

## Supporting information for

# ‘Size and size distribution balance the dispersion of colloidal CeO<sub>2</sub> nanoparticles in organic solvents’

*Toshihiko Arita\**, *Jungwoo Yoo*, *Yu Ueda*, *Tadafumi Adschiri*<sup>#</sup>

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,  
2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

<sup>#</sup>WPI Research Center: Advanced Institute for Materials Research, Tohoku University,  
2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

Corresponding author email address: tarita@tagen.tohoku.ac.jp

### **1. Experimental details:**

Materials: Cerium hydroxide (Ce(OH)<sub>4</sub>) and cyclohexane(99%) were obtained from Aldrich while decanoic acid (99%), dodecanoic acid (99%), *n*-hexane (96%), ethanol (99%), acetone (99%) from Wako were used as received. Purified water was purchased from Daiwa Yakuhin was used after filtration.

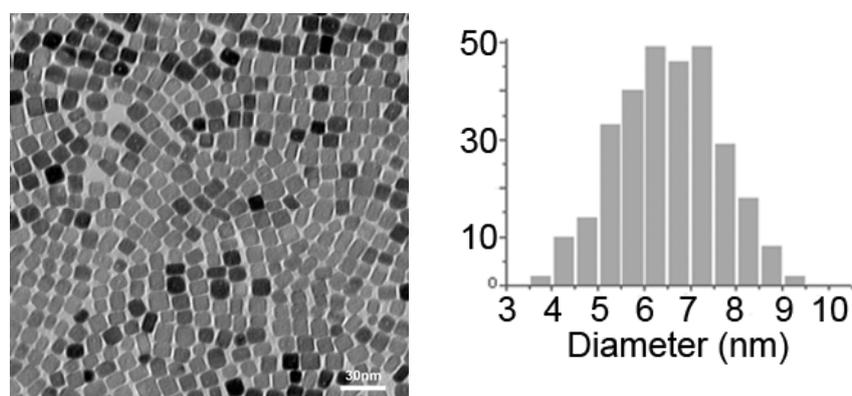
Synthesis and purification of HNPs: Surface modified CeO<sub>2</sub> NPs were obtained basically by the supercritical hydrothermal method.<sup>1</sup> In brief, 2.5 ml of the 0.1 M aqueous cerium hydroxide suspension and 0.258g of decanoic acid/0.050g of dodecanoic acid were loaded to a pressure resistant hastelloy reactor (inner volume was 5 ml). The supercritical hydrothermal reaction was performed at 400 °C for 10 min then terminated by immersing the reactor into a water bath. The surface modified NPs were extracted from the aqueous product mixture with hexane (3 ml). The organic portion was collected and ethanol (12 ml) was added to remove the residual fatty acid. HNPs were collected by centrifugation and carefully dried by freeze drying. Further purification was conducted to remove the residual and/or free modifiers from HNPs. The antisolvent precipitation method was used to remove free decanoic/dodecanoic acid from HNPs. 1 g of dried HNPs powder was dissolved into 30 ml of cyclohexane then the cyclohexane solution was dropped into an excess amount of acetone (500 ml). The HNPs was collected by centrifugation and dried by freeze drying. The precipitation method was repeated several times to perfectly remove non bound decanoic/dodecanoic acid on the surface of HNPs.

Characterization of HNPs: The average size, size distribution and morph of HNPs were measured by transmission electron microscopy (TEM). The THF solution of HNPs was dropped on a standard carbon coated copper grid and dried. Electron micrographs were taken by a Hitachi H-7650

micrometer at an accelerating voltage of 100kV. The particle sizes were calculated from the average of more than 250 particles using an image analysis software program (SigmaScan Pro4, Jandel Scientific). Fourier transfer infrared spectroscopy (FTIR) was employed to analyze how the surface modifiers bound to the surface of HNPs. A KBr disc deposited HNPs was settled in the a FT-IR spectrometer (Jasco FT/IR 680 plus) and measured spectrum at a resolution of  $4\text{ cm}^{-1}$ . The amount of grafted surface modifier was measured from the weight loss of the thermo gravimetry (TG). The temperature dependent weight loss of HNPs was recorded under Ar atmosphere (flow rate = 30 ml/min) with temperature sweep at  $10\text{ }^{\circ}\text{C}/\text{min}$  by Rigaku TG8120 system. Dynamic light scattering (DLS) was employed to analyze the size of the dispersed HNPs in cyclohexane. DLS experiments were performed with a Malvern Zetersizer Nano ZS. In this study, the General Purpose (GP) analysis functions in the Zetasizer Nano software, a non-negative least squares (NNLS) algorithms, was employed to deconvolute the particle size distribution to obtain the gross average diameter of the dispersants in organic solvents. The concentration of the HNPs solution for DLS was restricted up to 5 wt-% of HNPs. The zeta potential of HNPs was also measured by the Malvern Zetersizer Nano ZS. The concentration of HNPs for zeta potential measurement was varied from 0.5 to 2 wt-% of HNPs. The dispersity of HNPs in cyclohexane was also measured through the ultra violet and visible spectrometer (UV-VIS, Jasco V-570) and our eyes (taking photographs by Canon digital camera Powershot G2)

## 2. The calculation of the surface coverage of the modifier.

Here, we show the calculation detail of the surface coverage of decHNPs. The surface coverage of dodHNPs was carried out applying the same procedure shown below.



