Electronic Supplementary Information

Reversible Phase Transfer and Fractionation of Au Nanoparticles by pH change

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ESI 1

Materials:

All chemicals used were reagent grade and obtained from Aldrich or Kanto chemicals. Methyl acrylate (Kanto Chemicals) was purified by distillation. Octadecylamine (Aldrich) was recrystallized twice from hexane. Milli-Q Water (18.2 MΩ) was used for all experiments.

Synthesis of C18AA:[1]

10.22 g (0.12 mol) of methyl acrylate was added to 2.0 g (7.12 mmol) of octadecylamine in 15 mL of methanol. The solution was stirred at 40 °C for 3 days and then the solvents and excess methyl acrylate were removed from solution by rotary evaporation. 3-[(2-methoxycarbonyl-ethyl)-octadecyl-amino]-propionic acid methyl ester (C18ME) was obtained as a viscous liquid. Yield: 95%.

^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, $CH_2\mathbf{CH_3}$), 1.25 (br, 28H, CH_2), 1.42 (br, 4H, $\mathbf{CH_2}CH_3$, $CH_2\mathbf{CH_2}CH_2N$), 2.37 (t, 4H, $CH_2\mathbf{CH_2}CO$), 2.43 (t, 2H, CH_2N), 2.76(t, 4H, $N\mathbf{CH_2}CH_2CO$), and 3.66 (s, 6H, $O\mathbf{CH_3}$) ppm. HRMS: calcd for C18ME ($M+Na^+$) 464.37, found 464.38.

C18ME (3.2 g) and ethylenediamine 17.8 g (0.30 mol) were dissolved in 15 mL of methanol and the mixture was stirred for 1 week at room temperature. Upon removal of the solvent and ethylenediamine by evaporation and freeze-drying, C18AA was obtained as a light yellow solid. The crude solid was recrystallized from a mixed solvent of toluene and methanol. Yield: 90%.

^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, CH_3), 1.25 (br, 28H, CH_2), 1.45 (br, 4H, $\mathbf{CH_2}CH_3$, $CH_2\mathbf{CH_2}CH_2N$), 2.36 (t, 4H, $CH_2\mathbf{CH_2}O$), 2.42 (t, 2H, $\mathbf{CH_2}N$), 2.73 (t, 4H, $N\mathbf{CH_2}CH_2CO$), 2.82 (t, 4H, $\mathbf{CH_2}NH_2$), and 3.29 (q, 4H, $NH\mathbf{CH_2}$) ppm. HRMS: calcd for C18AA ($M+H^+$) 498.47, found 497.48.

NMR spectra were recorded in $CDCl_3$ using a Bruker 400 Ultrashield spectrometer operating at 400 MHz.

1) (a) Imura, Y.; Matsue, K.; Sugimoto, H.; Ito, R.; Kondo, T.; Kawai, T. *Chem. Lett.* **2009**, 38, 778-789. (b) Kawai, T.; Ito, R.; Kondo, T., Gold 2006, New Industrial Applications for Gold, University of Limerick, Abstract p. 113 (2006).

Synthesis of Au nanoparticles:

Au NPs were prepared by the standard citrate reduction method. 80 mL of 0.625 mM $HAuCl_4$ aqueous solution and 20 mL of 15 mM trisodium citrate aqueous solution were mixed at 100 °C and stirred for >10 min to obtain a wine-red colored solution. The diameter of the Au NPs was estimated to be 15.7 nm by TEM observation.

ESI 2

The difference in the transfer yield of Au NPs present in water and remained in chloroform.

