Triton X-114 Based Cloud Point Extraction: a Thermoreversible Approach for Separation/Concentration and Dispersion of Nanomaterials in Aqueous Phase

Supplementary Information

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Experimental Section

Materials and Chemicals

The C_{60} fullerene with purity > 99.5% was obtained from Aldrich (Steinheim, Germany). Single-walled carbon nanotubes (SWCNTs) with purity >90% (outer diameter 1-2 nm, inner diameter 0.8-1.6 nm, length 5-30 μm) were purchased from Chengdu Organic Chemistry Co. Ltd, Chinese Academy of Sciences (Chengdu, China). TiO_2 nanoparticles (NPs) powders (AEROXIDE® TiO_2 P 25) were bought from Evonik Degussa China (Beijing, China). CdSe/ZnS core/shell structure quantum dots, with diameter ranged from several nm to about 10 nm and photoluminescence at ~590 nm, were purchased from Jia Yuan Quautum Dots (Wuhan, China). Other nanomaterials (NMs) were synthesized in our laboratory.

Triton X-114 (TX-114) and polyvinylpyrrolidone (PVP) were purchased from Acros Organics (Geel, Belgium), Hydrogen tetrachloroaurate hydrate ($HAuCl_4 \bullet H_2O$) was obtained from Stream Chemicals (Newburyport, MA).

Preparation and Characterization of NMs

Monodispersed Au NPs. The aqueous solution of mono-dispersed Au NPs was prepared by the standard technique of citrate reduction of $HAuCl_4$ [1]. Briefly, 100 mL of 2.5 mM auric acid ($HAuCl_4$) aqueous solution in a 250-mL flask was heated to boil while being stirred for 30 min, and then 0.5 mmol sodium citrate was added. The solution color changed from yellow to black and wine red in seconds, indicating the formation of Au NPs.

The concentration of the synthesized of mono-dispersed Au NPs in aqueous solution was calculated based on equation (1) given by Leff [2]:

$$n = 4\pi(R - \delta)^3/3V_g \qquad (1)$$

where n is the number of Au atoms, R is the radius of Au NP (R = 203 Å for NPs with a diameter of D = 40.6 nm), δ is the length of the protecting ligand (in this case, δ << R), and V_g is the volume of one Au atom (17 Å^3).

The calculated number of Au atoms per Au NP is 2.06 x 10^6, and the concentration of Au NPs in the synthesized solution is 1.21 nM (2.5 mM/(2.06 x 10^6) = 1.21 nM).

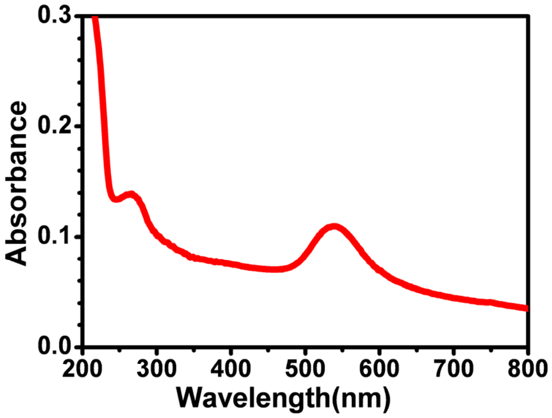

Figure S1. UV-vis absorption spectra of the synthesized Au NPs solution after diluted 30 times.

PVP stabilized Ag NPs. The PVP (polyvinylpyrrolidone) stabilized Ag nanoparticles were synthesized by one step reduction of $AgNO_3$ with sodium hypophosphite modified from literature [3]. Briefly, solution A was prepared by dissolving 0.44 g NaH_2PO_2, 0.4 g PVP, and 0.2 g sodium hexametaphosphate in 50 mL water, and adjusting to pH 2.0. Solution B was prepared by dissolving 1.6 g $AgNO_3$ in 10 mL of water. Both solutions were thermostated at 40 ± 1 ºC, and solution B was added to solution A dropwise while stirring. Then the mixture was allowed to react for an additional 30 min 40 ± 1 ºC with stirring. The resulting Ag colloid was centrifuged at 6000 rpm for 20 min to precipitate Ag nanoparticles. Unreacted reactants were removed by washing with 1% (w/v) aqueous solution of 1,2,3-benzotriazole, and rinsed with acetone and ethanol. The washed Ag NPs were dried in a vacuum oven at 50 ºC for 3 h.

