

Facile Size-control and Fabrication of Spherical Morphology Based on Amphiphilic Ionic Platinum(II) Complexes

Shin A Kim, Hye Ji Yoon, Hyun Ji Kang, Jong Pil Kim,[‡] and Ok-Sang Jung^{*}

Department of Chemistry, Pusan National University, Pusan 609-735, Korea. *E-mail: oksjung@pusan.ac.kr

[‡]Pusan Center, Korea Basic Science Institute, Pusan 609-735, Korea

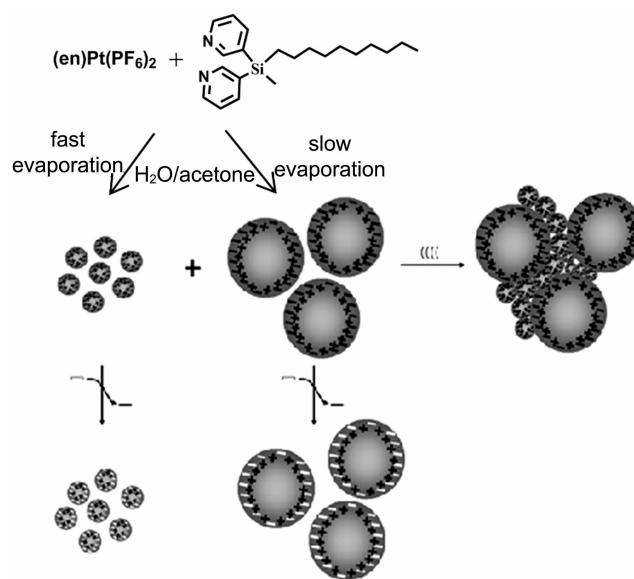
Received March 24, 2008

Key Words : Bimodal spheres, Platinum(II) complexes, Size-control, Submicrospheres, Surface modification

The morphological control by means of chemical triggers is of central importance in the recent development of advanced functional micromaterials.¹⁻⁵ A unique morphology from molecular building blocks promises to provide size- and shape-dependent materials with task-specific properties such as photo-electronic devices, pigments, ion exchangers, desiccants, molecular recognizers, drug delivery chemicals, biomimetics, cosmetics, chromatographic materials, and catalysts.⁶⁻¹³ Facile methods for the formation of nano- and micro-spherical morphology *via* surface tension, capillary effects, electric and magnetic forces, and hydrophilic interactions have been highly desired.¹⁴⁻²⁰ Thus, the size-control of spheres is one of the most important issues.²¹ Fabrication of multiple submicrospheres offers additional potentials such as photonic, phononic band gap materials, and multi-scale porous materials.^{22,23} Our previous communication reported that formation and coatings of submicrospheres based on ionic platinum(II) complexes, [(en)Pt(L.)₂(PF₆)₄] (en: ethylenediamine; L – decylmethylbis(*m*-pyridyl)silane (L.)) without the addition of any additives.²⁴ In order to expand the chemistry of the submicrospheres, the size-control of submicrospheres *via* evaporation rate of acetone along with the modification including fabrication and anion exchange was carried out.

For [(en)Pt(L.)₂(PF₆)₄] (7.5 mM, 10 mL) in a mixture (1:1) of acetone and water, evaporation of acetone produces a uniform spheres as shown in Scheme 1. The spherical morphology was characterized by elemental analysis, ¹H NMR, IR, thermal analyses, SEM, TEM, and X-ray powder diffraction. The part around platinum(II) cation and PF₆⁻ counter anions seems to be hydrophilic, and L moiety with a long aliphatic chain seems to be hydrophobic. The spheres were not formed without water as a mediator. The spheres are hardly in water or acetone, but are soluble in a mixture of water and acetone. The spherical materials are stable up to 250 °C. Moreover, the size of uniform spheres (300 nm - 4 μm) is significantly affected to the evaporation rate of acetone (Figure 1). Slow evaporation of acetone at room temperature produces ~4 μm diameter microspheres. As the evaporation rate of acetone increases, the size of spheres decreases. Fast evaporation of acetone using a rotary evaporator affords ~300 nm diameter submicrospheres.