Average diameter =  $6.5\text{nm} (\pm 1\text{nm})$

**Figure S1.** TEM image and the size distribution of the decHNPs used in this study.

#### Calculation of coverage (decHNPs)

Assumption – the surface of HNPs is a regular cubic.

The total surface area corresponding to the HNPs in the TEM picture was obtained by using an image analysis software program (SigmaScan Pro4, Jandel Scientific) and turned out to be  $A_{\text{HNP}} = 260.88 \text{ nm}^2$ . In addition, the total volume corresponds to the HNPs shown in the TEM picture was calculated as  $V_{\text{core}} = 298.44 \text{ nm}^3$ .

Density of ceria (from literature) =  $7.215 \text{ g/cm}^3$ , Density of modifier (from literature) =  $0.893 \text{ g/cm}^3$ .

Molecular weight of ceria ( $MW_{\text{ceria}}$ ) =  $172.115 \text{ g/mol}$ , Molecular weight of modifier ( $MW_{\text{modifier}}$ ) =  $172.26 \text{ g/mol}$ .

The weight loss in TG analysis was 14.40%.

$$W_{\text{core}} = V_{\text{core}} \times D_{\text{core}} = 2.15 \times 10^{-18} [\text{g}]$$

$$W_{\text{modifier}} = W_{\text{core}} \times 0.144/0.856 = 3.62 \times 10^{-19} [\text{g}]$$

$$V_{\text{modifier}} = W_{\text{modifier}} / D_{\text{modifier}} = 405.63 \text{ nm}^3$$

$$\text{Total number of modifier per HNP} = W_{\text{modifier}} / MW_{\text{modifier}} \times N_{\text{A}} = 1265.89$$

$$\text{Coverage} = \text{Total number of modifier} / A_{\text{HNP}} = 1265.89 / 260.88 = \underline{\underline{4.85 / \text{nm}^2}}$$

#### Calculation of coverage (dodHGNPs)

Assumption – the surface of HNPs is a regular cubic.

The total surface area corresponding to the HNPs in the TEM picture was obtained by using an image analysis software program (SigmaScan Pro4, Jandel Scientific) and turned out to be  $A_{\text{HNP}} = 577.48 \text{ nm}^2$ . In addition, the total volume corresponds to the HNPs shown in the TEM picture was calculated as  $V_{\text{core}} = 975.63 \text{ nm}^3$ .

Density of ceria (from literature) =  $7.215 \text{ g/cm}^3$ , Density of modifier (from literature) =  $0.88 \text{ g/cm}^3$ .

Molecular weight of ceria ( $MW_{\text{ceria}}$ ) =  $172.115 \text{ g/mol}$ , Molecular weight of modifier ( $MW_{\text{modifier}}$ ) =  $200.32 \text{ g/mol}$ .

The weight loss in TG analysis was 11.0%.

$$W_{\text{core}} = V_{\text{core}} \times D_{\text{core}} = 7.04 \times 10^{-18} [\text{g}]$$

$$W_{\text{modifier}} = W_{\text{core}} \times 0.11/0.88 = 8.8 \times 10^{-19} [\text{g}]$$

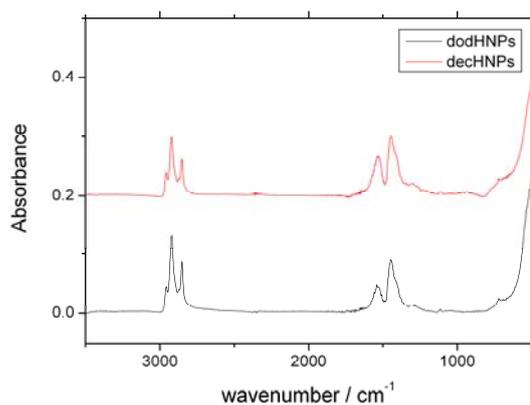
$$V_{\text{modifier}} = W_{\text{modifier}} / D_{\text{modifier}} = 988.65 \text{ nm}^3$$

$$\text{Total number of modifier per HNP} = W_{\text{modifier}} / MW_{\text{modifier}} \times N_{\text{A}} = 3040.44$$