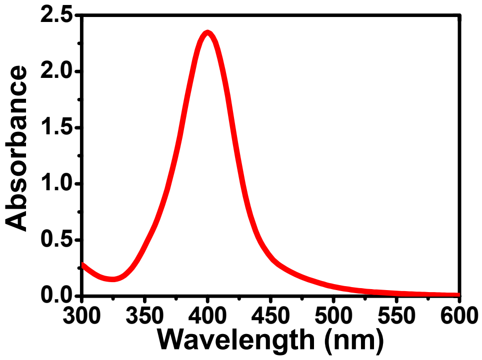

Figure S2. UV-vis absorption spectra of the synthesized Ag NPs.

Humic acid capped Fe_3O_4 magnetic NPs. The Humic acid capped Fe_3O_4 (Fe_3O_4/HA) magnetic NPs were prepared with a method modified from references [4]. Briefly, 6.1 g $FeCl_3{\cdot}6H_2O$ and 4.2 g $FeSO_4{\cdot}7H_2O$ were dissolved in 100 mL water and heated to 90 °C, and then two solutions, 10 mL ammonium hydroxide (25%) and 0.5 g humic acid sodium salt dissolved in 50 mL, were rapidly added in sequence. The mixture was stirred at 90 ºC for 30 min and then cooled to room temperature. The black precipitate was collected by filtrating and washed to neutral pH with water. The obtained black precipitate consists of Fe_3O_4/HA NPs and was ready for use.

Preparation of Aqueous Dispersions of NMs

TiO_2 dispersions. TiO_2 colloids were prepared by dissolving TiO_2 powder in deionized water. The mixture was ultrasonicated with an Ultrasonic Cleaner (Crest Model 275HT, 38.5 KHZ, USA) for 10 min, then centrifuged at 4000 rpm for 20 min, and the resulting supernatant colloid was collect for further experiment.

C_{60} dispersions. A reproducible and relatively simple method modified from reference [5] was developed for preparing the aqueous nC_{60} suspensions. Briefly, 20 mL of 1 g/L C_{60} in toluene was added into a mixture of 50 mL water and 1.5 mL ethanol. Thereafter, the mixture was ultrasonicated with a Ultrasonic Cleaner (Crest Model 275HT, 38.5 KHZ, USA) until all of the toluene had evaporated. The aqueous suspensions were stable for at least 8 weeks at room temperature.

SWCNT dispersions. Sodium dodecylbenzene sulfonate was used to stabilize SWCNT in water at a weight ratio (1:10) of SWCNT [6]. To 100 mL water was added 0.1 g of SWCNT and 1.0 g of sodium dodecylbenzene sulfonate, and the resulting mixture was sonicated for 24 h (Crest Model 275HT, 37.5 KHZ, USA). The resulting suspension was diluted with 100 mL water and used as SWCNT stock suspension (500 mg/L).

Other NM dispersions were prepared by direct dispersing the NMs in water.

General Separation/Dispersion Procedure

The prepared solution or suspensions of NMs were centrifuged at ~ 2700 g for 10 min (dispersions of SWCNTs was centrifuged at ~9300 g for 20 min) to exclude the possibility of precipitation during the extraction process, and the clear supernatant was collected for further experiment. For SWCNTs; 0.2% (w/v) TX-114 was added into 10 mL of the clear supernatant. For the other NMs, an aliquot of supernatant (50 μL for Au NPs, 100 μL each for quantum dots, Fe_3O_4/HA, TiO_2, Ag, and C_{60}) was pipetted into 9.5 mL deionized water in a long tapered centrifuge tube, and TX-114 was added to reach a concentration of 0.2% (w/v). The solution was mixed and incubated at 35 °C in water bath for 30 min. After 3.4 mM NaCl was added, the tube was centrifuged at ~170 g at room temperature to facilitate the phase separation. The TX-114 rich phase could be collected with a microsyringe if necessary. The tube, containing both the TX-114 rich phase and surfactant depleted phase, could then be further placed in ice-bath for 5 min or in 4 °C refrigerator for 30 min, and shook for a few seconds, upon which the NMs were re-dispersed and a homogenous phase was obtained.

