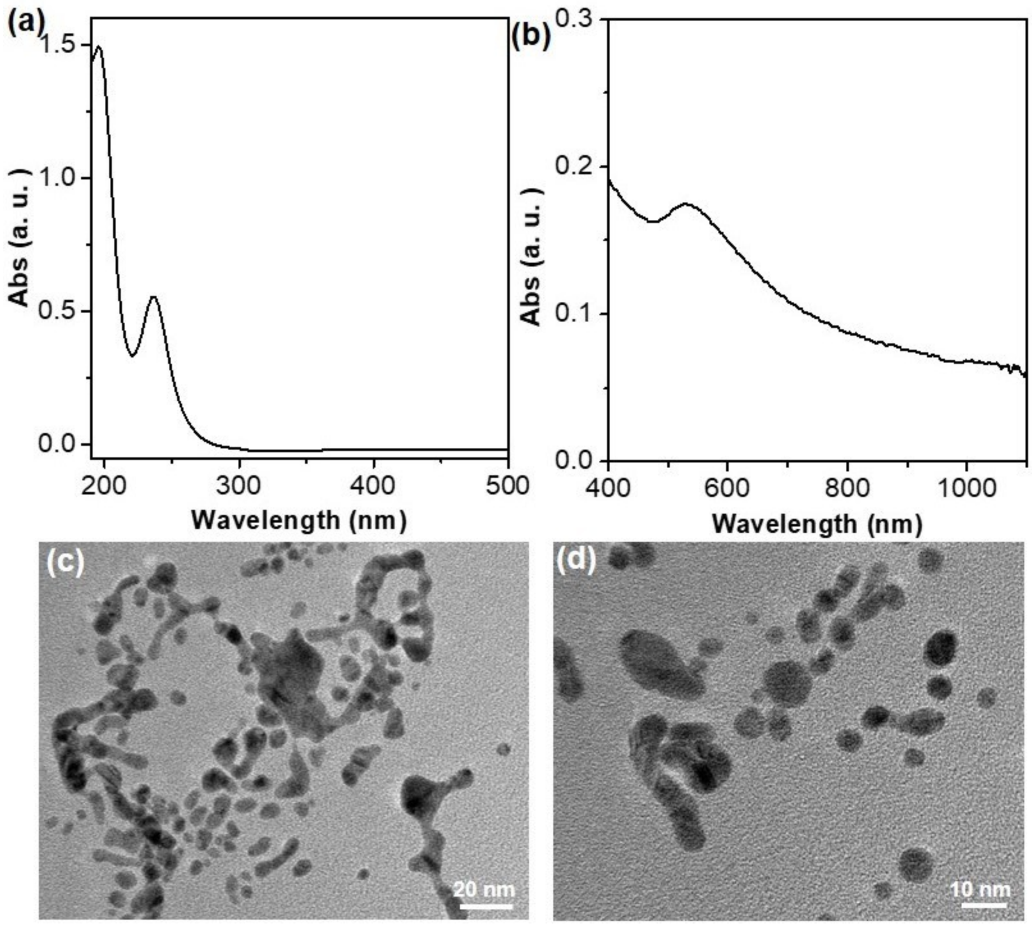

Figure S10. Au nanostructures synthesized with the mixed surfactants of thiourea and $C_{22}TAC$. UV-vis spectra of (a) solution of thiourea/$C_{22}TAC/HAuCl_4$ and (b) resultant nanostructure, and (c, d) corresponding TEM images.