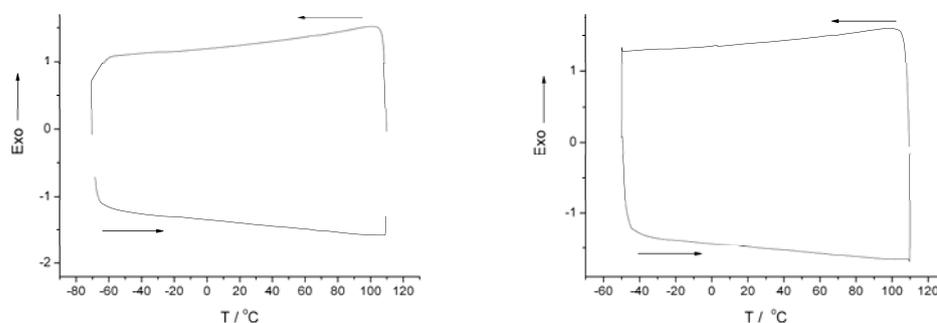
$$\text{Coverage} = \text{Total number of modifier} / A_{\text{HNP}} = 3040.44 / 577.48 = \underline{\underline{5.27 / \text{nm}^2}}$$

### **3. The crystalline state of the SAMs on the HNPs.<sup>2</sup>**

Here, we show the important information about determining the crystalline structure of the HNPs. Figure S2 depicts the FTIR spectra of the HNPs synthesized and used in this study. There was no peak corresponding to free carboxylic acids around  $1700\text{ cm}^{-1}$  in both spectra. In addition the result of dry state differential scanning calorimetry (DSC, Q100, TA instruments) of HNPs (Figure S3) did not show any peaks, i.e., no phase transition was induced. If the fatty acid SAM was in the semi-crystalline state (graft density of the fatty acids was smaller), a small endothermic peak(exothermic peak) due to the activation(deactivation) of the chain motion in the SAM would appear in the heating(cooling) curve. Furthermore, if the SAM includes unbound fatty acids in it, an endothermic peak(exothermic peak) due to the melting(freezing) of the free fatty acid would appear in the heating(cooling) curve. Combining this with the calculated graft density of the HNPs, we concluded both of the SAM on the HNPs were in the quasi-crystalline state.



**Figure S2.** FTIR spectra of the decHNPs (red) and the dodHNPs (black).



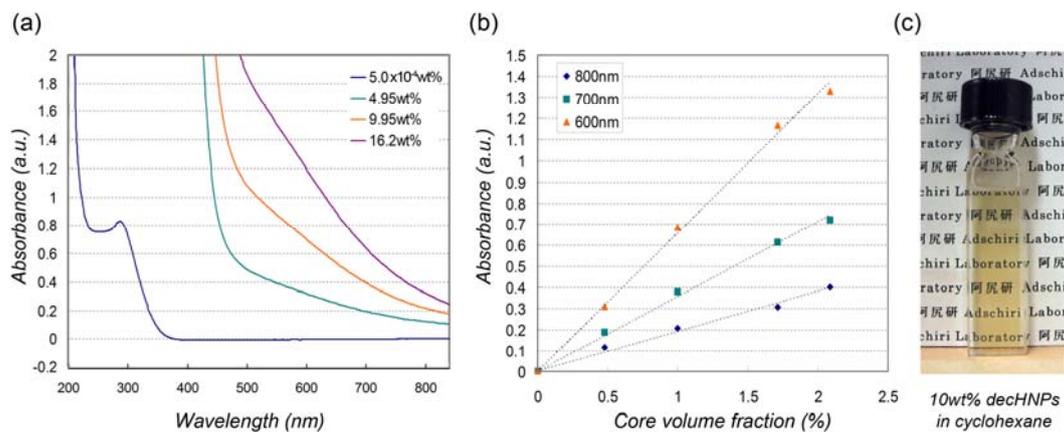
**Figure S3.** DSC curves of the decHNPs (left) and the dodHNPs (right). The speed of temperature sweep was set to  $10\text{ }^{\circ}\text{C}/\text{min}$ .

#### **4. Perfect dispersion up to 20 wt%.**

Because perfect dispersion is defined as the state in which all NPs remain in the solvent without forming any aggregations, we need to check whether HNPs are dispersed in cyclohexane with a single NP size or not. When we think about a highly concentrated single nano-sized particle's solution, the DLS and UV-VIS absorption spectrum would not be efficient for measuring the concentration of the NP. DLS is not effective for measuring highly concentrated solutions and the time-series stability of solutions. In the case of UV-VIS absorption, because strong absorption corresponds to the band gap of CeO<sub>2</sub>, most of the UV light was absorbed at a high concentration. Therefore, it is difficult to perform an accurate measurement. However, it is well known that single nano-sized particles show Rayleigh scattering, depending on the sizes of the NPs.<sup>3</sup> This might make it possible to measure the concentration and examine the dispersion state of the highly concentrated NPs solutions by measuring the strength of Rayleigh scattering in the solution. The strength of Rayleigh scattering can be measured by using UV-VIS transmittance spectrometer to measure the intensity loss of light.<sup>4</sup> The intensity loss of light by Rayleigh scattering due to the randomly dispersed spherical NPs with the particle radius  $r$ , which do not absorb at the wavelength  $\lambda$ , can be estimated by equation SE1.