Transmission Electron Microscopy

TEM was carried out with H-7500 (Hitachi, Japan) at 80 kV for Au NPs, Ag NPs, TiO_2 NPs, C_{60} and SWCNTs, and JEOL-2010 (JEOL, Japan) at 200 kV for CdSe/ZnS quantum dots and humic acid coated Fe_3O_4 (Fe_3O_4/HA) NPs. TEM samples were prepared by loading 5-µL aliquots of the aqueous sample or the TX-114 rich phase at 30 times dilution (with 1:1 water and methanol) onto carbon-coated grid sample holders, except for TX-114 rich phase with SWCNTs that was diluted 100 times with water. After sample loading, the sample holders were dried at room temperature. In order to preserve the morphology of the TX-114 micelles, however, the sample holders for Figure 2 were firstly frozen at -52 ºC for 3 h after sample loading, and then freeze dried (-52 ºC) with vacuum for 24 h by using a freeze dryer (Model FD-1A-50, Beijing Boyikang Lab Instrument Co., Beijing, China). The size distribution of the nanoparticles was estimated using Image-Pro plus software and Gaussian fitting. At least 300 particles were counted from multi-picture in each case.

Determination of the Hydrodynamic Diameter of Particles

The particle size distribution of Au NPs dispersions at varied aqueous conditions was determined by laser particle size analyzer (Mastersizer 2000, Malvern Co., UK).

Extraction Efficiency of Au and Fe_3O_4/HA NPs

To study the parameters that influence the extraction of Au NPs, an aliquot of Triton X-114 (0.05-0.3%, w/v) was added into 10 mL of 6.05 pM Au NPs (a 200 times dilution of the as-synthesized Au NPs) in a long tapered centrifuge tube. After the centrifuge tube containing the mixture was incubated at desired temperature (30-55 ºC) for prescribed time (5 -120 min), NaCl was added to reach a salinity of 3.4 mM, and then centrifuged at 1000 rpm (about 170 g) for 10 min. The TX-114 rich phase was collected and diluted by methanol, and then the absorbance was recorded with a UV-vis spectrophotometer (Model UV-1102, Techcomp, Shanghai) at 535 nm.

The extraction efficiency of Fe_3O_4/HA NPs was studied in a similar way. However, quantification of Fe_3O_4/HA NPs was conducted by measuring the Fe content after dissolution with 5 M HCl with ICP-MS (Agilent 7500ce, USA).

References

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[3] A. B. R. Mayer, W. Grebner, R.Wannemacher, *J. Phys. Chem. B* **2000**, *104,* 7278-7285.

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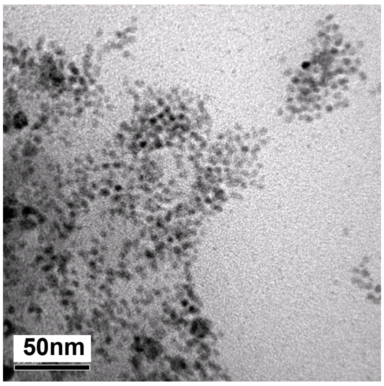
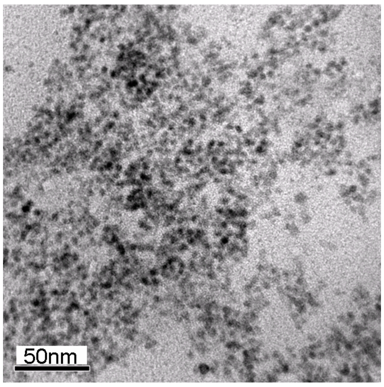
[6] M. F. Islam, E. Rojas, D. M. Bergey, A. T. Johnson, A.G. Yodh, *Nano Lett.* **2003**, *3*, 269-273.