The PF₆⁻ anions on the surface of the spheres could be exchanged by ClO₄⁻ in aqueous suspension. The surface-



Scheme 1

exchanged species was characterized by IR (ClO₄⁻) and contact angles of a water-droplet. The surface-exchanged spheres have the completely different surface. For instance, the average inter-spherical distance of the exchanged spheres is relatively shorter than the original spheres as shown in Figure 2, indicating that the counteranion is strongly dependent on the packing of spheres. An array of bimodal spheres was also accomplished in water suspension *via* sonication as shown in Figure 3. The packed bimodal spheres were not easily dissociated in aqueous media, presumably owing to the presence of electrostatic interactions between anions and cations²¹ on the surface of spheres consisting of ionic platinum(II) complexes. This process is an advanced method for reproducibly forming bimodal spheres. Such a sonication in aqueous suspension is the good method to form fast and reproducibly well-ordered bimodal colloidal spheres. The ionic characters of the complex seem to be an important factor in the formation of anion exchange and bimodal array.

In conclusion, the assembly of amphiphilic ionic metal complexes with a long aliphatic chain in a mixture of water and acetone was proved to be an effective strategy for the preparation of submicro- microspheres without the addition of any templates. The spherical size can be controlled *via*

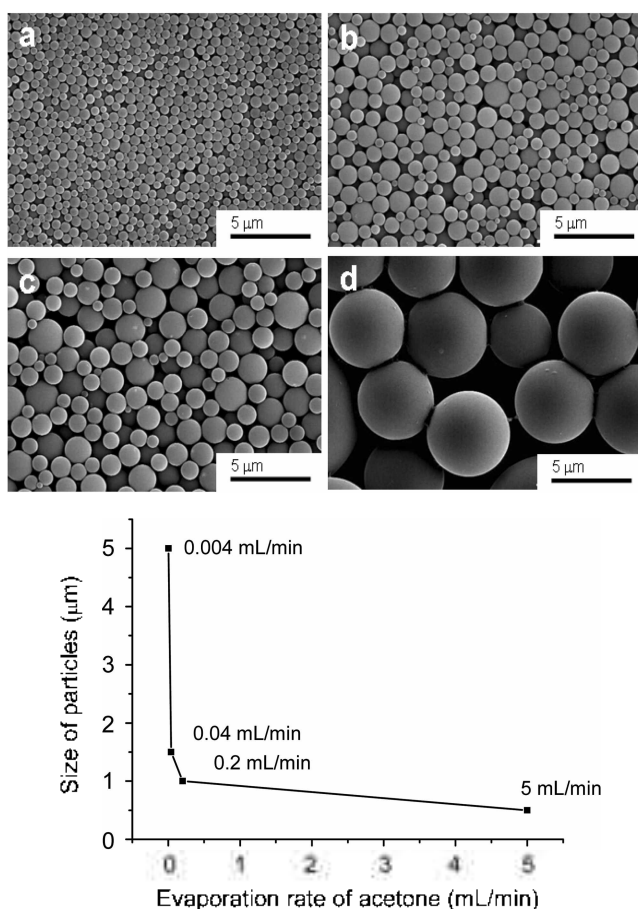


Figure 1. SEM images of spheres *via* evaporation rate of acetone at 70 °C by rotary evaporator (a); simple evaporation of solvent at 70 °C (b); simple evaporation of solvent at 40 °C (c); simple evaporation of solvent at room temperature (d).

evaporation of solvents. An array of bimodal spheres might be explained by interspherical electrostatic interaction. The size-control and modification of spherical morphology may be useful to clinical diagnosis, catalysis, and the transport of drugs or proteins.