$$\frac{I}{I_0} = \exp \left\{ -32\pi^4 r^3 \Phi l \left( \frac{n_0}{\lambda} \right)^4 \left( \frac{n_p^2 - n_0^2}{n_p^2 + 2n_0^2} \right)^2 \right\} \quad (\text{SE1})$$

where  $I$  is the intensity of the transmitted,  $I_0$  is the incident light,  $n_p$  is the refractive index of the NPs,  $n_0$  is the refractive index of the solvent,  $\Phi$  is the volume fraction of the NPs and  $l$  is the path length of the solution. We measured the UV-VIS spectra of the HNPs' cyclohexane solution at different concentrations in order to confirm whether HNPs solution obeyed equation SE1 or not. Figure S4 depicts the UV-VIS spectra of the decHNPs cyclohexane solution at various concentrations. Since the HNPs used in this study do not have any absorption at the wavelength range 600-800 nm, we have verified the linearity between volume fraction of the core of the HNPs and absorbance measured at each concentration. As a result, good linear relationships between them at 600, 700 and 800 nm were found. We then successfully drew analytical curves for the HNPs cyclohexane solution up to 20 wt% of the HNPs. In addition, as shown in the image in Figure S4(c), we could see no precipitation or turbidity. The detailed study is on going on this topic.



**Figure S4.** UV-VIS transmittance spectra of the deCHNPs in cyclohexane (a), analytical curves for the deCHNPs in cyclohexane (b) and the picture of the deCHNPs cyclohexane solution at 10 wt% (c).

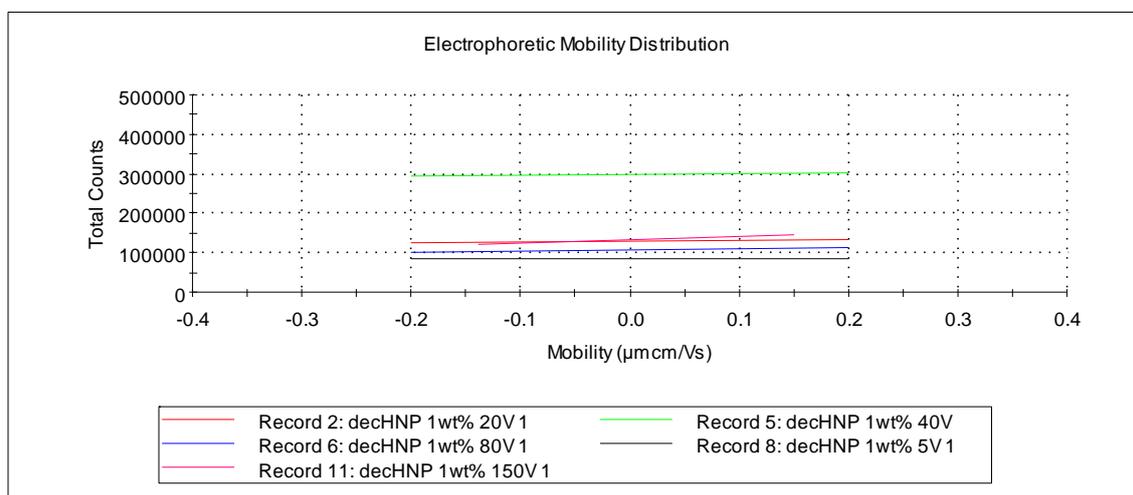
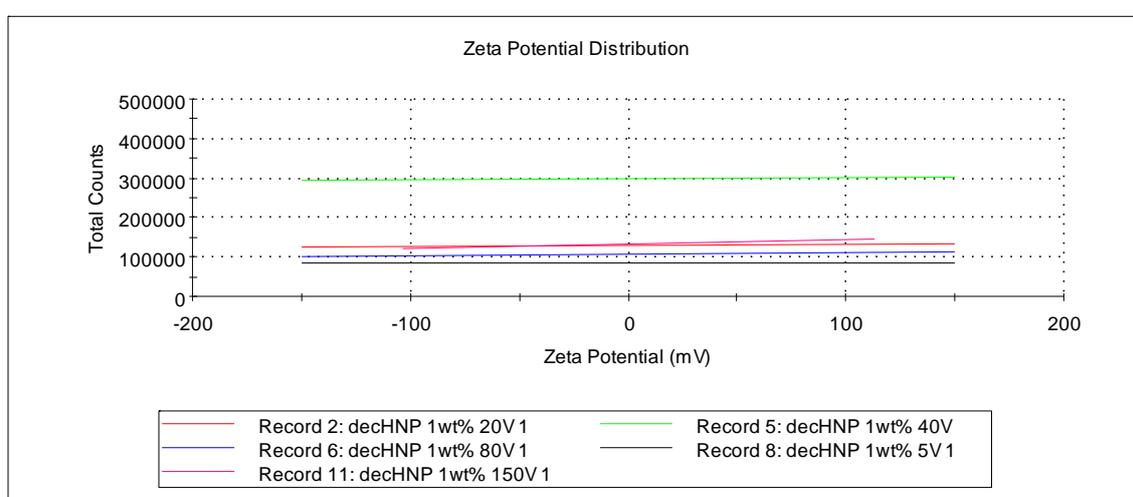
### **5. The zeta potential measurement of the decHNPs in cyclohexane.**

