

Supplementary Information

Three dimensional gold nanodendrimers: never conglomerating nanocatalyst

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Materials

Potassium persulfate ($K_2S_2O_8$), Hydrochloroauric acid ($HAuCl_4$) and ascorbic acid (AA) were analytic grade and purchased from Alfa Aesar. Maleic anhydride (MA), polyethylene glycol 400 (PEG400), Nitrobenzene (NB) and polyethylene glycol 600 (PEG600) were obtained from Shanghai Chemical Reagent Industry. Octadecyl alcohol (OA) and methacrylic acid 2-(diethylamino) ethyl ester (DEAEMA) were used as received from Aldrich.

Synthesis

2-butenedioic acid (Z)-, monoctadecyl ester (O-Be) 13.5 g of Maleic anhydride (0.05 mol) and 4.9 g of octadecyl alcohol (0.05 mol) were dissolved in methylbenzene (0.5 mol, 53 mL). The reaction mixture was refluxed 4 h, the disappearance of peaks at 1850 and 1780 cm^{-1} (C=O stretch vibration of Maleic anhydride) in IR spectrum indicated that the reaction was carried out completely. After evaporating methylbenzene by rotary evaporator, O-Be was obtained (18.1 g, 98%). 1H NMR (400 MHz, $CDCl_3$, ppm) δ 0.89 ($-CH_3$, 3H), 1.20-1.42 ($(-CH_2-)$ ₁₅, 30H), 1.78 ($-CH_2-$, 2H), 4.30 ($-OCH_2-$, 2H), 6.40 (=CH, 1H), 6.50 (=CH, 1H).

O-B-EG400 5.0 g of PEG400 (0.0125 mol) and *p*-toluene sulphonic acid (0.172g, 1 mmol) was dissolved in methylbenzene (0.3 mol, 31.8 mL), and 4.6 g of O-Be (0.0125 mol) was dissolved in 21.2 mL of methylbenzene (0.2 mol). O-Be solution was dropwised into PEG400 solution under a stirring condition, the reaction mixture was refluxed 6h, and a water segregator was used to remove the generated water. Then methylbenzene was evaporated by rotary evaporator. The product was dialyzed in water using a dialytic-bag (molecular weight cutoff 3500) to remove unreacted materials (O-B-EG400 can form micelles in water and can not pass though the dialytic-bag). Final product (O-B-EG400) was obtained after drying at a temperature of 60 °C for several days (9.6 g, 79%). 1H NMR (400 MHz, $CDCl_3$, ppm) δ 0.89 ($-CH_3$, 3H), 1.20-1.40 ($(-CH_2-)$ ₁₅, 30H), 1.68 ($-CH_2-$, 2H), 3.60-3.80 ($(-OCH_2)$ ₁₇, 34H), 4.18 ($-OCH_2-$, 2H), 4.35 ($-OCH_2-$, 2H), 6.28 (=CH, 2H). O-B-EG600 was synthesized via the same route using PEG600 as material.

P(DEAEMA-co-O-B-EG400) 2.0 ml of DEAEMA (0.01 mol) and 3.75 g of O-B-EG400 (0.005 mol) were dissolved in 40 mL of deionized water (2.2 mol). After stirring for 30 min, 0.01 g of $K_2S_2O_8$ (0.037 mmol) was added in N_2 atmosphere. The reaction mixture was stirred 12 h at a temperature of 72 °C. Then the mixture containing product was evaporated by rotary evaporator to eliminate unreacted DEAEMA and water, and

P(DEAEMA-co-O-B-EG400) was prepared. P(DEAEMA-co-O-B-EG600) was also synthesized using the same route from O-B-EG600.

3D Au NDs 0.05 g of P(DEAEMA-co-O-B-EG400) or P(DEAEMA-co-O-B-EG600) was dissolved in 40 mL of deionized water (2.2 mol) to obtain an adulescent solution. Then, HAuCl₄ (0.5 mL, 10 mM) and ascorbic acid (AA, 0.75 mL, 0.1M) were added to the solution at room temperature. The reaction mixture was shaken, and then allowed to stand undisturbedly at room temperature for hours. 3D Au NDs were prepared accordingly. In order to remove the polymer template, the mixture containing the key product was centrifugated at 10000 rpm for 30 min, followed by consecutive washing/centrifugation cycles three times with water. To control the diameter and the morphology of the 3D Au NDs, different reaction time such as 2, 12, 24 and 48 h were used.

