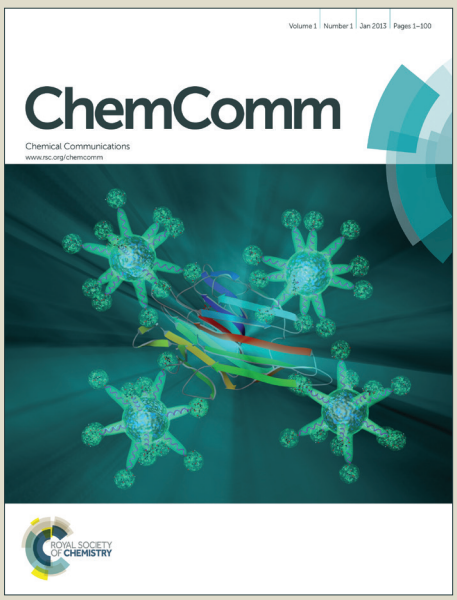
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name

RSCPublishing

COMMUNICATION

Recovery and redispersion of gold nanoparticles using a self-assembly of pH sensitive zwitterionic amphiphile

Cite this: DOI: 10.1039/x0xx00000x

Clara Morita-Imura [a*], Yoshiro Imura [b], Takeshi Kawai [b] and Hitoshi Shindo[a*]

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

The pH-responsive self-assembly of zwitterionic amphiphile C16CA was expanded to recovery gold (Au) nanoparticles for environmentally friendly chemistry applications. Multilayered lamellae at pH ~4 successfully incorporated nanoparticles from the dispersion. Redispersion of nanoparticles was available under basic condition by transition of self-assembly.

Noble metal nanomaterials have been studied extensively because of their potential for applications in nano-science, including catalysis, electronics, and biotechnology.[1] However, the cost of the materials requires their limited use or the development of a reuse method.[2] The sedimentation method using centrifugation or a stimuli-responsive stabilizer[3-6] has been used to recover dispersed nanoparticles (NPs). Since strong interparticle interactions are likely to cause coagulation of NPs, especially those with a large diameter,[5] the redispersion of coagulated NPs[3] for convenient reuse without the consumption of additional energy is of interest. Therefore, a novel recovery method allowing the redispersion and reuse of noble metal nanomaterials is needed.

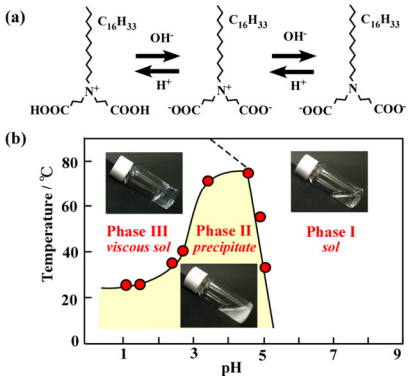


Figure 1. (a) Zwitterionic amphiphile of C16CA. (b) Phase diagram of an aqueous solution of C16CA. Inset shows the molecular structure of C16CA and photographs of the aqueous C16CA solution.

In addition, supramolecular assemblies based on noncovalent bonds are interesting candidates for encapusulation applications[7-9] and the release of substances upon specific stimuli.[10-12] Kumar et al. investigated dipeptide–based low-molecular-weight gelators that adsorb dye molecules, resulting in gelator-dye composites that precipitated allowing the removal of dye molecules from a suspension.[8] Esch et al. reported the release of enzymes from a gel matrix upon heating.[10] The encapsulation-release method incorporating supramolecular assemblies is potentially useful for other materials involving Au nanomaterials, although few studies have reported the incorporation of noble metal nanomatrials in assemblies with a multi- or bilayer structure.[13, 14]

To develop a new recovery system for noble metal, an amphiphile must be developed that can adsorb onto the metal surface,[15, 16] form highly ordered self-asssembled structures similar to supramolecules,[17, 18] and exhibit a response to stimuli[19-22]. Our previous report indicated that amphiphiles derived from amines[23-27] could adsorb onto Au nanomaterials and act as a pH-responsive stabilizer to phase-transfer Au nanoparticles between aqueous and organic media using the transition of the adsorption state on Au surface.[23, 24] Other reports demonstrated that amphiphiles with hydrogen-bonding sites could form self-assembled lamellar gels in nonpolar solvents,[26] but these self-assembled gels became unstable in aqueous solution due to hydration of the amphiphile. However, the introduction of an oppositely charged moiety, such as a zwitterionic structure, has been found to promote the formation of supramolecules in polar solvents.[28-30] The present report describes a zwitterionic amphiphile, 3-[(2-carboxy-ethyl)-hexadecyl-amino]-propionic acid, containing amine and carboxyl groups (C16CA, Fig. 1a, ESI), and its pH-responsive transition on assembly. In addition, lamellar assembly of C16CA is obtained at a specific pH range and recovery of Au NPs with the lamellar precipitation through pH adjustment is demonstrated. The pH-sensitive transition of C16CA assemblies enabled the reversible precipitation-redispersion of Au NPs through pH regulation without further heating, sonication, or stirring. This method is very different from the conventional coagulation

method, because Au NPs are adsorbed and incorporated in the C16CA assemblies with a sufficient interparticle distance.