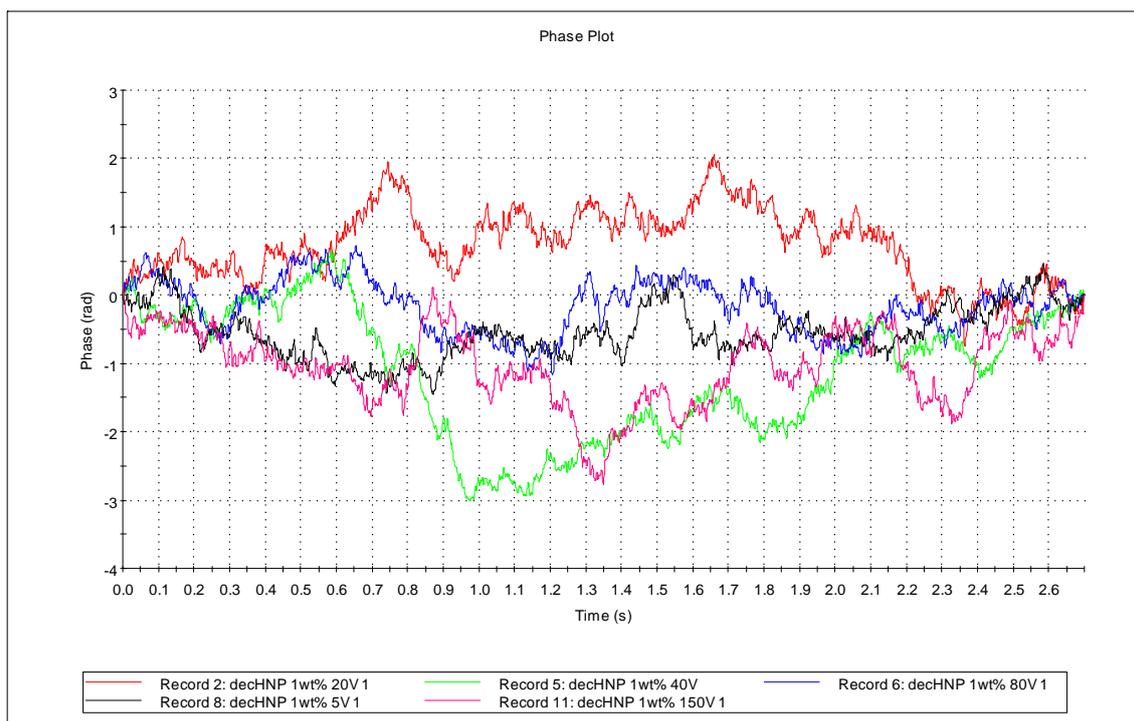
Zeta potential distribution (Malvern)

decHNPs in cyclohexane 1wt% solution at room temperature.

As we can clearly see in following figures (Figure S5), there was no change on the intensity of the light scattering with zeta potential and mobility. Furthermore, there was no significant phase change with time. The zeta potential of the decHNPs in cyclohexane must be 0.

For the dodHNPs in cyclohexane, the similar result was obtained.





**Figure S5.** The report obtained for the measurement of the zeta potential of the decHNPs in cyclohexane.

### **6. The rough estimation of potential curves between HNPs in cyclohexane.**

As writenn in main text, the total potential between to NPs can be written as below

$$V_t = V_{vW} + V_R + V_{Elas} + V_{Osm}$$

In our case,  $V_R=0$  and we employed assumption  $V_{Elas}=0$  because the contribution of elastic repulsion is smaller than the others. Then  $V_t$  can be written in

$$V_t = V_{vW} + V_{Osm}$$

$$V_{vW} = -\frac{A}{6} \left[ \frac{2R^2}{r^2 - 4R^2} + \frac{2R^2}{r^2} + \ln \left( \frac{r^2 - 4R^2}{r^2} \right) \right]$$

According to the theory proposed by Vincent et al,  $V_{Osm}$  was expressed as following.

$$V_{Osm} = \frac{4\pi R k_B T}{v_{solvent}} \phi^2 \left( \frac{1}{2} - \chi \right) \left[ l^2 \left( \frac{r-2R}{2l} - \frac{1}{4} - \ln \left( \frac{r-2R}{l} \right) \right) \right] \quad r-2R < l$$