Experimental Section

Materials and Measurements. Potassium tetrachloroplatinate(II) and ethylenediamine (en) were purchased from

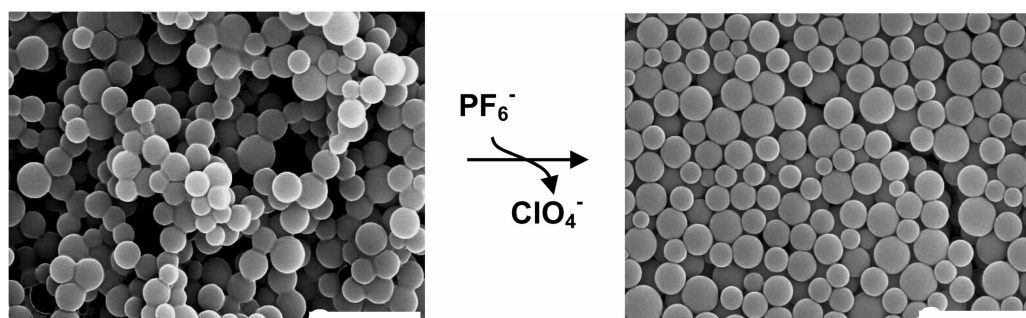


Figure 2. Surface-anion exchange of $[(\text{en})\text{Pt}(\text{L})_2](\text{PF}_6)_4$ spheres with ClO_4^- . Bar = 2 μm.

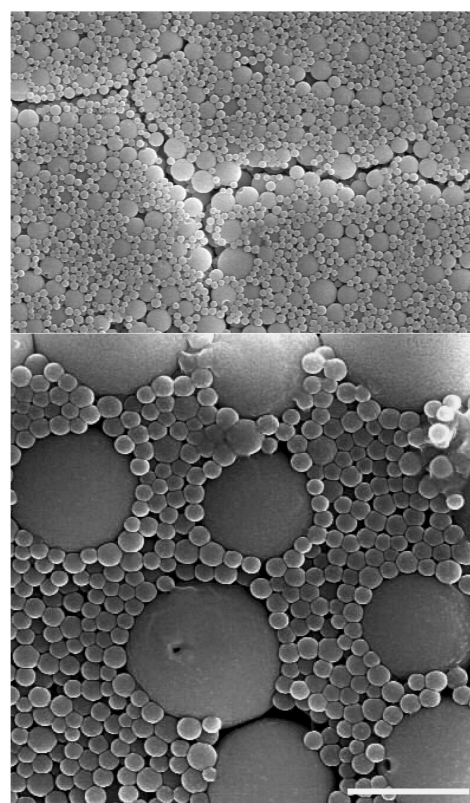


Figure 3. Array of bimodal spheres (~400 nm and ~4 μm) in aqueous suspension *via* sonication, bar, 5 μm.

Aldrich, and used without further purification. $[(\text{en})\text{Pt}(\text{L})_2](\text{PF}_6)_4$ was prepared by the literature procedure.²¹ ^1H NMR spectra were recorded on a Varian Gemini 300 operating at 300.00 MHz, and the chemical shifts were relative to internal Me_4Si . Infrared spectra were obtained on a Perkin Elmer 16F PC FTIR spectrophotometer with samples prepared as KBr pellet. Elemental microanalyses (C, H, N) were performed on solid samples at the Busan Center at KBSI using a Perkin Elmer 2400 CHNS analyzer. Thermal analyses were performed under a dinitrogen atmosphere at a scan rate of 10 °C/min with a Stanton Red Croft TG 100. Sonication was carried out using a Branson Ultrasonic 2510R-D1H. Scanning electron microscope (SEM) images were obtained with a JEM 2011.

Surface-Anion Exchange. An aqueous suspension of the

submicrospheres (0.03 mmol) was mixed with the aqueous solution of NaClO₄ (0.05 mmol). The mixture was stirred for 10 min. The exchanged products were washed with water several times.