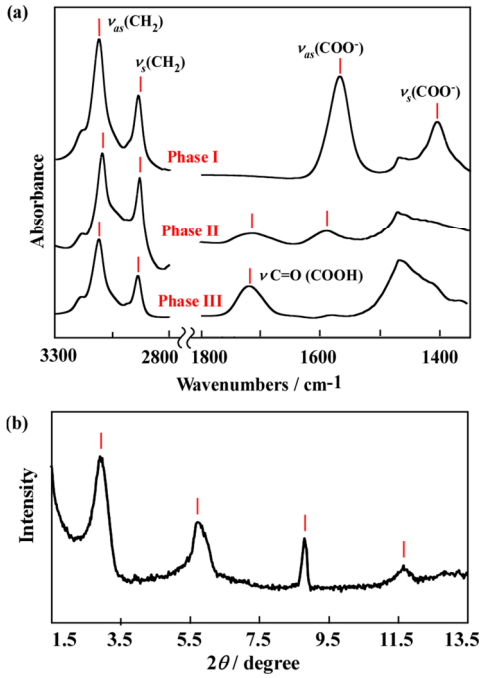


Figure 2. (a) FT-IR spectra of C16CA solution at various phases. (b) XRD profile of the C16CA precipitate at Phase II.

As shown in the phase diagram in Fig. 1b, aq. C16CA exhibited three pH-dependent states: a transparent solution with low viscosity above pH ~5 (Phase I), a phase-separated precipitate at pH 2 - 5 (Phase II), and a highly viscous solution below pH ~2 (Phase III). The C16CA molecule is protonated-deprotonated as shown in Fig. 1a, so that this phase transition appeared to occur *via* a change in the self-assembly structure of C16CA, which was related to electrostatic interactions or to the hydrogen bonds of the hydrophilic moiety. At the high pH values of Phase I, FT-IR analysis was used to investigate the terminal carboxyl groups dissociated to COO^- (Figs. 1a and 2a),[31] which revealed that negatively charged C16CA dissolved in water to form micelles with a strong electrostatic repulsion. At the middle pH values, the amino moiety protonated ($pK_a \approx 6.6$), and C16CA precipitated as shown in Fig. 1b (Phase II) due to the approach of the isoelectric point at pH ~4, where the electrostatic charge between the amine and carboxylate is neutralized. A specific periodic pattern on XRD at 2.9, 5.8, and 8.8° (Fig. 2b) indicated that the precipitates at Phase II had a lamellar structure, which contains a hydrophilic-hydrophobic multilayer.[25-27] The lamellar spacing was estimated to be 3.0 nm using the Bragg's equation.[18, 26, 27] FT-IR spectra showed the antisymmetric and symmetric CH stretching bands of an alkyl chain at 2918 and 2850 cm^{-1}, respectively, indicating methylene chains in an all-trans state (Fig. 2a).[26, 27] Thus, strong hydrophobic interactions in addition to ion-pair interactions between the amine and carboxylate resulted in molecular packing in the lamellar assembly of C16CA. In contrast, at low pH (Phase III), carboxyl groups ($pK_a \approx 2.0$, 1.6) protonated, and C16CA redissolved. Interestingly, the solution at Phase III possessed high viscosity, unlike that at Phase I (Fig. 1) and Maxwell-like dynamic viscoelastic property was observed (Fig. S1). This result implies that C16CA formed worm-like micelles, which has an equilibrium entanglement point.[32, 33] According to FT-IR spectra, the C=O stretching mode of COOH appeared at 1716 cm^{-1} in Phase III (Fig. 2a), indicating lateral hydrogen-bonded carboxyl groups.[34] Thus, formation of C16CA worm-like micelles occurred through biaxial intermolecular packing of carboxyl groups. The self-assembly of C16CA occurred reversible structural transitions through changes in pH, which allows control of the dispersion-precipitation state. This pH-sensitive transition for the self-assembly of amphiphiles is expected to be useful for the design of many stimuli-responsive composite materials. Furthermore, amphiphiles and their self-assemblies exhibit great affinity toward nano-materials. Therefore the pH-responsive precipitation phenomenon at Phase II was applied to the recovery of Au NPs.