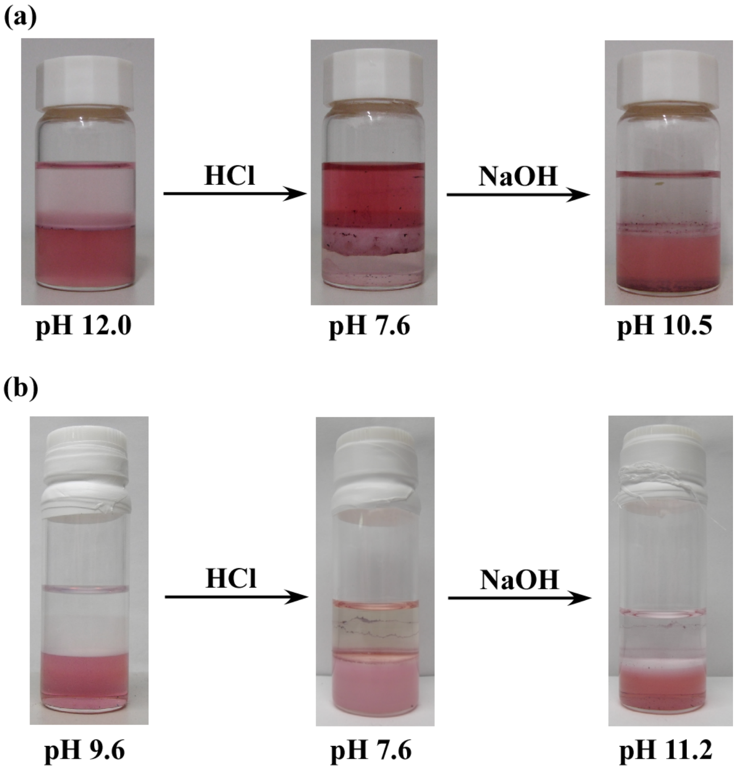

Figure S1. Photographs of the phase transfer behavior of Au NPs (a) present in water phase and (b) remaining in chloroform phase in Figure 2d.

Au NPs dispersed in water and chloroform (Figure 2d) were collected by centrifugal sedimentation. The respective Au NPs were re-dispersed into water and chloroform, and then 1.5 wt% chloroform and aqueous solution of C18AA were poured into the corresponding water and the chloroform phases, because the surfactant concentration was adjusted to the original condition.

UV-vis spectra of Au NPs in each phase were obtained to examine the transfer yield at pH 7.6, as shown in Figure S1. The band intensity shown in Figure S2 indicates that the transfer yield of Au NPs remained in chloroform phase was 0%. However, the transfer yield from the chloroform to water phase for Au NPs present in water phase was evaluated as 92%. This indicates that the Au NPs present in water in Figure 2 can transfer easily between water and chloroform phases. Thus, the transfer nature of Au NPs present in water differs from that remaining in the chloroform phase.

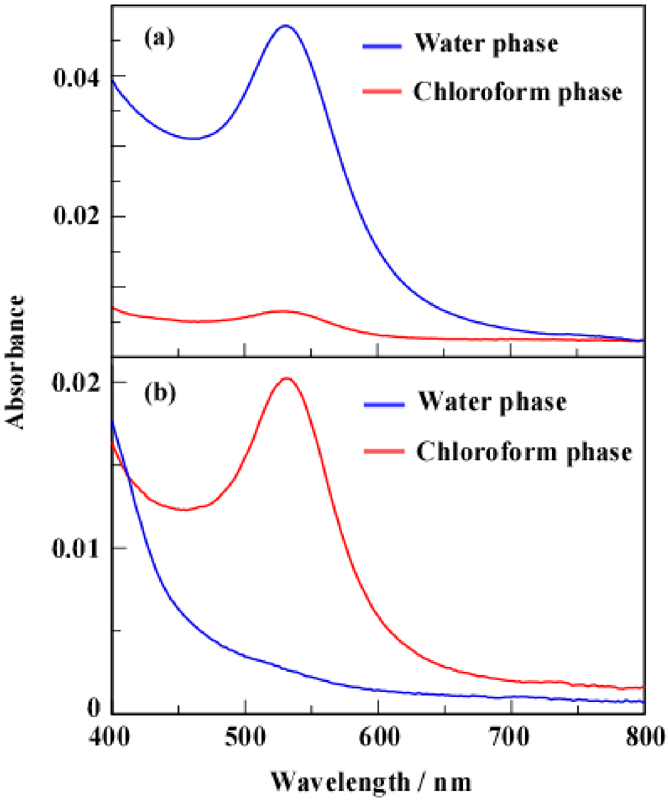

Figure S2. UV-vis spectra of Au NPs in each phase in the samples shown in (a) Figure S2a and (b) Figure S2b at pH 7.6.