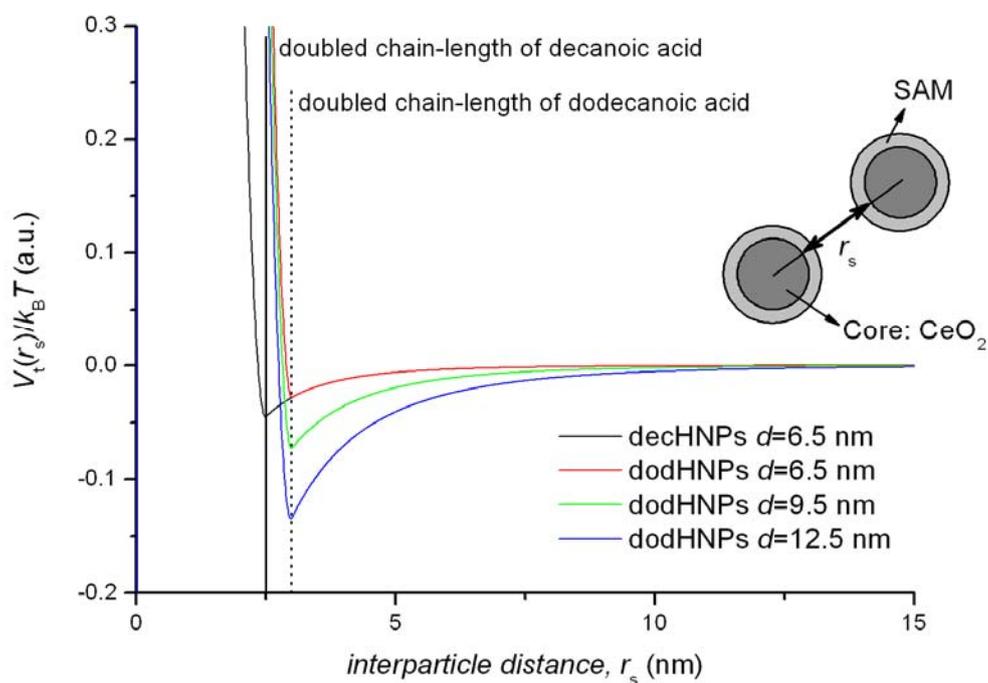
$$V_{Osm} = \frac{4\pi R k_B T}{v_{solvent}} \phi^2 \left( \frac{1}{2} - \chi \right) \left( l - \frac{r-2R}{2} \right)^2 \quad l < r-2R < 2l$$

where  $v_{solvent}$  is the volume of a solvent molecule,  $r$  is the separation distance between two cores,  $R$  is the radius of NP,  $A$  is Hamaker constant,  $l$  is the contour length of the modifier,  $\phi$  is the volume fraction of the modifier layer in the HNP and  $\chi$  is Flory-Huggins interaction parameter.

The actual values we used for the calculation were listed in Table S1. We assumed the temperature of the system was 25 °C and  $\chi$  parameter was 0.4.  $v_{solvent}$  was calculated to be  $1.81 \times 10^{-28} \text{ m}^3$ . Hamaker constant was  $A=A_{131}=1.62 \times 10^{-20} \text{ J}$ .

**Table S1.** The parameters used for the calculation of the potential curves

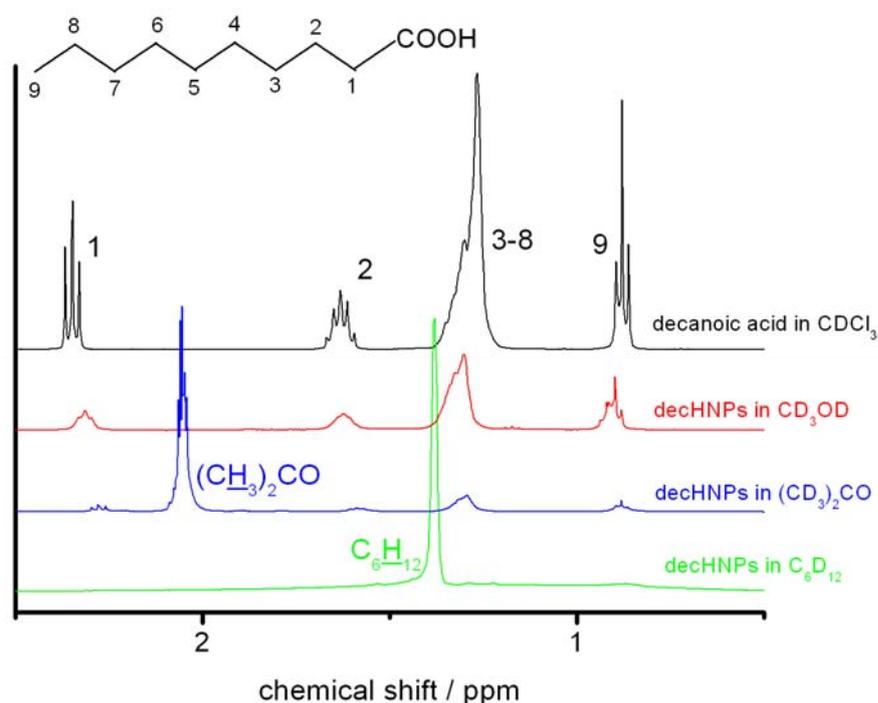
	decHNPs 6.5 nm	dodHNPs 6.5 nm	dodHNPs 9.5 nm	dodHNPs 12.5 nm
$R$ (nm)	3.25	3.25	4.75	6.25
$l$ (nm)	1.25	1.5	1.5	1.5
$\phi$ (a.u.)	0.62	0.67	0.56	0.48



**Figure S6.** The calculated total potential energy curves between two identical sized HNPs. The interparticle distance,  $r_s$ , used here was defined as the distance between two core surfaces of HNPs. As clearly seen in the Figure, the repulsive forces arise at the distance the SAMs of the HNPs contact each other.

