Supporting Information

A phyto-reduction Route for Selective Synthesis of Highly Stable Ag and Ag:AgCl Hybrid Nanocolloids

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1. Vernonia anthelmintica (L.) wild seed

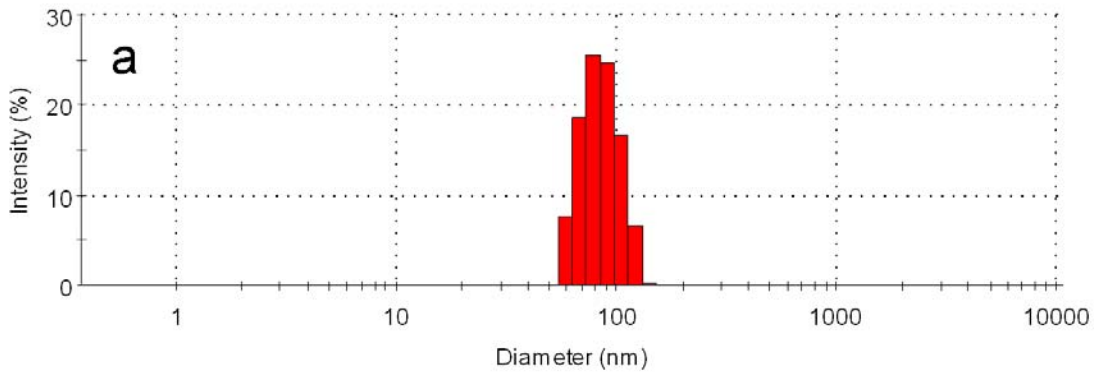
The *Vernonia anthelmintica* (L.) willd (VW) seed (Figure S1) is a famous folk medicine in china, India, Pakistan, and certain countries of Africa.[34-35] It is widely used for medicinal purpose, especially treatment skin disease. Science 1960, another major consideration about this plant is its oil-rich seed giving the plant potentiality as a new bio-oil crop.[36-37]

Figure S1. A photo of the *Vernonia anthelmintica* (L.) willd seeds was taken by a digital camera. (The one VW seed is about 0.5 centimeters long)

2 Effect of VW extract and NaOH on the size distribution of Ag NPs (Malvern Instruments Ltd, Malvern, UK)

The particle size distribution of silver nanoparticles was evaluated using dynamic light scattering (DLS) measurements conducted with a Malvern Zeta-sizer Nanoseries compact scattering spectrometer (Malvern Instruments Ltd, Malvern, UK). Data obtained were analyzed using Zeta-sizer software. Each test sample is original colloid solution without ultrasound or filtration. Each DLS measurement was run at least in triplicate using automated, optimal measurement times and laser attenuation settings.

Increasing the amount of seed extract in the synthesis didn't show apparent effect on the size distribution of product particles, but would led to mildew of the colloidal solution after placed for 2-3 months (Figure S2a). On the other hand, a smaller amount of seed extract could not ensure complete reduction of silver ions as well as effective capping of product particles, and NPs with a smaller average size and a wider size distribution would form, which tend to aggregate in the solution (Figure S2b). It was also found that the size of NPs decrease with the increase of the amount of NaOH due to enhanced nucleation induced by NaOH, and the size distribution of the particles becomes wider, which might result from the occurrence of aggregation of the smaller NPs with higher surface energy (Figure S2c). Moderate decrease of the amount of NaOH would result in a larger average size of NPs with fine size distribution (Figure S2d).