Normal Au nanoparticles The synthetic route of the normal Au nanoparticles is almost the same with that of the 3D Au NDs. The only difference between these two synthetic methods is the reaction temperature. We synthesized the normal Au nanoparticles by standing the reaction mixture at 60 °C for 2 h. Here, P(DEAEMA-co-O-B-EG400) was used as template, and the dosage of all the chemicals are the same as that of the synthesis of 3D Au NDs. The product was also purified by removing the polymer template using centrifugation.

Characterization

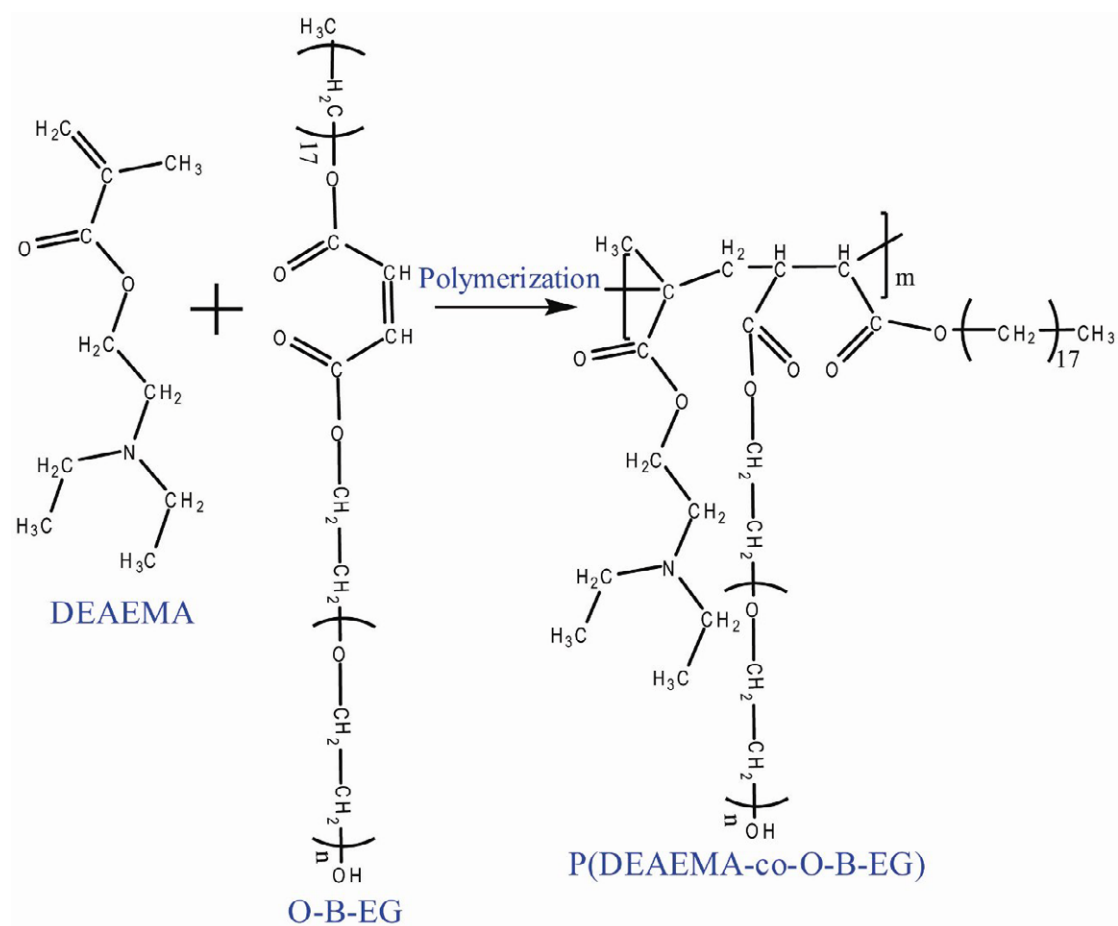
The ¹H NMR spectra of O-Be, O-B-EG400, O-B-EG600, P(DEAEMA-co-O-B-EG400) and P(DEAEMA-co-O-B-EG600) were measured on a Bruker ARX 400MHz spectrometer with 1000 scans at a relaxation time of 2 s.