Formation of Various Microspheres. The solution (7.5 mM, 10 mL) of [(en)Pt(L)]₂(PF₆)₄ in a mixture of water and acetone (1:1) was prepared. Evaporation of acetone was carried out for 30 h at room temperature, 12 h at 40 °C, 2 h at 70 °C, 1 min at 70 °C using a rotary evaporator.

Array of Bimodal Spheres in H₂O. Equimolar microspheres and submicrospheres (10 mg) were sonicated in 10 mL of water at room temperature for 3 min.

Acknowledgments. This work is supported by the KRF2007-314-C00157.

References

1. Busch, S.; Dolhaine, H.; DuChesne, A.; Heinz, S.; Hochrein, O.; Laeri, F.; Podebrad, O.; Vietze, U.; Weiland, T.; Knief, R. *Eur. J. Inorg. Chem.* **1999**, 643.
2. Mann, S. *Angew. Chem. Int. Ed.* **2000**, *39*, 3392.
3. Yoon, H. J.; Chun, I. S.; Na, Y. M.; Lee, Y.-A.; Jung, O.-S. *Chem. Commun.* **2007**, 492.
4. Chun, I. S.; Kwon, J. A.; Yoon, H. J.; Bae, M. N.; Hong, J.; Jung, O.-S. *Angew. Chem. Int. Ed.* **2007**, *46*, 4960.
5. Chun, I. S.; Lee, K. S.; Hong, J.; Do, Y.; Jung, O.-S. *Chem. Lett.* **2007**, *36*, 584.
6. Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353.
7. Liu, B.; Zeng, H. C. *J. Am. Chem. Soc.* **2004**, *126*, 8124.
8. Cölfen, H.; Mann, S. *Angew. Chem. Int. Ed.* **2003**, *42*, 2350.
9. Vekilov, P.; Christova, C. G.; Dullens, R. P. A.; van Blaaderen, A. *Science* **2002**, *296*, 106.
10. Sun, X.; Li, Y. *Chem. Eur. J.* **2003**, *9*, 2229.
11. Li, M.; Schnablegger, H.; Mann, S. *Nature* **1999**, *402*, 393.
12. Peng, Q.; Dong, Y.; Li, Y. *Angew. Chem. Int. Ed.* **2003**, *42*, 3027.
13. Shi, T.; Qi, L. M.; Ma, J. M.; Cheng, H. M. *J. Am. Chem. Soc.* **2003**, *125*, 3450.
14. Bowden, N.; Terfort, A.; Carbeck, J.; Whitesides, G. M. *Science* **1997**, *276*, 233.
15. Gracias, H.; Tien, J.; Breen, T. L.; Hsu, C.; Whitesides, G. M. *Science* **2000**, *289*, 1170.
16. Whitesides, M.; Grzybowski, B. *Science* **2002**, *295*, 2418.
17. Thalladi, V. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **2002**, *124*, 3520.
18. Kovtyukhova, N. I.; Mallouk, T. E. *Chem. Eur. J.* **2002**, *8*, 4355.
19. Whang, D.; Jin, S.; Wu, Y.; Lieber, C. M. *Nano Lett.* **2003**, *3*, 1255.
20. Dinsmore, A. D.; Hsu, M. F.; Nikolaides, M. G.; Marquez, M.; Bauseh, A. R.; Weitz, D. A. *Science* **2002**, *298*, 1006.
21. Yano, K.; Fukushima, Y. *J. Mater. Chem.* **2003**, *13*, 2577.
22. Wang, J.; Li, Q.; Knoll, W.; Jonas, U. *J. Am. Chem. Soc.* **2006**, *128*, 15606.
23. Kitaev, V.; Ozin, Z. A. *Adv. Mater.* **2003**, *15*, 75.
24. Yoon, H. J.; Chun, I. S.; Kim, J. P.; Lee, Y. S.; Jung, O.-S. *Mater. Lett.* **2008**, *62*, 2883.