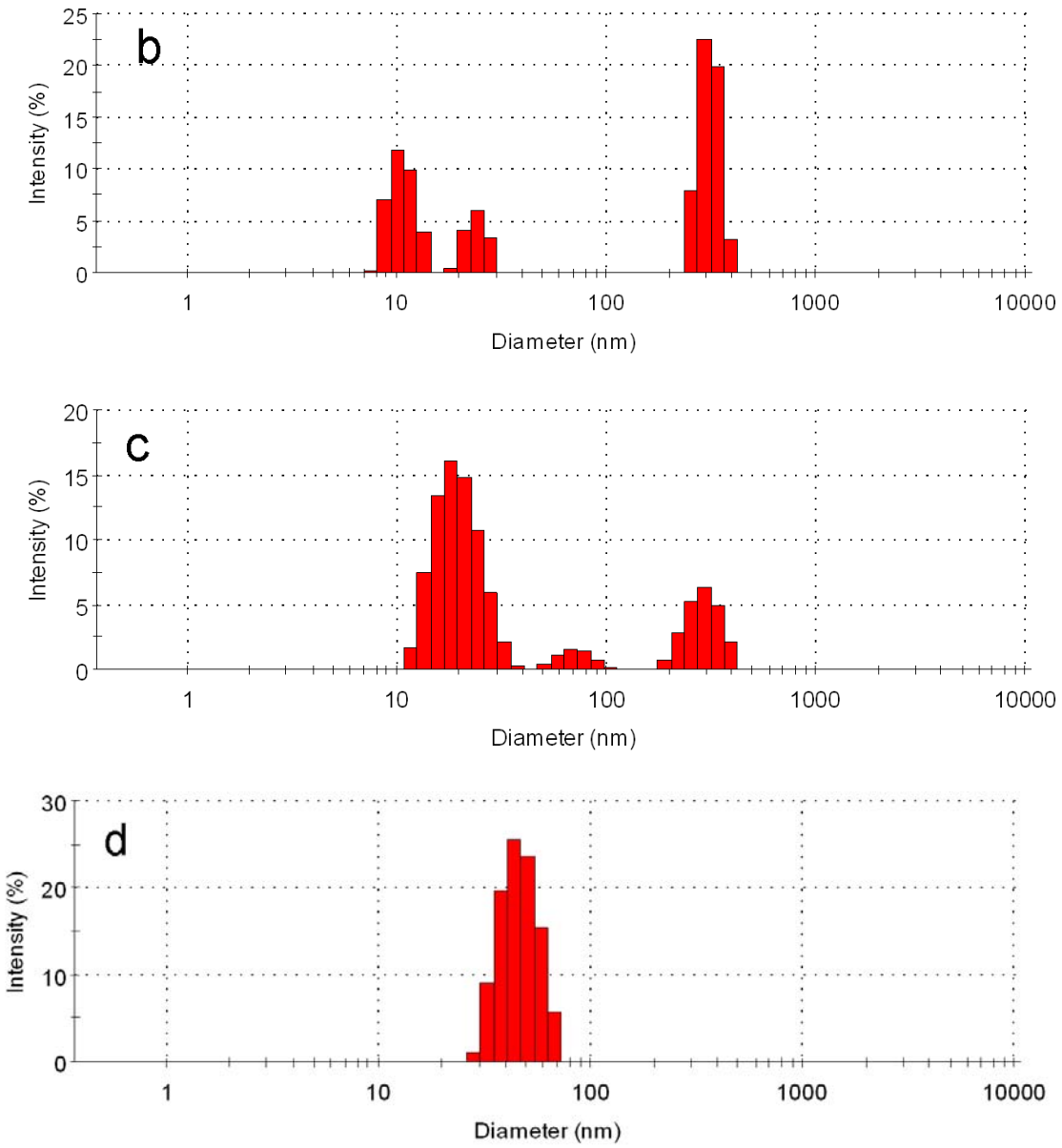


Figure S2. Particle size distribution histogram of Ag NPs obtained at different amount of seed extract and NaOH. a) $V_{Extract} : V_{AgNO3} : V_{NaOH} = 4 : 5 : 1$; b) $V_{Extract} : V_{AgNO3} : V_{NaOH} = 0.25 : 5 : 1$; c) $V_{Extract} : V_{AgNO3} : V_{NaOH} = 1 : 5 : 4$; d) $V_{Extract} : V_{AgNO3} : V_{NaOH} = 1 : 5 : 0.25$.

3 Particle size (DLS) analysis of Ag NPs at different storing time (Malvern Instruments Ltd, Malvern, UK)

Each test sample is original colloid (VExtract : VAgNO3 : VNaOH = 1 : 5 : 1) solution after different storing time (not the same batch) without ultrasound or filtration. Although the different batches typically have some fluctuation in size , the results will not influence the evaluation of colloidal stability. The frequency distribution observed from the Figure S3a, b, c shows that almost 80% of the particles are in the 20 to 50 nm range. This particle size measured by DLS technique is larger than that observed by TEM (Figure 2e) due to the different working principles of the two instruments.[38] It is important to note that the colloids have no obvious particle

aggregation over the 100nm size after long period of storage at ambient temperature (Figure S3b, c). This further proves the high stability of the colloidal products synthesized by our approach.