ESI 3

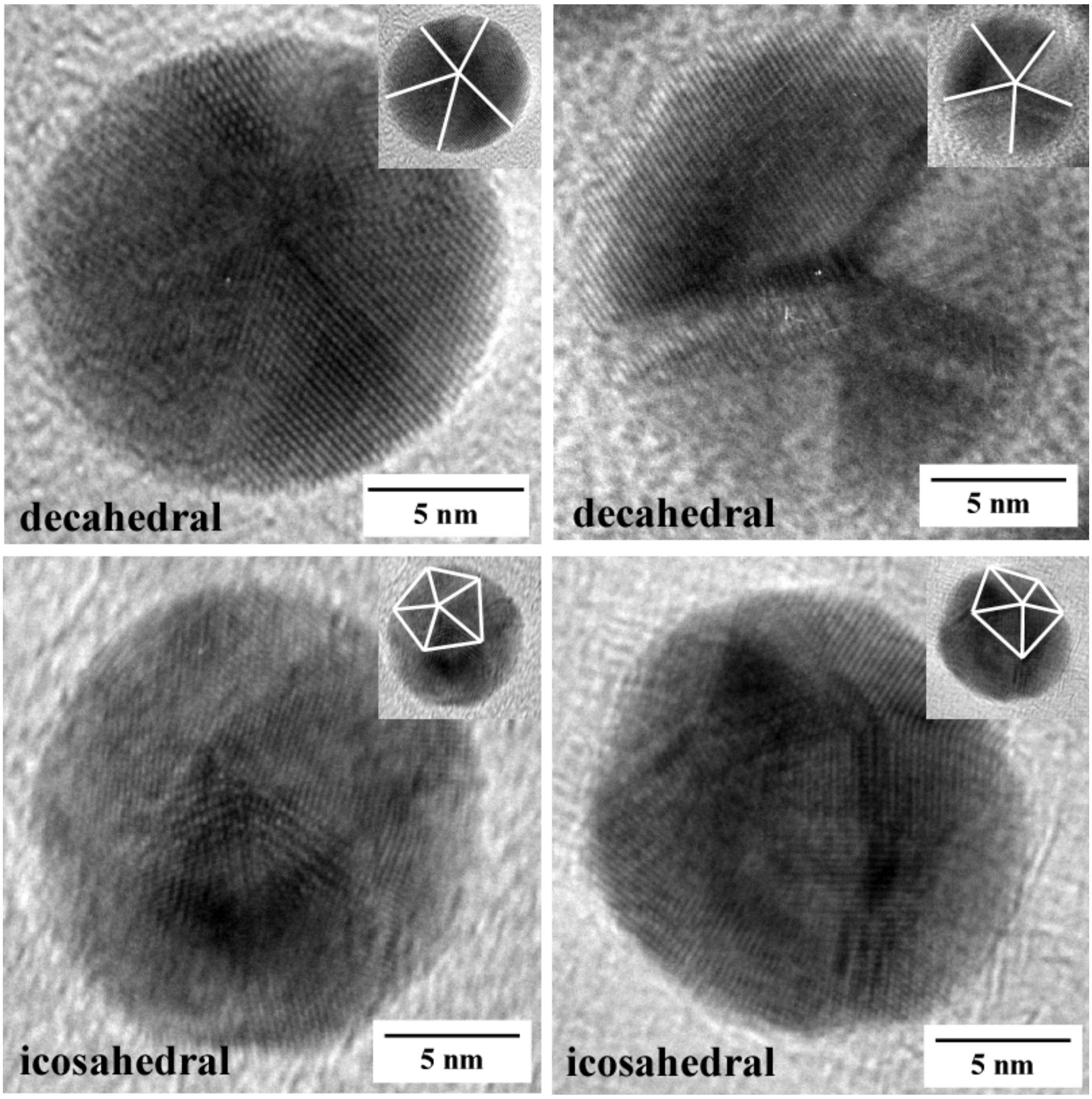

Figure S3. HRTEM images of Au NPs in the chloroform phase in Figure 2d.