TEM measurements and electron diffraction experiment were performed with a JEM2100 at an acceleration voltage of 200 kV. To prepare the TEM samples, a small drop of product solution was deposited onto a carbon-coated copper electron microscopy (EM) grid and then dried at room temperature. The energy dispersion spectroscopy analysis was also carried out on an energy dispersive spectrometer (ZNCA Energy TEM 100 x-ray energy spectrum) assembled on JEM2100.

SEM images were obtained from a field emission scanning electron microscope (FE-SEM, LEO-1530). Samples were dispersed in deionized water. Then the mixture was dropwised on aluminium sheets. After air-drying for 24 h at room temperature, the samples were gold sputtering treated.

Catalytic reduction of nitrobenzene (NB)¹⁻⁴: The reduction reactions of NB by NaBH₄ were chosen as model reactions to test the selective catalytic activity of both 3D Au NDs and normal Au nanoparticles. Aqueous solution of NB (0.04 mL, 0.01M) and NaBH₄ (0.4 mL, 0.1M) was added into a quartz cuvette filled with 2.0 mL deionized water under magnetic stirring. Then aqueous solutions of 3D Au NDs and normal Au nanoparticles (0.1 mL, 0.05 mg mL⁻¹) were added to the quartz cuvettes. UV/Vis spectra were recorded at regular intervals to monitor the

progress of the reaction. To test the service life of these Au nanocatalysts, both dry 3D Au NDs and normal Au nanoparticles were firstly exposed in the air for 3 months, and then dispersed in deionized water using ultrasonic vibration to prepare dispersion solution (0.05 mg mL^{-1}). The catalytic activity of the long time air exposed catalysts was also tested using the method mentioned above.



Scheme 1S. Chemical structures of DEAEMA, O-B-EG and P(DEAEMA-co-O-B-EG).