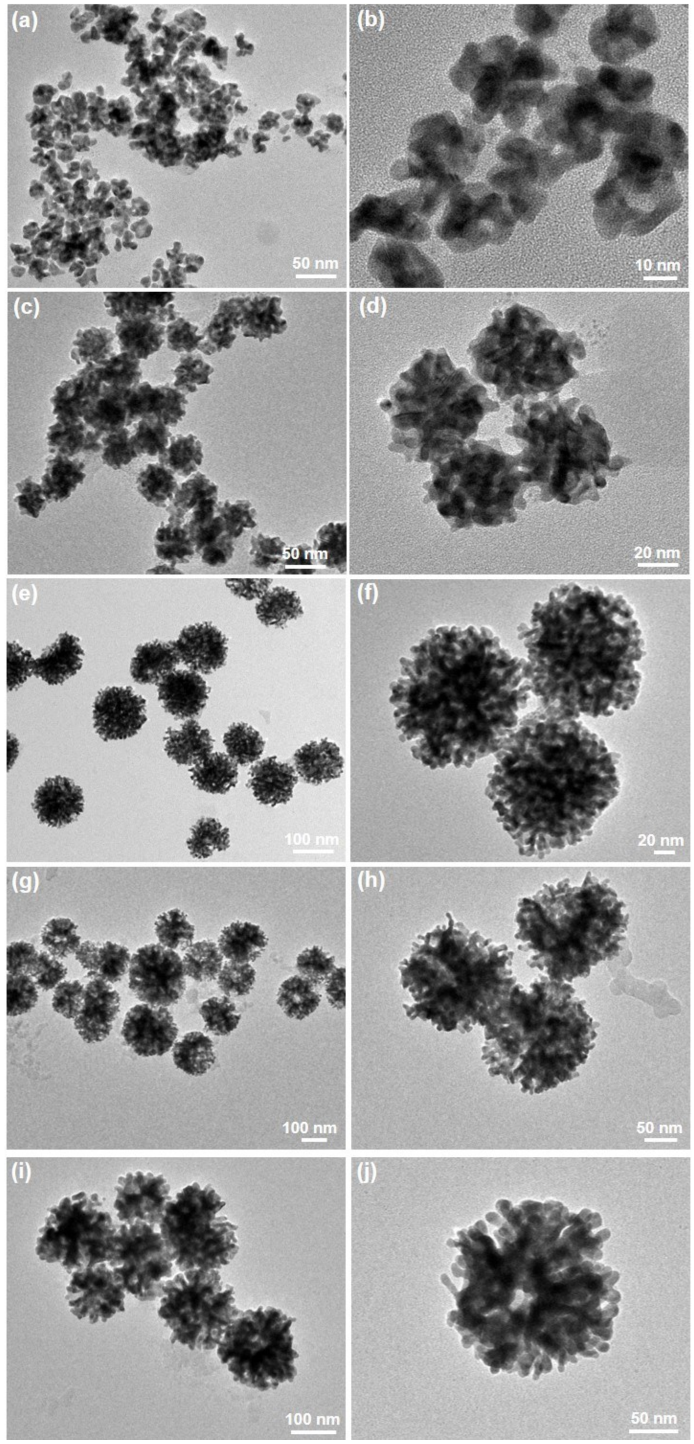

Figure S11. Synthesis of mesoAu nanospheres with different sizes and porosities under different reaction temperatures. TEM images of mesoAu nanoshperes synthesized under the temperature of (a, b) 0 ^{o}C, (c, d) 25 ^{o}C, (e, f) 50 ^{o}C, (g, h) 75 ^{o}C, and (i, j) 95 ^{o}C.