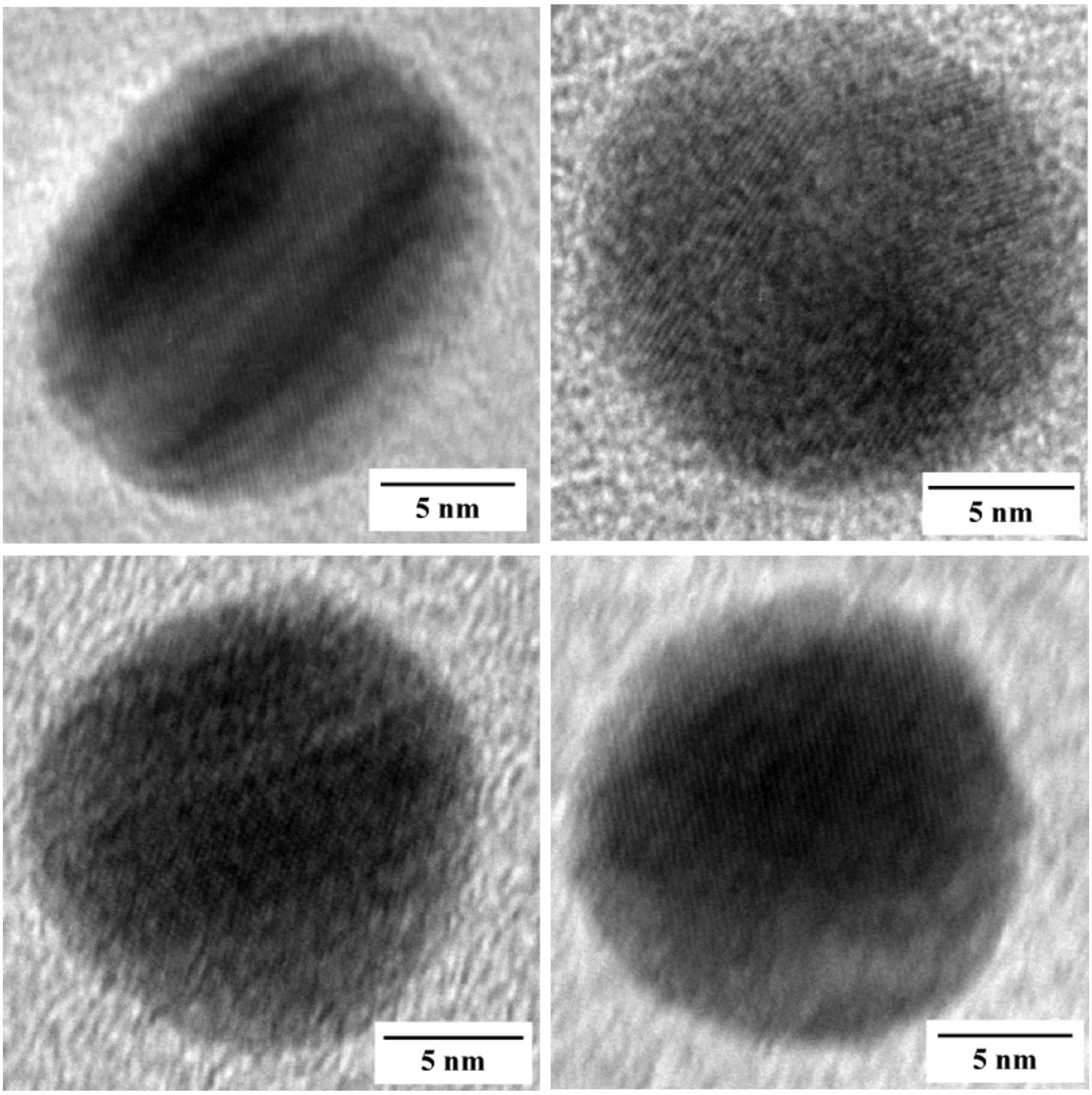

Figure S4. HRTEM images of Au NPs in water phase in Figure 2d.

ESI 4

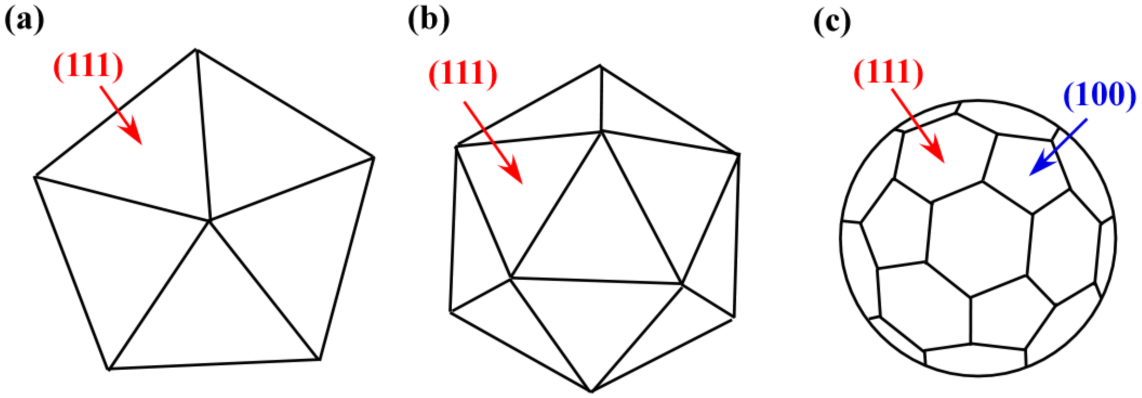

Figure S5 Crystal structure of (a) decahedral, (b) icosahedral, and (c) truncated icosahedral NPs.