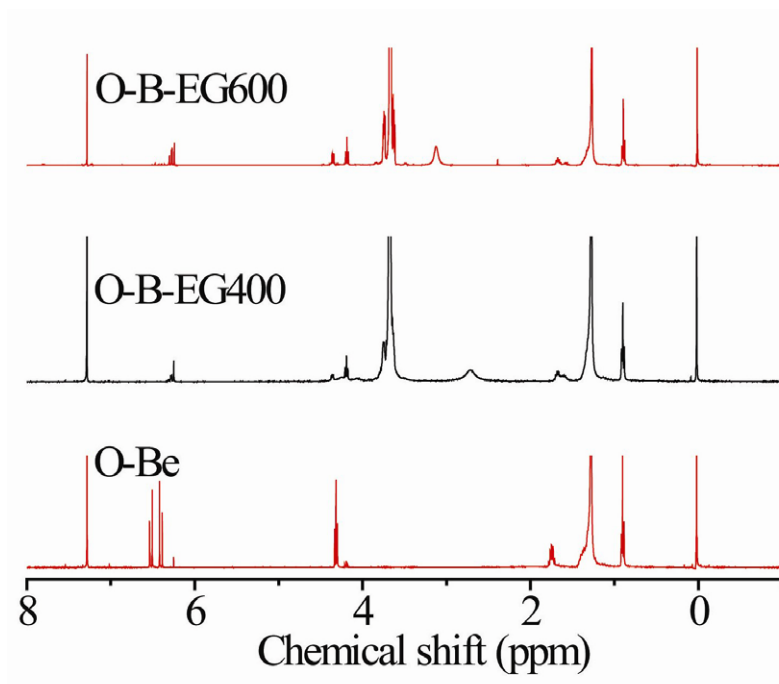


Figure 1S. ^1H NMR spectra of O-B-EG400 and O-B-EG600

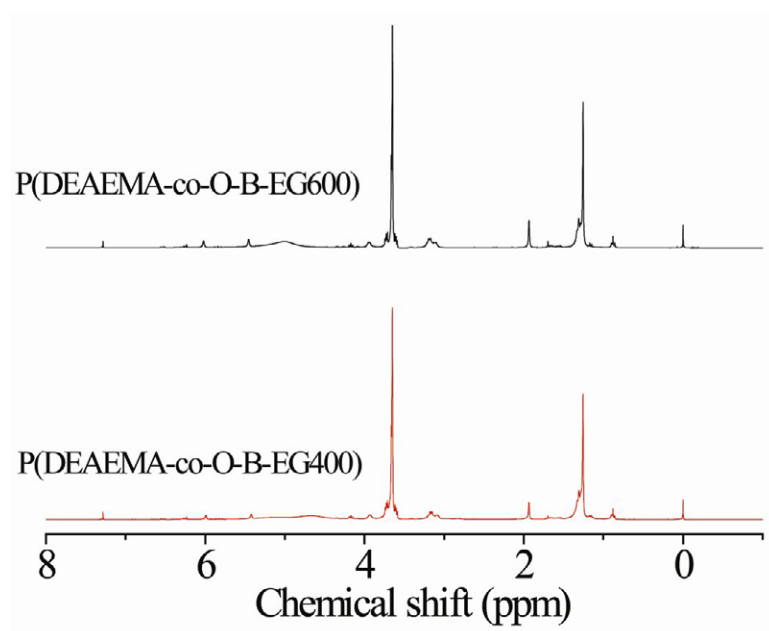


Figure 2S. ^1H NMR spectra P(DEAEMA-co-O-B-EG400) and P(DEAEMA-co-O-B-EG600). H proton signals at δ 0.89, 1.20-1.40, 1.68, 3.60-3.80, 4.18 and 4.35 are assigned to P(O-B-EG), while H proton signals at δ 1.12, 1.96, 3.15 and 3.96 are derived from PDEAEMA.