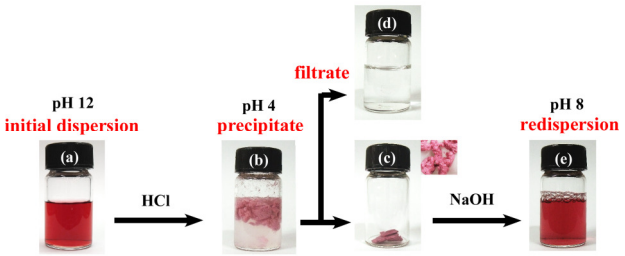


Figure 3. (a-e) Photographs of pH-responsive removal and redispersal of Au NPs.

The Au NPs with an average diameter of 15 nm were prepared as follows. A 15 mM aqueous citric acid solution (20 mL) was added to 80 mL of 0.625 mM aq. $HAuCl_4$ and heated to 90°C (ESI, Fig. S2).[23] Then, aq. C16CA was added to the Au NPs dispersion, and the solution ([C16CA] / [Au] = 100) obtained was used for dispersion-precipitation evaluation. Under the basic conditions at pH 12, the C16CA - Au NPs solution (Fig. 3a) was a homogeneous red dispersion that produced an absorption spectra of surface plasmon (SP) band at 522 nm (Fig. 4a), indicating that the Au NPs were well dispersed.[23] Next, the solution pH was adjusted to pH 4 using 1 M HCl. Similar to the aq. C16CA solutions, the C16CA lamellae precipitated immediately out of the C16CA - Au solution (Fig. 3b). Simultaneously, Au NPs were incorporated into the lamellar precipitate. Filtration enabled separation of the light reddish-purple precipitates from the transparent solution (Figs. 3c-d). The UV-Vis spectra of the filtrate did not contain any absorbance in the visible region (such as for the Au SP band) (Fig. 4a), indicating that the Au NPs were incorporated in the precipitate completely and were absent in the filtrate. These results suggest that the Au NPs were removed by the C16CA self-assembled lamellae. The C16CA molecule has an amino moiety that adsorbs onto Au, allowing the insoluble precipitate of C16CA lamellae to act as an adsorbent of the Au NPs at pH 4.

Adding 1 M NaOH to the Au NPs-C16CA composite precipitate caused dissolution of the lamellae at pH > 6 and redispersion of the Au NPs to solution without heating or sonication (Fig. 3e). The wavelength of the SP band remained constant at 523 nm (Figs. 4a and 6a), indicating that the Au NPs could redisperse without coagulation. The TEM images demonstrate that the Au NPs did not change diameter or shape during the dispersion-redispersion procedure (Figs. 5a-b), confirming that the Au NP recovery technique involved a pH change that affected C16CA.

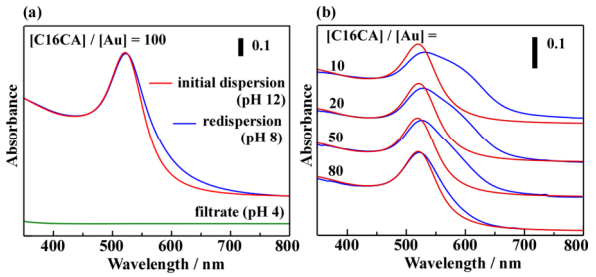


Figure 4. UV-Vis spectra of the initial Au NPs dispersion at pH 12 (red), redispersed solution at pH 8 (blue), and the filtrate at pH 4 (green) at various [C16CA] / [Au] ratios.

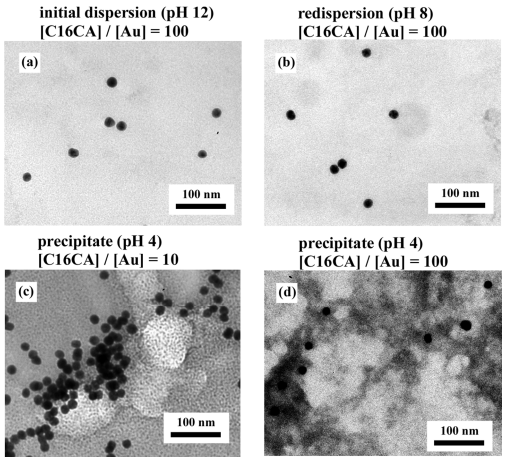


Figure 5. TEM images of Au NPs in (a) the initial dispersion at pH 12, (b) redispersed solution at pH 8, and (c, d) the precipitate at pH 4. [C16CA] / [Au] = 100 except for (c) where [C16CA] / [Au] = 10.