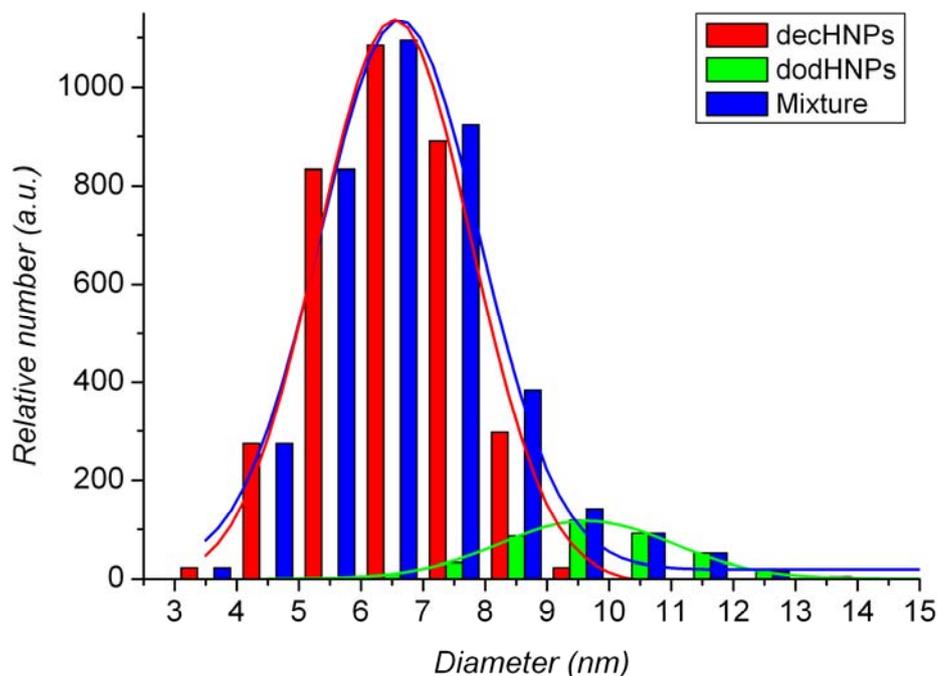
### 7. Estimation of the amount of desorbed decanoic acids from the decHNPs in solvents.<sup>2</sup>

Solution state <sup>1</sup>H NMR was measured using a 400-MHz FTNMR system (JEOL) at 25 °C. 30 mg of HNPs dissolved in 0.7 mL of the desired deuterated solvent was loaded into an NMR tube for NMR measurements. 4 mg of decanoic acid was dissolved in 0.7 mL of CDCl<sub>3</sub> was loaded into an NMR tube and measured NMR spectrum. Because the dec HNPs possesses 14 wt% of decanoic acid to its weight, that is, 4.2 mg of 30 mg so that the NMR spectrum of 4 mg of decanoic acid in 0.7 mL of CDCl<sub>3</sub> was measured. The results were shown in Figure S7. As one can clearly see that the peaks of desorbed (free) decanoic acid in the decHNPs in cyclohexane was negligible in the NMR spectrum whereas the very broad signals due to chemisorbed decanoic acids were able to be seen. The concentration of the free decanoic acids in CD<sub>3</sub>OD and (CD<sub>3</sub>)<sub>2</sub>CO was calculated to be 1.63 mg and 0.017 mg, respectively. This amount (0.017 mg in 0.7 mL) is equal to 0.14 mM. (For NMR measurement, the concentration of the HNPs in solvents were around 5 wt%.) The concentration of desorbed decanoic acids in acetone is already quite low level, furthermore, the signal of desorbed decanoic acid in cyclohexane is much smaller than that in acetone. Our presumption that the equilibrium concentration of desorbed decanoic acid has to be quite low is reasonable.



**Figure S7.** The <sup>1</sup>H-NMR spectra of decanoic acid in CDCl<sub>3</sub> (black), decHNPs in *d*4-methanol (red), decHNPs in *d*6-acetone (blue) and decHNPs in cyclohexane (green).

### 8. The calculation of the size distribution of the mixed solution $\beta$ .



**Figure S8.** The size distributions (filled blocks) and Gaussian fitting results (lines) of the mixture of decHNPs and dodHNPs in cyclohexane (Blue), 1 wt% of the dodHNPs in cyclohexane (Green) 2.5 wt% of the decHNPs in cyclohexane (Red).