ESI 5

FT-IR external reflection spectra of C18AA adsorbed on Au (100), (110) and (111) crystal faces (MaTeck GmbH, Germany) were obtained to reveal the adsorption properties of C18AA on gold surfaces. Gold pellets with the respective single crystal faces were immersed in a dilute ethanol solution of C18AA (ca. 50 mM) for 30 min and then gently washed with ethanol prior to IR spectral measurements.

The spectra of the Au (100), (110) and (111) crystal faces show antisymmetric and symmetric CH_2 stretching bands at 2920 and 2850 cm^{-1}, respectively, however, these intensity of (111) crystal face are weaker than (100) and (110) faces. This indicates that C18AA molecules were hardly adsorb on the (111) crystal facet, just like CTAB.[2)]

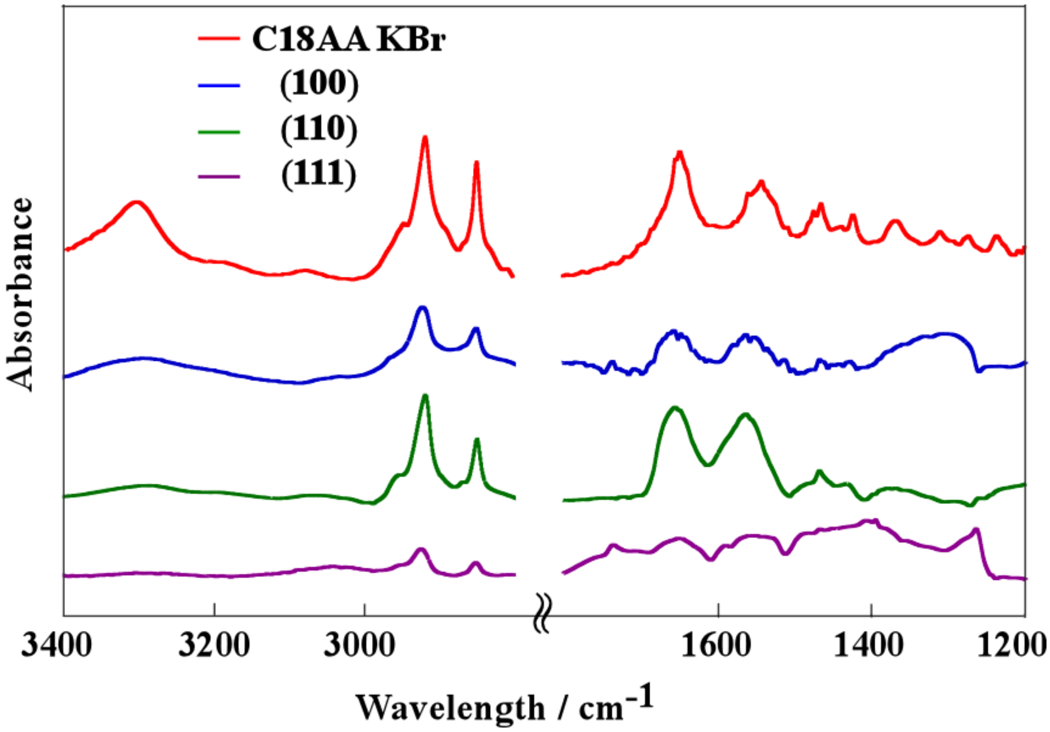

Figure S6. FT-IR spectra of Au (100), (110) and (111) single crystals after the addition of C18AA.

2) (a) Murphy, C. J.; Sau, T. K.; Gole, A. M.; Orendorff, C. J. *MRS Bull.* **2005**, 30, 349-355. (b) Murphy, C. J.; Sau, T. K.; Gole, A. M.; Orendorff, C. J.; Gao, J.; Gou, L.; Hunyadi, S. E.; Li, T. *J. Phys. Chem. B* **2005**, 109, 13857-13870. (c) Johnson, C. J.; Dujardin, E.; Davis, S. A.; Murphy, C. J.; Mann, S. *J. Mater. Chem.* **2002**, 12, 1765-1770.