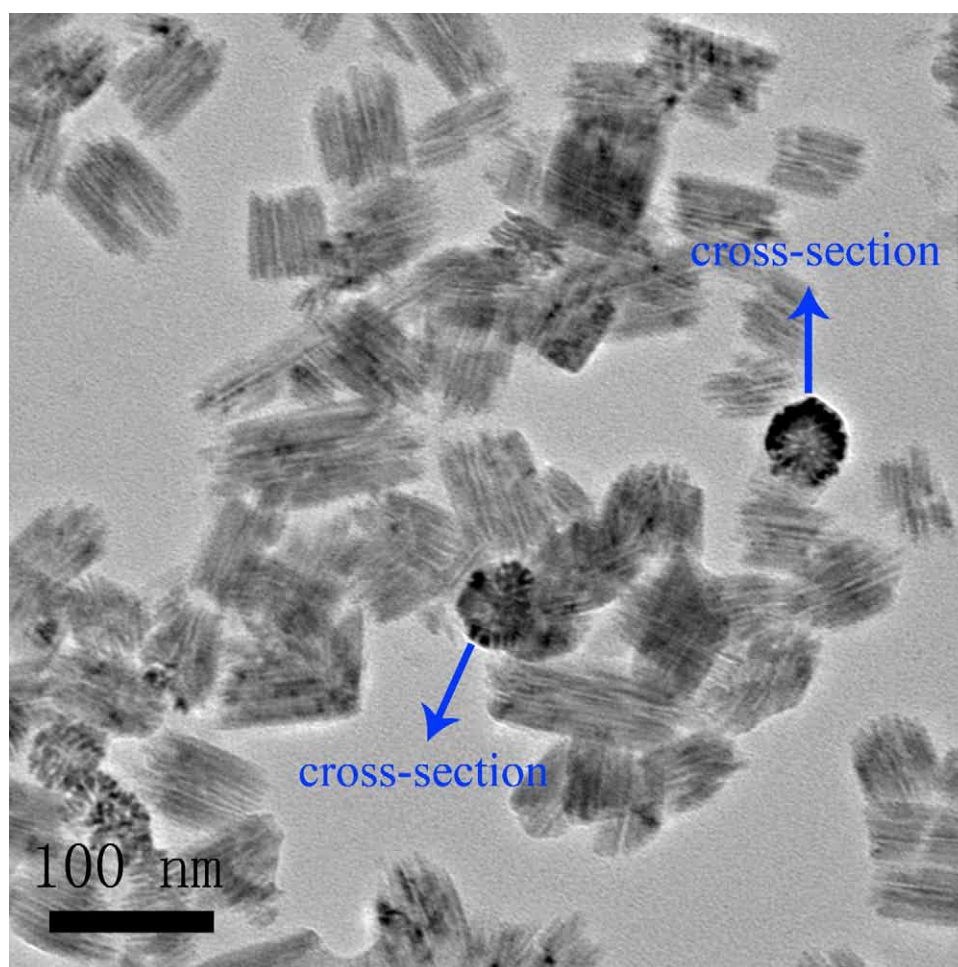


Figure 3S. Overview TEM image of 3D Au NDs containing both the columniform lateral face and the hyper-branched cross-section prepared from 24 h reaction time using P(DEAEMA-co-O-B-EG400) as template.

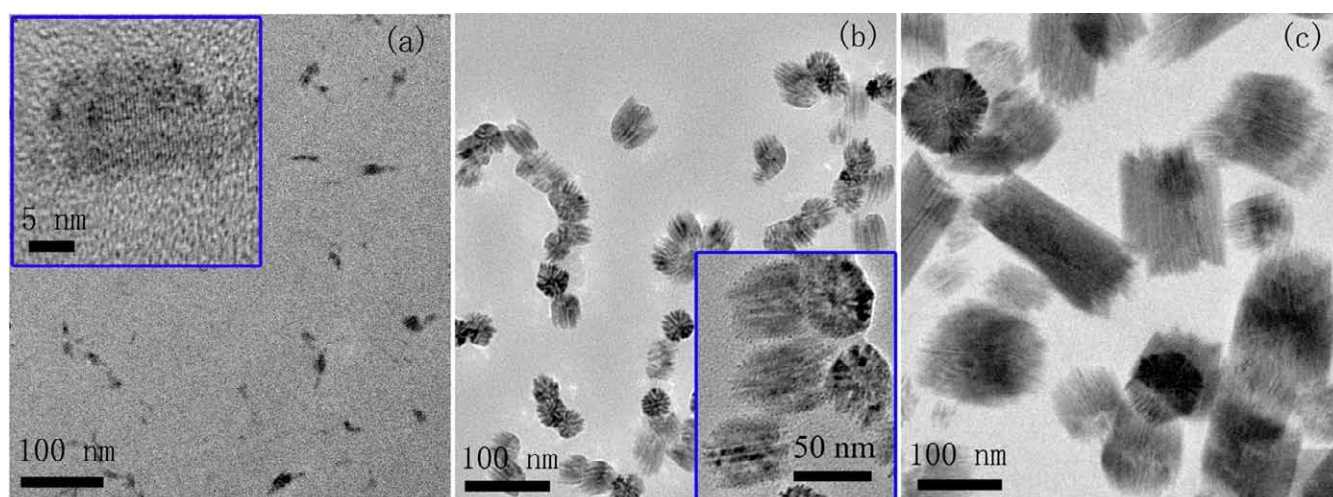


Figure 4S. TEM images of 3D Au NDs prepared from (a) 2, (b) 12 and (c) 48 h reaction time using P(DEAEMA-co-O-B-EG400) as template; the inset of (a) and (b) represent the magnified TEM images of the resultant products obtained from 2 and 12 h reaction time, respectively.