#### Gaussian fitting

$$\text{Equation: } y = y_0 + \frac{A}{w \cdot \sqrt{\pi/2}} \cdot \exp(-2 \cdot ((x - x_c)/w)^2)$$

Weighting:

y No weighting

#### of decHNPs

$$\text{Chi}^2/\text{DoF} = 8.01715$$

$$R^2 = 0.99512$$

$$y_0 = -0.88468 \pm 1.10462$$

$$x_c = 6.54269 \pm 0.03333$$

$$w = 2.47784 \pm 0.07642$$

$$A = 312.0166 \pm 10.22598$$

#### of dodHNPs

$$\text{Chi}^2/\text{DoF} = 8.12922$$

$$R^2 = 0.99652$$

$$y_0 = 0.60293 \pm 1.20443$$

$$x_c = 9.63298 \pm 0.03053$$

$$w = 2.78323 \pm 0.07327$$

$$A = 408.1692 \pm 11.81301$$

#### of mixture

$$\text{Chi}^2/\text{DoF} = 1697.71516$$

$$R^2 = 0.99181$$

$$y_0 = 19.17553 \pm 16.35197$$

$$x_c = 6.62378 \pm 0.04443$$

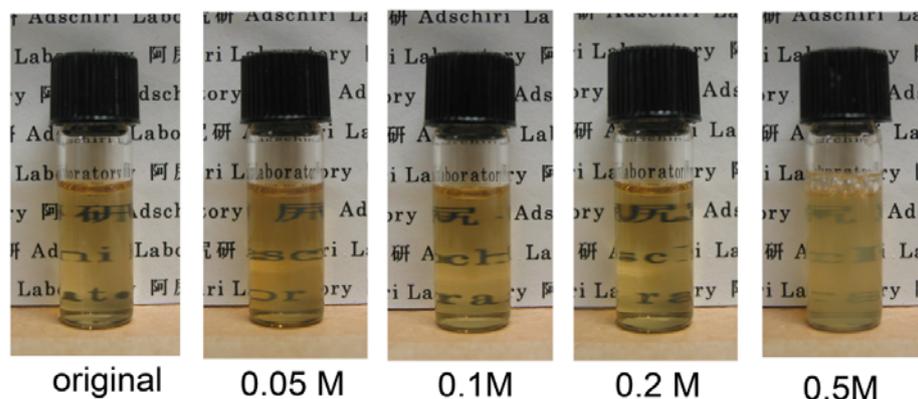
$$w = 2.57061 \pm 0.10271$$

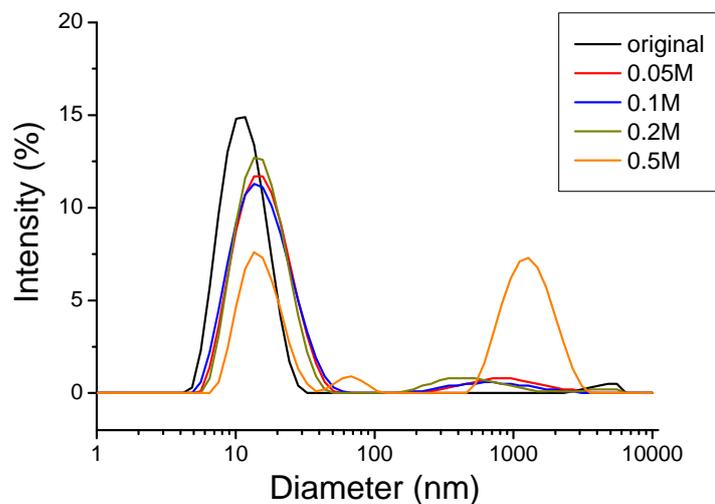
$$A = 3598.545 \pm 154.20641$$

### 9. The examination of the surfactant effect on the dispersion of the HNPs.

As written in main text, surfactant effect on the dispersion of decHNPs was investigated by adding dodecanoic acid in decHNPs solution.

The result was shown in Figures S9. One can clearly see there was no improvement on the dispersion of the decHNPs. This implies that even though the SAM of the decanoic acid on the decHNPs exchanges the modifier into dodecanoic acid forming the jagged surface (it may increase the interaction with solvent molecules), the dispersion does not improve. In other words, this indicates the jagged surface of modifier exchanged decHNPs did not enhance the dispersion of the decHNPs. In addition, we added too much decanoic(dodecanoic) acid in the dodHNPs(decHNPs) solution, the dispersion became worse and worse.





**Figure S9.** Images (upper) and DLS results (lower) of decHNPs in cyclohexane. All the images and DLS measurements were finished within 15 min. after the sample solution preparation. Dodecanoic acid was added to the 1 wt% dodHNPs cyclohexane solution (800  $\mu$ l) until the final concentration of dodecanoic acid becomes 0.05 M (1.3 wt%), 0.1 M (2.6 wt%), 0.2 M (5.2 wt%) and 0.5 M (14.3wt%).

**References (for Supporting information):**

1. J. Zhang, S. Ohara, M. Umetsu, T. Naka, Y. Hatakeyama and T. Adschiri, *Adv. Mater.*, 2007, **19**, 203-206.
2. T. Arita, J. Yoo and T. Adschiri, *J. Nanopart. Res. published online.*, 2009.
3. H. C. v. d. Hulst, *Light scattering by small particles*, 2 nd (Dover edition) edn., John Wiley & Sons, Inc., New York, 1957.
4. W. R. Caseri, *Mater. Sci. Technol.*, 2006, **22**, 807-817.