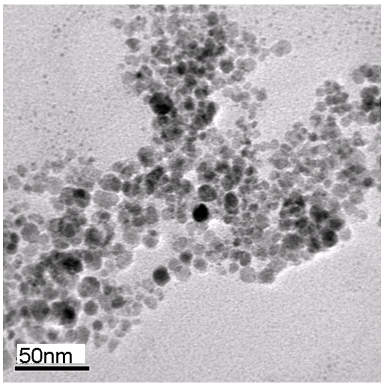
Results and Discussion

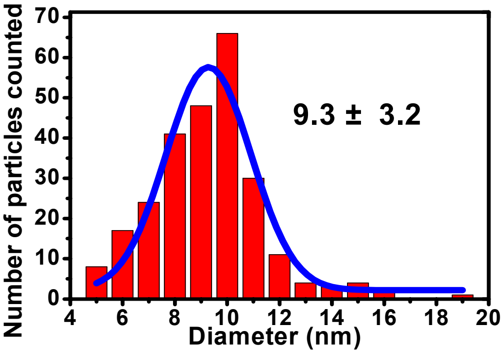
(a) Quantum Dots

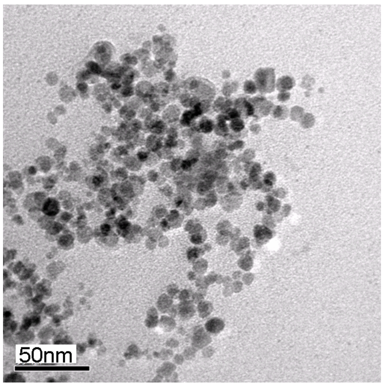


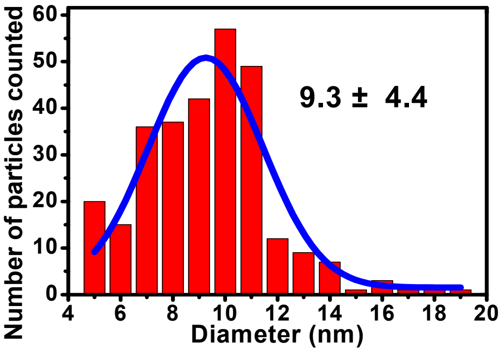


(b) Fe_3O_4/HA

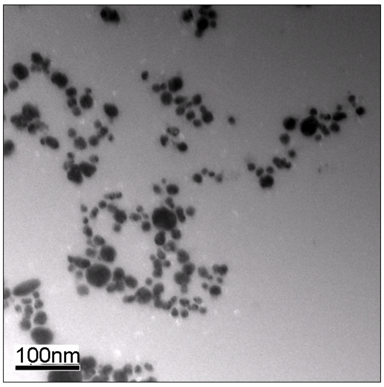








(C) TiO_2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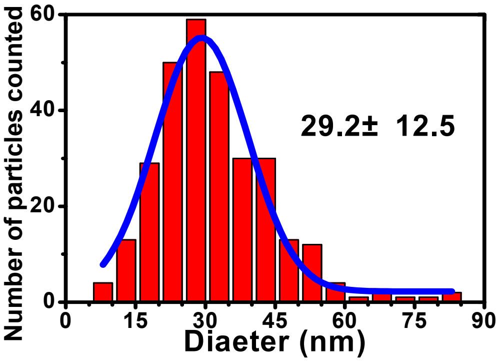
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30
45
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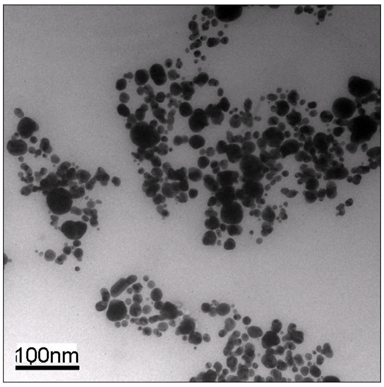
75
90
Diaeter (nm)