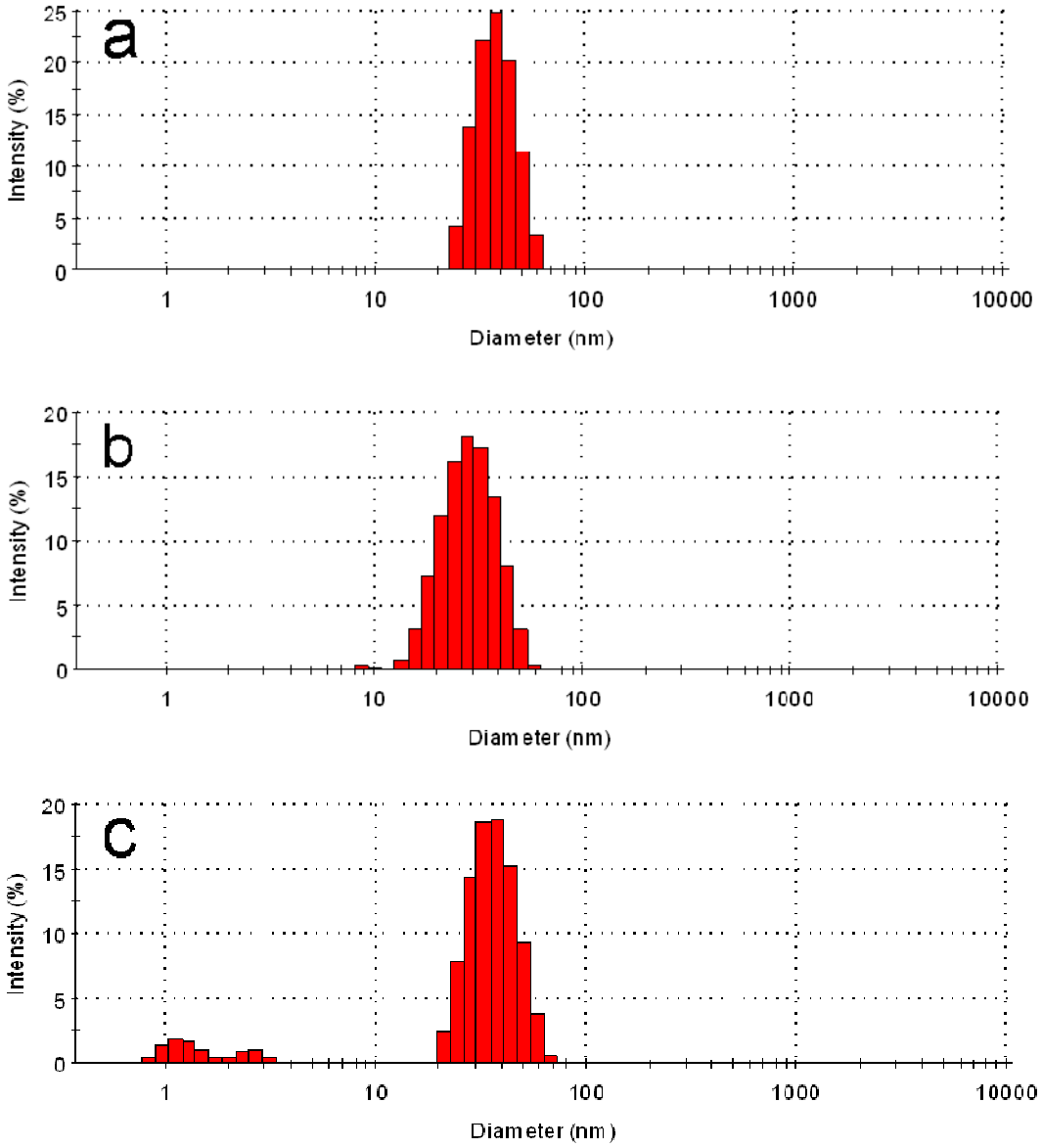


Figure S3. Particle size distribution histogram of Ag NPs obtained from Zeta-size analysis. a) fresh colloidal solution, b) the colloidal solution after placed for 3 months, c) the colloidal solution after placed for 20 months.