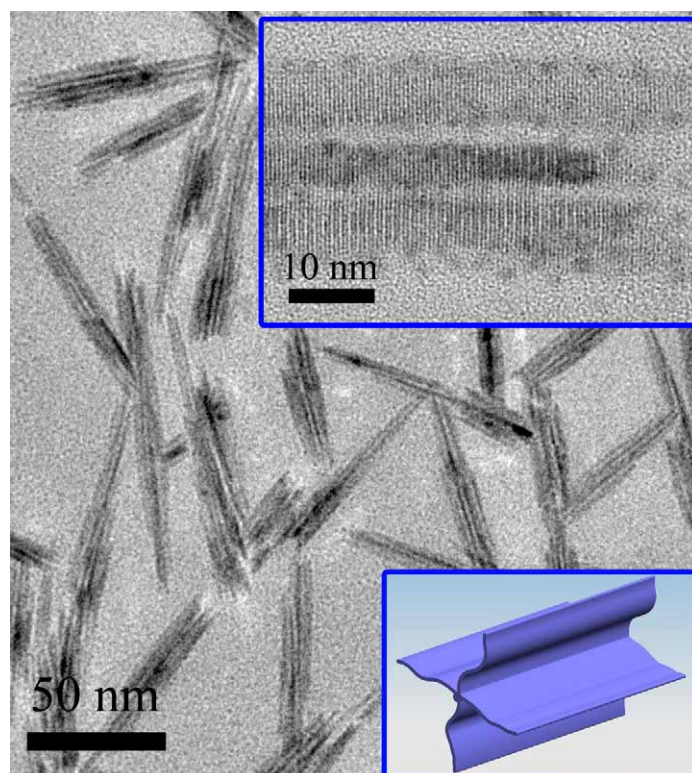


Figure 5S. TEM image of 3D Au NDs prepared from 2 h reaction time using P(DEAEMA-co-O-B-EG600) as template, the top right inset is the high resolution TEM image of a 3D Au ND, the down right inset is the quadripetalous 3D model of this resultant product.

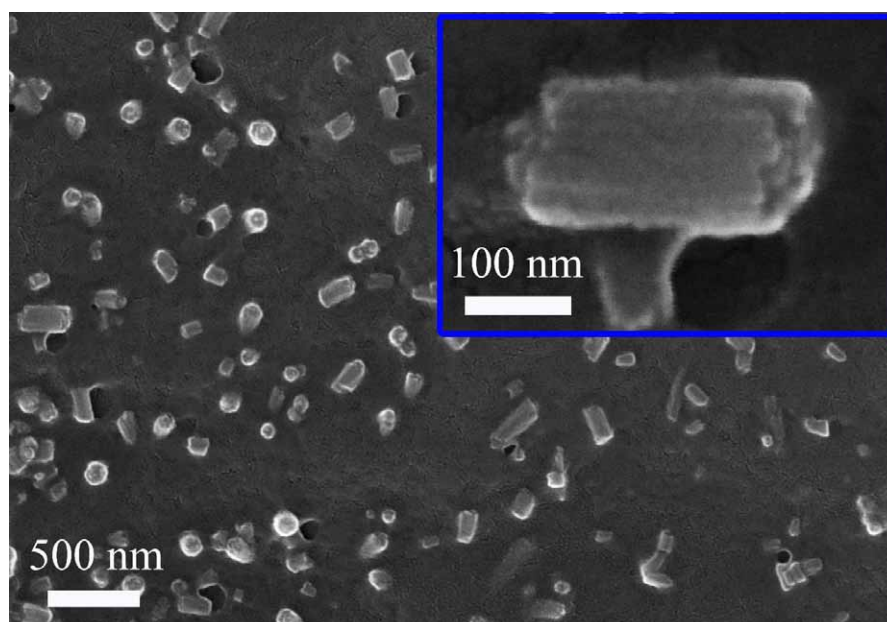


Figure 6S. SEM image of the 3D Au NDs prepared from 48 h reaction time using P(DEAEMA-co-O-B-EG400) as template, the inset is the magnified SEM image of one 3D Au ND. Ravine-like stripes arranging along the column axial direction can be observed clearly, though the sample was gold sputtering treated, indicating that the 3D Au NDs is constructed by nano-sheets.