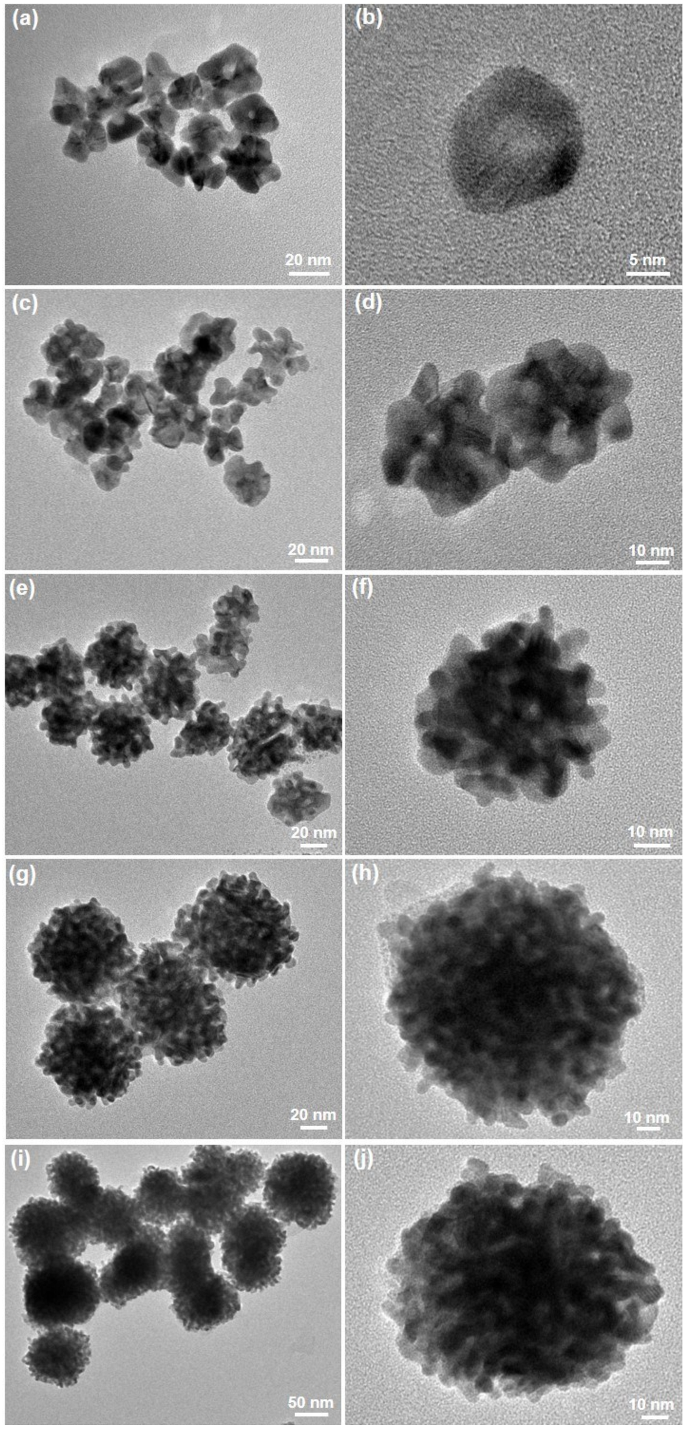

Figure S12. Synthesis of mesoAu nanospheres with different sizes and porosities under different pH at 25 ^{o}C. TEM images of mesoAu nanospheres synthesized under the pH of (a, b) 1.2, (c, d) 1.8, (e, f) 3.4, (g, h) 4.2, and (i, j) 4.8.

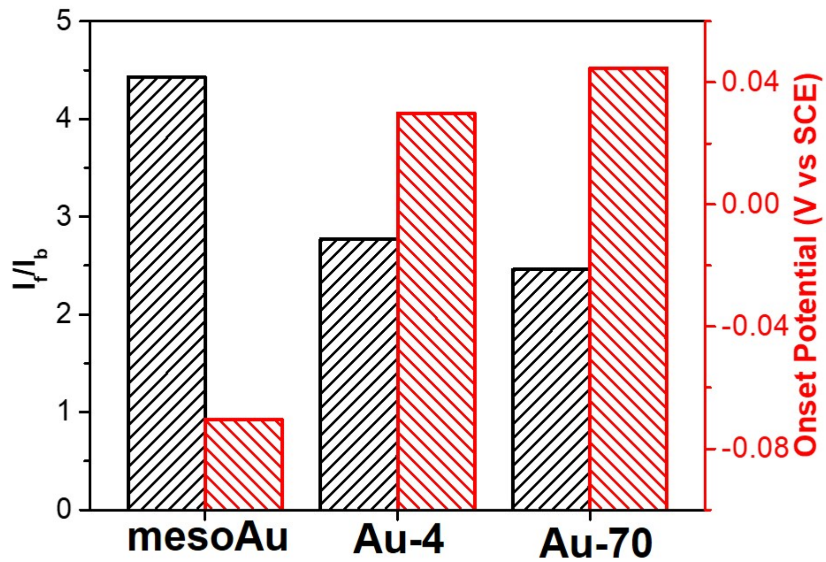

Figure S13. Summarized I_f/I_b values and onset potentials of the mesoAu nanospheres, non-porous Au-4 and Au-70 NPs.

Table S1. Summarizations of the activity of nanostructured Au catalysts in the electrocatalytic MOR.

Nanocatalysts	Measurement Conditions			Activity		Ref.
	Scan rate (mV s^{-1})	CH_3OH con. (M)	KOH con. (M)	Mass activity (μA $μg^{-1}$)[a]	Specific activity (mA cm^{-2})	
mesoAu nanospheres	20	2.0	0.5	30.7	0.32	This work
mesoAu network	10	2.0	0.5	13.1	0.21	*Nat. Commun.* **2018**, *9*, 521
Au nanobowls	10	2.0	0.5	26	0.09	*Small*, **2016**, *12*, 4531
Nanoporous Au	10	1.0	0.5	28	0.25	*ACS Appl. Mater. Interfaces* **2016**, *8*, 23920
MesoAu film	20	2.0	1.0	-	0.2	*Nano Res.* **2016**, *9*, 1752
Fern-like Au film	50	1.0	0.5	-	0.16	*Electrochim. Acta* **2016**, *216*, 88
Nanoporous Au nanoparticles	20	2.0	0.5	16.8	0.117	*Nat. Commun.* **2014**, *5*, 4947
Au nanoparticles on carbon	50	1.0	0.1	~21	0.14	*Electrochim. Acta* **2013**, *94*, 159
Nanoporous Au film	10	1.0	0.5	-	0.11	*J. Phys. Chem. C* **2007**, *111*, 10382
Au nanoparticles	50	1.0	1.0	~20	0.12	*Electrochim. Acta* **2006**, *52*, 1662

[a] No mass activity for Au films