29.2± 12.5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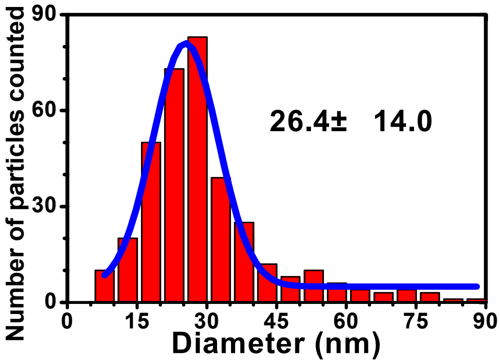
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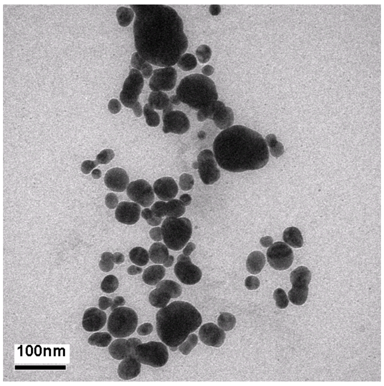
Diameter (nm)
26.4± 14.0

(d) Ag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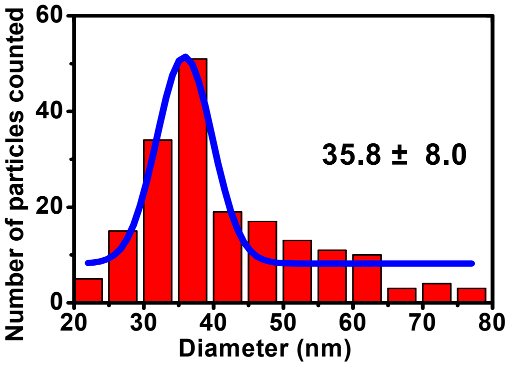
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Diameter (nm)
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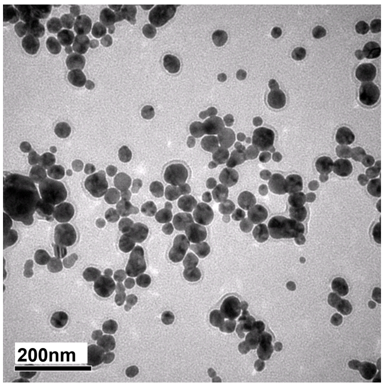
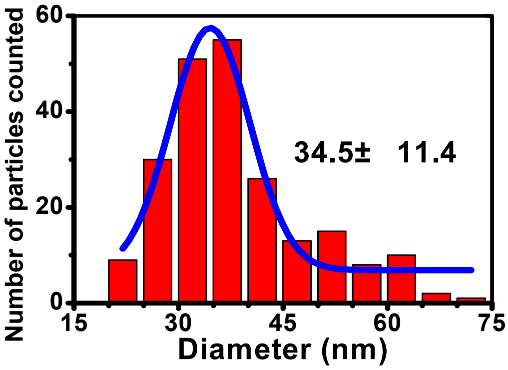

200nm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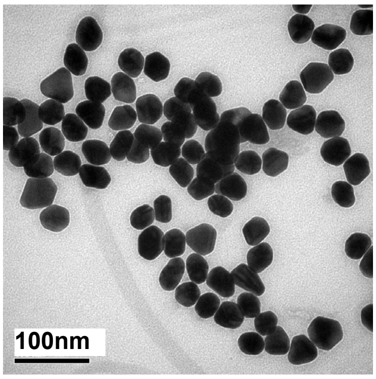
Diameter (nm)
34.5± 11.4