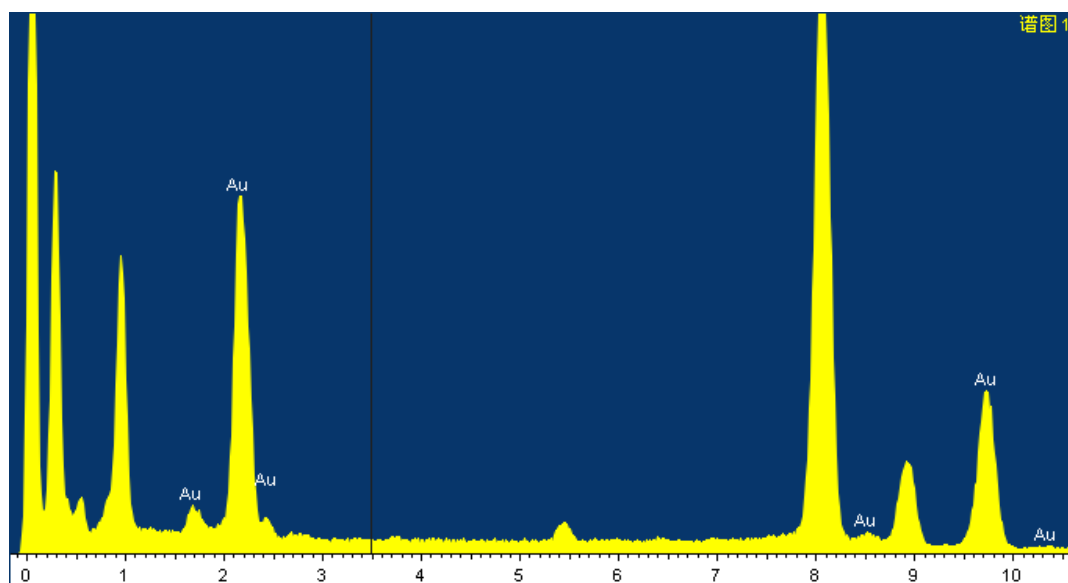


Figure 7S. EDS spectrum of 3D Au NDs prepared using P(DEAEMA-co-O-B-EG400) as template from 48 h reaction time.