4. EDX analysis of AgCl:Ag hyrbid particles（EDX acessory of JEOL-2100F TEM）

Elemental analysis of the AgCl:Ag hybrid nanoparticles is carried out with energy dispersive X-ray spectroscopy (EDS). AgCl:Ag sample for EDS was washed several times with deionized water to remove the adsorbed plant ingredient. It clearly shows the dominating elements in the product particles are Ag and Cl. The presence of Cu and other trace amount of metals is due to the substrate. The mole ratio between Ag

and Cl is about 12.5, and the mole ratio of Ag to AgCl should be about 11.5.

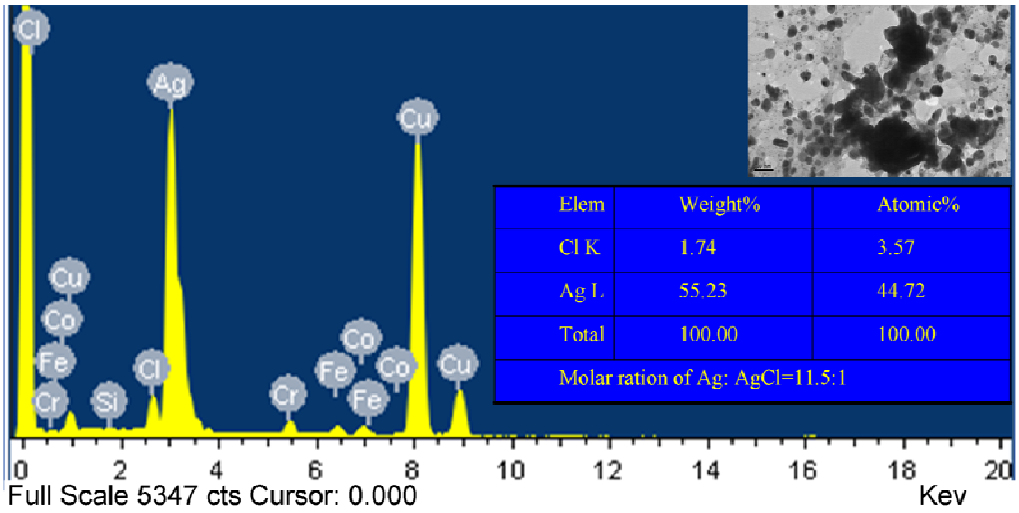


Figure S4. EDS spectra of the as-synthesized AgCl:Ag nanoparticles after washed with deionized water for several times to remove the adsorbed plant ingredient.

5. XRD patterns of the products at different reaction time

In our XRD investigations, a fixed amount of reaction solution of 24 mL was sampled at different time. The solution was centrifuged and the precipitate was then deposited on a holder for XRD measurement.

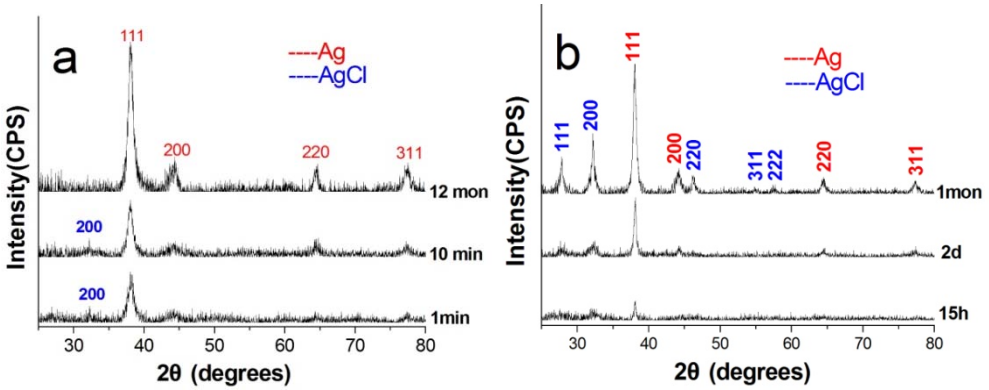


Figure S5. XRD patterns of the products at different reaction time when a) NaOH is present, and b) NaOH is absent.