(e) Au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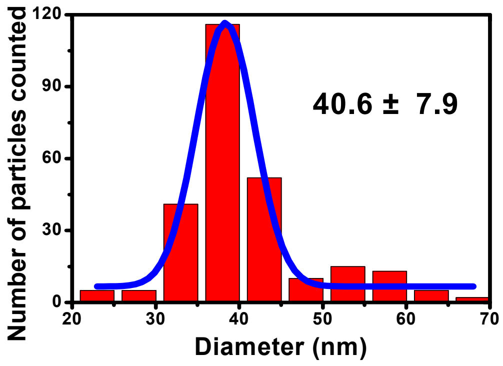
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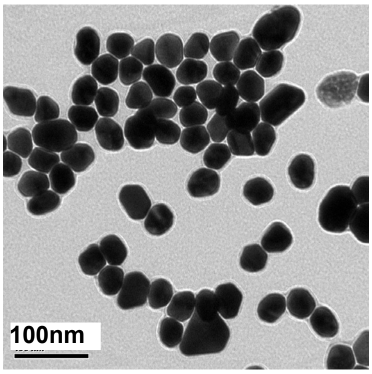
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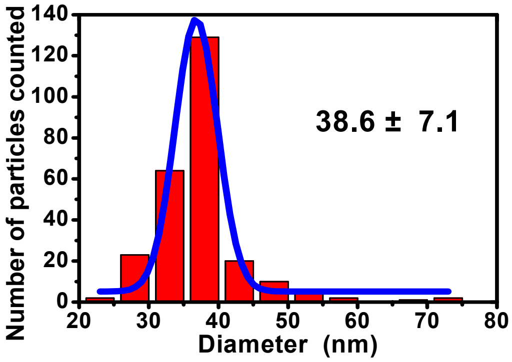
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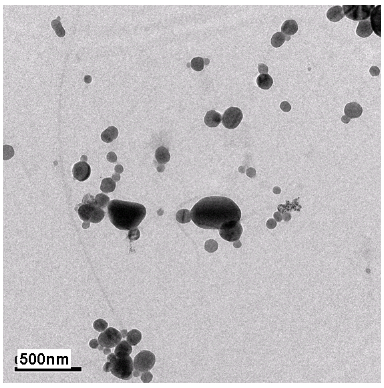
Diameter (nm)
38.6 ± 7.1

(f) C_{60}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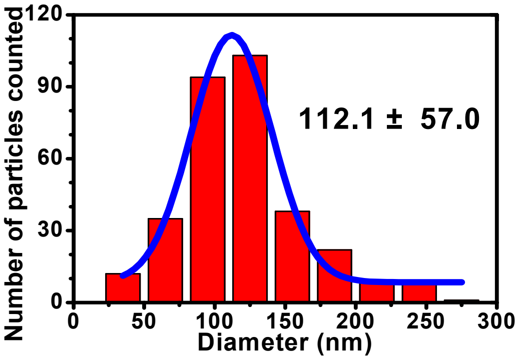
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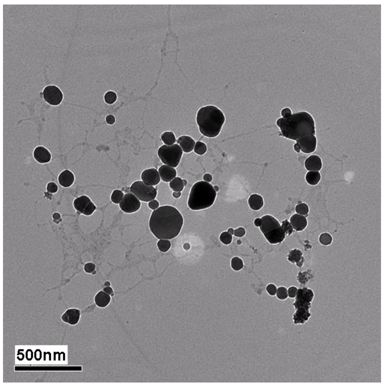
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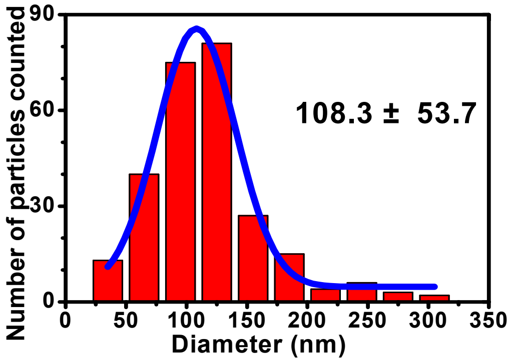
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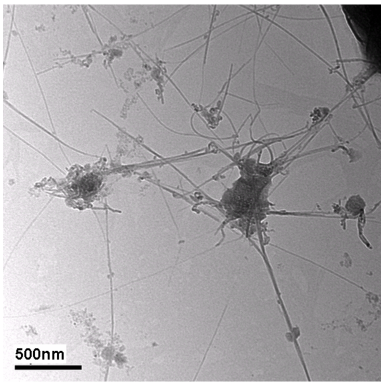
(g) SWCNT