To determine the effect of C16CA on pH-responsive redispersion phenomena, pH was adjusted under relatively low [C16CA] conditions. When the ratio of [C16CA] / [Au] was 10 to 50, Au NPs were well dispersed at pH 12 and precipitated at pH 4, although the SP band of the redispersed solution at pH 8 red-shifted (Fig. 4b), indicating that the dispersibility of Au NPs dropped slightly after precipitation at [C16CA] / [Au] ratios < 50. The red-shifts of SP band for redispersion were occurred not by the morphological change of Au NPs but by the coagulation of Au NPs (Figs. S3 and S4). The TEM observations indicated that Au NPs were closely coagulated during precipitation at pH 4 and could not redisperse at pH 8 (Fig. 5c). In contrast, at [C16CA] / [Au] =100, TEM images suggested that Au NPs at pH 4 were wrapped up with the C16CA lamellar assembly (Fig. 5d), which adsorbed and incorporated the Au NPs in its network. Thus, the C16CA lamellae give to Au NPs sufficient intermolecular distance and prevent coagulation of Au NPs. The pH-responsive recovery-redispersion of Au NPs was demonstrated over at least 3 cycles. The SP band peak of Au NPs remained at ~ 523 nm for any cycled redispersion, and no morphological changes of the Au NPs was observed, indicating that C16CA self-assemblies prevented coagulation by multicycle recovery-redispersion manipulations (Figs. 6 and S5).

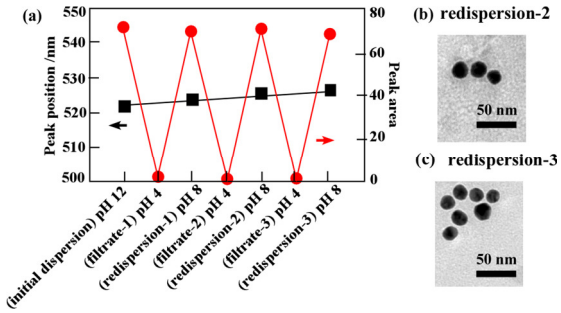


Figure 6. (a) Peak position (black) and peak area (red) of the SP band for multi-cycled recovery-redispersion of Au NPs at [C16CA] / [Au] = 100. (b, c) TEM images of multicycled redispersed Au NPs.

Conclusions

The zwitterionic amphiphile C16CA formed self-assemblies that could undergo reversible structural changes, spherical micelle - lamellae - wormlike micelle, by adjusting the pH. This pH-sensitive transition on self-assembly was developed to recover Au NPs. The C16CA acts as a unique NPs precipitant. The Au NPs were incorporated into the C16CA lamellar precipitate at pH 4 and separated from the suspension. The C16CA lamellae prevent coagulation of the Au NPs during precipitation, which enabled the Au NPs to redisperse by making the pH basic. This incorporation recovery technique using the C16CA assembly can be applied to other inorganic or organic nanomaterials with an affinity for amino or carboxyl groups. Self-assembly of the zwitterionic amphiphile is a powerful tool that permits recovery of Au nanomaterials but also has the potential to be applied to the handling of a variety of nanomaterials.

Acknowledgement

This work was supported by Grant-in-Aid for Scientific Research from Japan Society for the Promotion of Science (No. 24510144, 25886013) and the Institute of Science and Engineering of Chuo University.

Notes and references

[a] Department of Applied Chemistry, Chuo University, 1-13-27 Kasuga Bunkyo-ku, Tokyo 112-8551, Japan.
E-mail: cimura@kc.chuo-u.ac.jp, shindo@kc.chuo-u.ac.jp
[b] Department of Industrial Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8614, Japan.
Electronic Supplementary Information (ESI) available: [Synthesis of C16CA, Rheological measurements, Preparation of Au NPs capped with citric acid and Redispersion of Au NPs]. See DOI: 10.1039/c000000x/

1. Y. Xia, Y. Xiong, B. Lim and S. E. Skrabalak, *Angew. Chem. Int. Ed.*, 2009, **48**, 60-103.
2. D. Wang and Y. Li, *J. Am. Chem. Soc.*, 2010, **132**, 6280-6281.
3. Y. Shiraishi, K. Tanaka, E. Shirakawa, Y. Sugano, S. Ichikawa, S. Tanaka and T. Hirai, *Angew. Chem. Int. Ed.*, 2013, **52**, 8304-8308.
4. C. Raimondo, F. Reinders, U. Soydaner, M. Mayor and P. Samori, *Chem. Commun.*, 2010, **46**, 1147-1149.