6. XPS spectra collected for Ag colloids (Amicus, Shimadzu. Co., Japan)

X-ray photoelectron spectroscopy (XPS) was used to analyze the changes of the surface chemistry. For XPS measurments, the sample preparation method is similar to that in XRD analysis except that the precipitate was coated onto Al substrate. The binding energies of Ag samples are consistent with the values reported for metal Ag (368.3 and 374.3 eV)[39] and indicate the presence of zerovalent Ag only. This further proved the excellent chemical stability of the Ag nanocolloids.

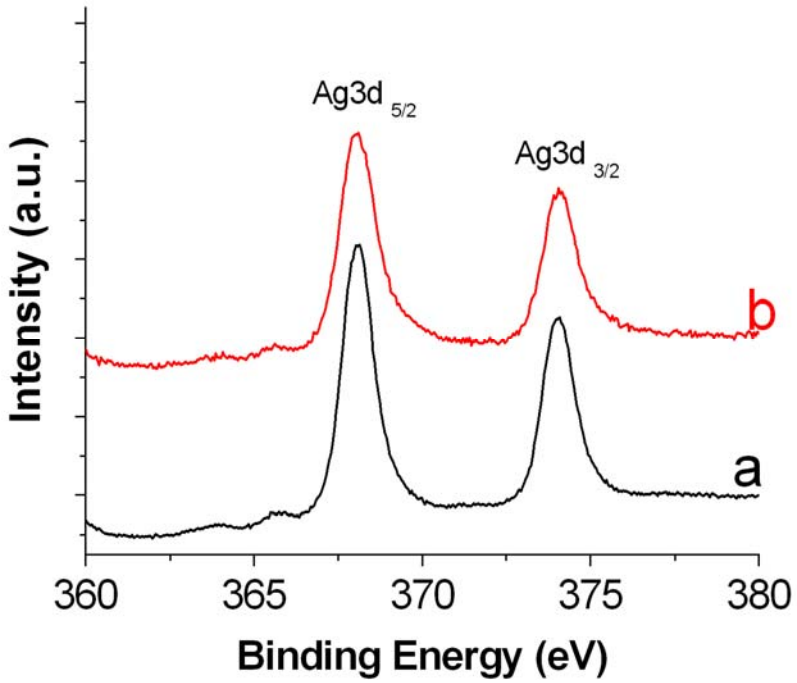


Figure S6. Ag 3d XPS spectra of NP samples after stored for a) 4 days and b) 10 months.

7. The GC-MS analyses may be prove the existence of vernolic acid in VW seed extract

In order to confirm the existence of long chain vernolic acid, 50 mL of fresh aqueous extract was extracted with diethyl ether, and about 220 mg of crude oil was obtained from diethyl ether fraction. The quantitative and qualitative analysis of the crud oil was also performed by gas chromatography-mass spectrometry (GC-MS) after methyl esterification treatment. Transesterification was carried out in 20% BF3/methanol as described by Tsevegsuren.[40] GC-MS analyses were performed using an Agilent Technologies (type 7890A, USA) gas chromatograph equipped with a mass selective detector (MSD) (type 5975C, Agilent, USA). In the case of the derivative of vernolic acid, the column temperature was initially kept at 200 °C, and then increased from 200 to 300°C at 5 °C/min. The final temperature was held for 5 min. The other operating conditions were: split/splitless injector in split mode (split ratio = 1:50) at a temperature of 310°C, an interface temperature of 280°C, and an ion source temperature of 230 °C.

From GC-MS analysis, it can be known that the extract oil contains a major proportion of vernolic acids (76.4%). Gas chromatogram for the methoxy derivative of the crude oil is shown in the lower left hand of Figure S7. Mass spectrum of the ring-opening derivative of vernolic acid is displayed in the upper right-hand of Figure S7.