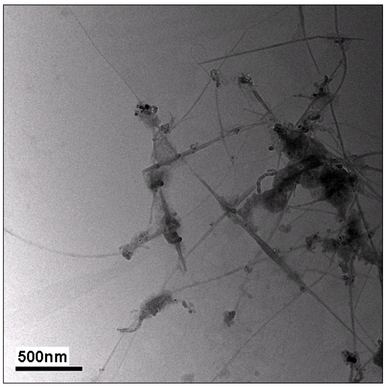


Figure S3. TEM images and particle-size distribution of NPs in the aqueous phase before extraction (up) and in the surfactant-rich phase after extraction (down). (a) quantum dots; (b) Fe_3O_4/HA; (c) TiO_2; (d) Ag; (e) Au; (f) C_{60}; (g) SWCNT. Note that the particle-size distribution of quantum dots was not analyzed due to the confined resolution of TEM.

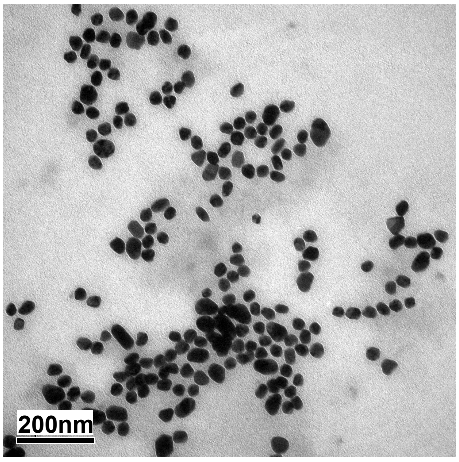


Figure S4. A representative TEM image of Au NPs after stored in TX-114 rich phase at room temperature for two months.

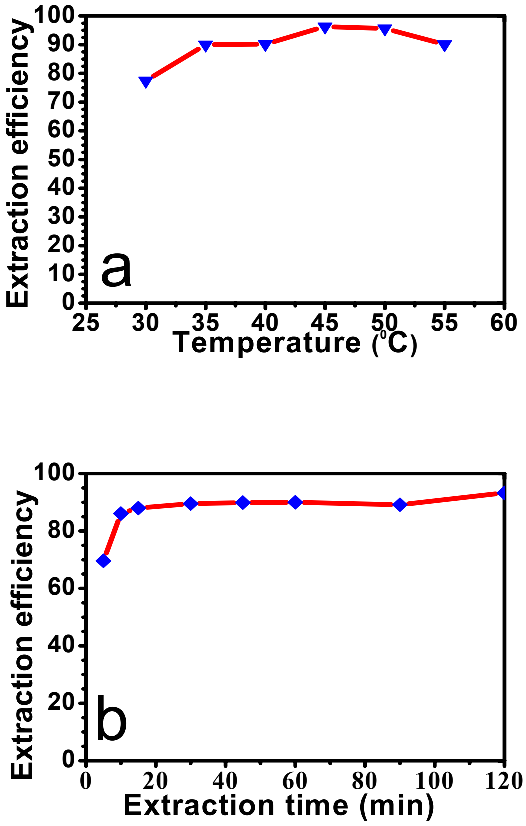


Figure S5. Effects of temperature (a) and incubation time (b) on the extraction efficiency of Au NPs.

Table S1. Effect of TX-114 concentration on extraction efficiency and enrichment factor of Au NPs

Concentration of TX-114 (%, m/v)	Volume of TX-114 rich phase (μL)	Extraction efficiency (%)	Enrichment factor
0.05	25	97	388
0.10	50	92	184
0.15	75	93	124
0.20	100	98	98
0.25	125	96	77
0.30	150	96	64