5. I. Ojea-Jiménez and V. Puntes, *J. Am. Chem. Soc.*, 2009, **131**, 13320-13327.
6. H.-C. Huang, A. Nanda and K. Rege, *Langmuir*, 2012, **28**, 6645-6655.
7. S. Dutta, D. Das, A. Dasgupta and P. K. Das, *Chem. Eur. J.*, 2010, **16**, 1493-1505.
8. S. Debnath, A. Shome, S. Dutta and P. K. Das, *Chem. Eur. J.*, 2008, **14**, 6870-6881.
9. H. Cao, P. Duan, X. Zhu, J. Jiang and M. Liu, *Chem. Eur. J.*, 2012, **18**, 5546-5550.
10. J. Boekhoven, M. Koot, T. A. Wezendonk, R. Eelkema and J. H. van Esch, *J. Am. Chem. Soc.*, 2012, **134**, 12908-12911.
11. X. Li, J. Li, Y. Gao, Y. Kuang, J. Shi and B. Xu, *J. Am. Chem. Soc.*, 2010, **132**, 17707-17709.
12. S. Ito, H. Takata, K. Ono and N. Iwasawa, *Angew. Chem. Int. Ed.*, 2013, **52**, 11045-11048.
13. A. Pal, A. Srivastava and S. Bhattacharya, *Chem. Eur. J.*, 2009, **15**, 9169-9182.
14. H.-Y. Lee, S. H. R. Shin, L. L. Abezgauz, S. A. Lewis, A. M. Chirsan, D. D. Danino and K. J. M. Bishop, *J. Am. Chem. Soc.*, 2013, **135**, 5950-5953.
15. J. P. Vivek and I. J. Burgess, *Langmuir*, 2012, **28**, 5031-5039.
16. J. P. Vivek and I. J. Burgess, *Langmuir*, 2012, **28**, 5040-5047.
17. H. Hoffmann, *Adv. Mater.*, 1994, **6**, 116-129.
18. T. Kar, S. Debnath, D. Das, A. Shome and P. Das, *Langmuir*, 2009, **25**, 8639-8648.
19. Z. Chu and Y. Feng, *Chem. Commun.*, 2010, **46**, 9028-9030.
20. Y. Lin, X. Han, X. Cheng, J. Huang, D. Liang and C. Yu, *Langmuir*, 2008, **24**, 13918-13924.
21. Y. Lin, X. Han, J. Huang, H. Fu and C. Yu, *J. Colloid Interface Sci.*, 2009, **330**, 449-455.
22. K. Sakai, K. Nomura, R. G. Shrestha, T. Endo, K. Sakamoto, H. Sakai and M. Abe, *Langmuir*, 2012, **28**, 17617-17622.
23. Y. Imura, C. Morita, H. Endo, T. Kondo and T. Kawai, *Chem. Commun.*, 2010, **46**, 9206-9208.
24. Y. Imura, S. Hojo, C. Morita and T. Kawai, *Langmuir*, 2014, **30**, 1888-1892.
25. C. Morita, T. Aoyama, Y. Imura and T. Kawai, *Chem. Commun.*, 2011, **47**, 11760-11762.
26. C. Morita, H. Sugimoto, K. Matsue, T. Kondo, Y. Imura and T. Kawai, *Chem. Commun.*, 2010, **46**, 7969-7971.
27. C. Morita, H. Tanuma, C. Kawai, Y. Ito, Y. Imura and T. Kawai, *Langmuir*, 2013, **29**, 1669-1675.
28. Y. Hisamatsu, S. Banerjee, M. B. Avinash, T. Govindaraju and C. Schmuck, *Angew. Chem. Int. Ed.*, 2013, **52**, 12550-12554.
29. B. Rybtchinski, *ACS Nano*, 2011, **5**, 6791-6818.
30. C. Schmuck and W. Wienand, *J. Am. Chem. Soc.*, 2002, **125**, 452-459.
31. S. Fiorilli, B. Onida, B. Bonelli and E. Garrone, *J. Phys. Chem. B*, 2005, **109**, 16725-16729.
32. D. P. Acharya and H. Kunieda, *Adv. Colloid Interface Sci.*, 2006, **123–126**, 401-413.
33. C. Morita, Y. Imura, T. Ogawa, H. Kurata and T. Kawai, *Langmuir*, 2013, **29**, 5450-5456.
34. J. Dong, Y. Ozaki and K. Nakashima, *Macromolecules*, 1997, **30**, 1111-1117.