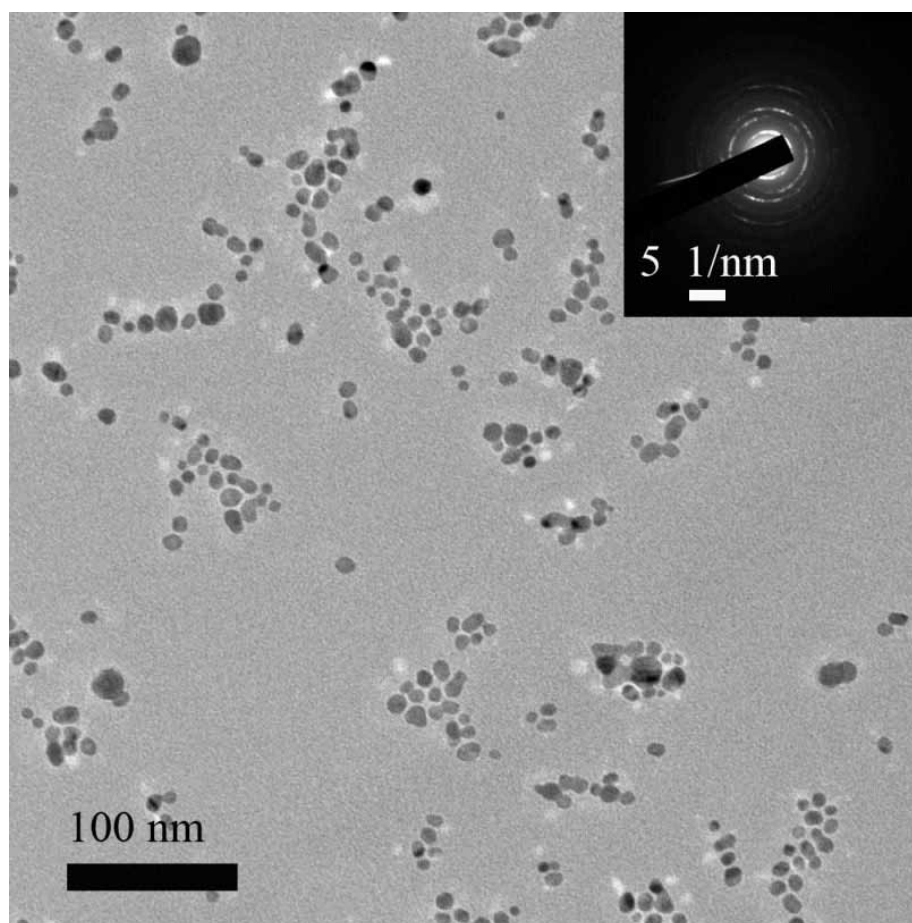


Figure 8S. TEM image of Au nanoparticles synthesized at 60 °C using P(DEAEMA-co-O-B-EG400) as the template, the average diameter calculated from 100 nanoparticles is 10 nm.

Theoretical Calculation of the specific surface area

To theoretically prove that the as-prepared 3D Au NDs have extremely high specific surface area, here we carry out the following calculation.

The Au volume which constructs one 3D Au ND is calculated using the following equation:

$$V = (l \times d \times h) \times n \quad (1)$$

Where V represents Au volume constructing one 3D Au ND; l , d , h and n represent the length, width, thickness, and number of the nano-sheets which construct one 3D Au ND.

The surface area of one 3D Au ND can be calculated according to the following equation:

$$S = (l \times d + l \times h + h \times d) \times 2n \quad (2)$$

Here S represents the surface area of one 3D Au ND; l , d , h and n also represent the length, width, thickness, and number of the nano-sheets which construct one 3D Au ND.

To simplify the calculation process, we suppose that all the 3D Au NDs are constructed by nano-sheets with 50 nm in length, 10 nm in width and 2 nm in thickness (this supposition is also based on the TEM images show in Figure 1). Accordingly, equations (1) and (2) can be changed to equations (3) and (4) which are listed as follows:

$$V = 1000n(\text{nm}^3) \quad (3)$$

$$S = 1240n(\text{nm}^2) \quad (4)$$

As the specific surface area is defined as the surface area of unit mass, the specific surface area (SS) of the 3D Au NDs can be calculated according to the following equation:

$$SS = \frac{1240n(\text{nm}^2)}{1000n(\text{nm}^3) \cdot \rho} \quad (5)$$

Here ρ represents the density of Au which is 19.3 g cm^{-3} . After unit conversion and calculation, the specific surface area of the 3D Au NDs is theoretically calculated to be $64 \text{ m}^2 \text{ g}^{-1}$.

For comparison, we also calculated the surface area (S) of spherical and cubic Au nanostructures which are constructed by the same Au volume with that of the 3D Au ND.

In the case of spherical Au nanostructure, its radius r can be calculated using the following equation:

$$1000n(\text{nm}^3) = \frac{4}{3} \pi r^3 \quad (6)$$

And r is calculated to be $6.2n^{\frac{1}{3}} \text{ nm}$. According to the sphere surface area calculation formula:

$$S = 4\pi r^2 \quad (7)$$

It is easily to calculate that the surface area of spherical Au nanostructure is $483.5n^{\frac{2}{3}}$. Comparing with equation (4), it is clear that the surface area of 3D Au NDs is almost $2.56n^{\frac{1}{3}}$ times that of spherical Au nanostructures. We also used the same method to calculate the surface area of cubic Au nanostructures. It is found that the surface area of 3D Au NDs is almost $2.06n^{\frac{1}{3}}$ times that of cubic Au nanostructures. The TEM images have indicated that the 3D Au NDs are constructed at least 4 pieces of nano-sheets, which means that the n in all the equations are greater than or equal 4. For example, in the case of $n=4$, the surface area of 3D Au NDs is about 3 and 4 times that of the cubic and spherical Au nanostructures, respectively; while in the case of $n=64$, the surface area of 3D Au NDs is about 8 and 10 times that of the cubic and spherical Au nanostructures, respectively. Accordingly, it is reasonable to believe that the 3D Au NDs have unexpectedly high specific surface area.

Reference:

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