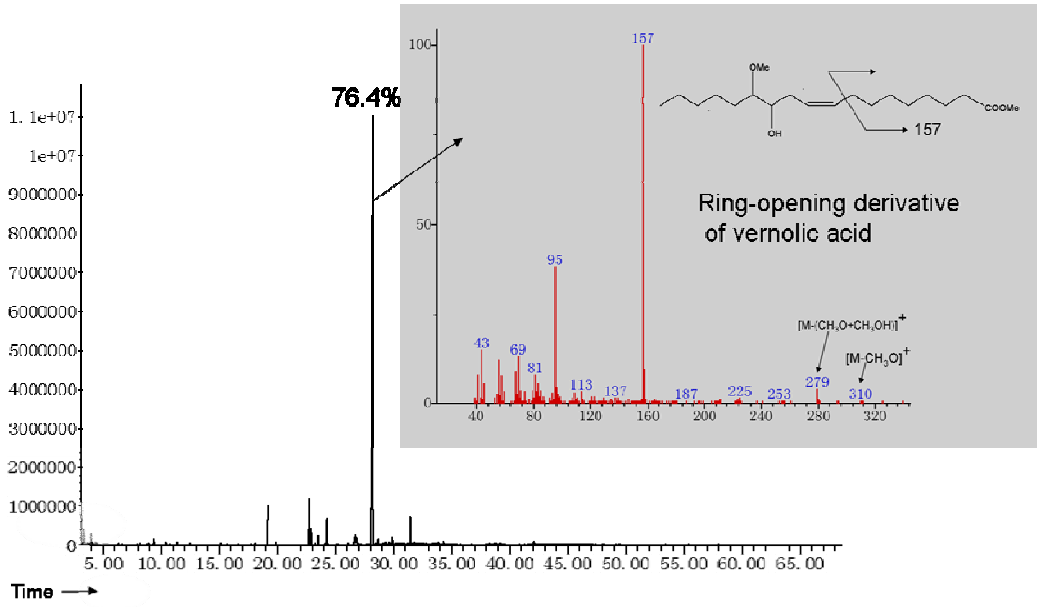


Figure S7 Lower left: gas chromatogram for the methoxy derivative of the oil. Upper right: mass spectrum of the ring-opening derivative of vernolic acid.

8. Energy dispersive X-ray spectroscopy of the VW seed extract

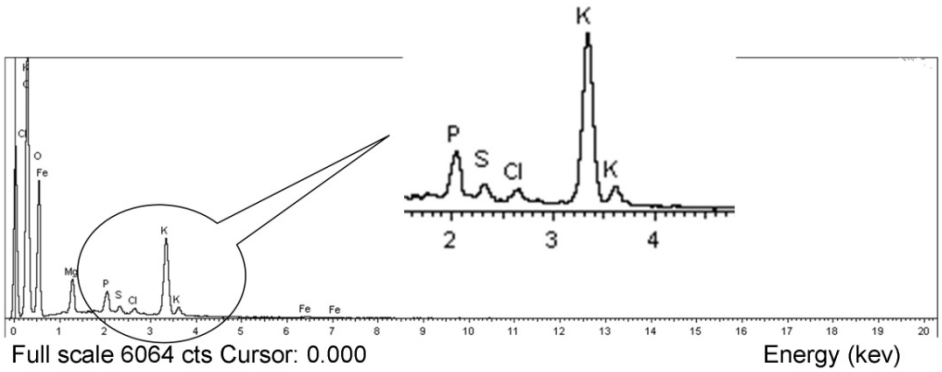


Figure S8. Energy dispersive X-ray spectroscopy of the VW seed extract confirmed the presence of Cl.

References

34. Iqbal, Z.; Lateef, M.; Jabbar, A.; Akhtar, M. S.; Khan, M. N., *Pharm. Biol.* **2006,** *44*, 563.

35. Hördegen, P.; Hertzberg, H.; Heilmann, J.; Langhans, W.; Maurer, V., *Vet. Parasitol.* **2003,** *117*, 51.

36. Krewson, C.; Luddy, F., *J. Am. Oil Chem. Soc.* **1964,** *41*, 134.

37. White, G. A.; Gardner, J. C.; Cook, C. G., *Industrial Crops and Products* **1994,** *2*, 259.

38. Bhattarai, S. R.; Kim, S. Y.; Jang, K. Y.; Lee, K. C.; Yi, H. K.; Lee, D. Y.; Kim, H. Y.; Hwang, P. H., *Nanomed. Nanotechnol. Biol. Med.* **2008,** *4*, 146.

39. Zaccheo, B. A.; Crooks, R. M., *Langmuir* **2011,** *27*, 11591.

40. Tsevegsuren, N.; Aitzetmuller, K.; Vosmann, K., *Lipids* **2004,** *39*, 571.

Electronic Supplementary Material (ESI) for CrystEngComm