

Uniform Submicro Spherical Morphology of Ionic Palladium(II) Complexes

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Spherical morphology with diameters of 300–500 nm is easily formed by a reaction of palladium(II) species in water with bis(nicotinoyl)-4,4'-thiophenolate in acetone and followed by evaporation of acetone. The surface hydrophilicity of the spheres is strongly dependent on the counter anions of the complexes.

The ability to systematically manipulate the morphology of materials remains an important goal since submicrometer or colloidal spheres play important roles in many applications such as catalysts, electronic devices, drug-delivery medicines, ceramics, pigments, biosensor, colloidal lithography, and cosmetics.^{1,2} Thus, considerable attention has been paid to strategies for fabricating monodisperse colloidal spheres.^{3,4} Steric effects, surface tension, capillary effects, electric and magnetic forces, permanent dipoles, van der Waals interaction, hydrophilic interactions, surfactant/precursor ratio, and shape anisotropy have been applied as driving forces in the formation of artificial morphology.^{5–9} Spherical morphology of metal oxides has been widely carried out, but the morphogenesis of metal complexes is rare. In particular, no attention has been focused on the preparation of submicrometer spheres of ionic metal complexes. To explore the formation of new conceptual submicro spherical materials, in this communication, we report the first formation of spherical colloids based on discrete ionic palladium(II) complexes of bis(nicotinoyl)-4,4'-thiophenolate (L) without addition of any additives. The counter anion effects on surface hydrophilicity of the spheres are investigated.

The ionic palladium(II) complexes were prepared by the reaction of an aqueous solution of (en)PdX₂ (en: ethylenediamine; X⁻ = NO₃⁻, ClO₄⁻, BF₄⁻, CF₃SO₃⁻, and PF₆⁻) with an acetone solution of L as shown in Figure 1. In a typical preparation, L (0.1 mmol) in 10 mL of acetone was added slowly to (en)Pd(NO₃)₂ (0.1 mmol) in 10 mL of distilled water. The mixture was refluxed for 2 h, and evaporation of acetone at ambient temperature gave a white spherical product of [(en)Pd(L)]₂(NO₃)₄ in 83% yield. The spheres were collected by the filtration using a membrane (membrane filter, Advantec MFS Inc.) for further characterization. The spherical product is a stable solid even under air and moisture. In order to measure the molecular weight of the product, the spheres were dissolved in *N,N*-dimethylformamide, and then the solution was mixed with 3-nitrobenzyl alcohol (Sigma, U.S.A.) on a FAB probe tip. The molecular weight was identified by the presence of the ion clusters at *m/z* = 1374 [M – NO₃]⁺ and 1314 [M – NO₃ – en]⁺ (Supporting Information).¹⁹ Thus, the skeletal structure of [(en)Pd(L)]₂(X)₄ is a cyclodimeric molecule consisting of two square planar palladium(II) units.

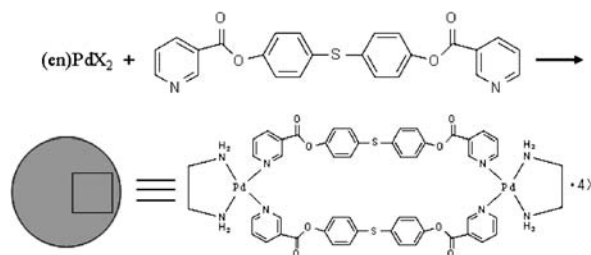


Figure 1. Synthetic scheme.

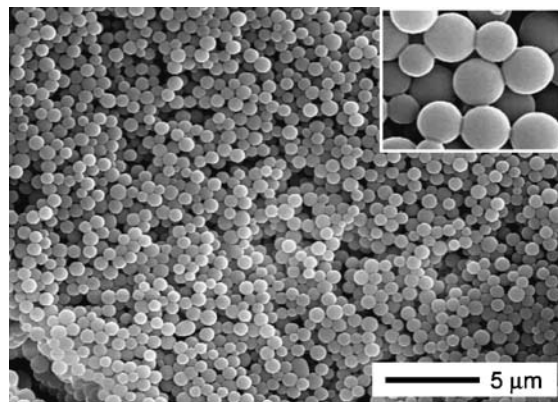


Figure 2. SEM image of [(en)Pd(L)]₂(NO₃)₄. Inset indicates high magnification.

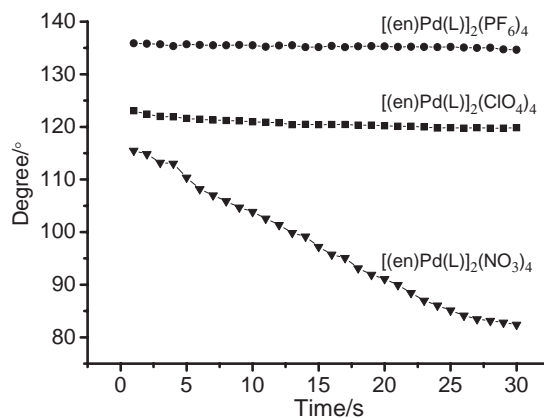


Figure 3. Contact angles of a water droplet on the monolayer of [(en)Pd(L)]₂(X)₄.

Scanning electron microscopy images show that the colloidal spheres have diameters in the range of 300–500 nm as shown in Figure 2. The spheres are hardly soluble in water or acetone but are soluble in a mixture of water and acetone (Supporting Information),¹⁹ indicating that the spheres are typical amphiphilic materials. Such an amphiphilic solubility may be a driving force for the formation of spherical morphology. The part around palladium(II) cation and NO_3^- counter anions seems to be hydrophilic, and L moiety seems to be hydrophobic. Of course, L itself does not show amphiphilic properties and formation of any spherical morphology. The ionic palladium(II) complexes easily form the submicro spheres, presumably owing to such amphiphilic properties. At this stage, the formation mechanism is not clear, the amphiphilic properties seem to play an important role in the formation of submicro spheres. The submicro spheres from the reaction of H_2PtCl_4 with *p*-phenylenediamine² may have both hydrophilic and hydrophobic moiety. According to thermogravimetric analysis (TGA) result, the spherical product contains about 5 wt% water and drastically decomposes at 285 °C. Water molecules on the surface of the spheres easily evaporate without a great change of the spherical shape. This easy evaporation of the water molecules on the surface in the wide range 45–100 °C suggests that the water molecules act as mediators in the formation of sphere rather than crystallization solvates. The water molecules on the surface evaporate at low temperature. Of course, water molecules are essential elements for the formation of the submicro spheres. Elemental analysis, the evaporation of water molecules, and $\nu(\text{OH})$ (3394 cm^{-1}) designate the presence and role of water molecules in the formation of the spherical morphology. When other counter anions such as ClO_4^- , BF_4^- , CF_3SO_3^- , and PF_6^- were used instead of NO_3^- , the similar spheres were obtained. We could not observe significant counter anion effects on the size and shape of the spheres. Preliminary results indicate the size of spheres is strongly dependent upon the evaporation-rate of organic solvent.

Recent developments on anion chemistry include exciting advances in anion template assembly, ion-pair recognition, surface properties, and the function of supramolecular materials.^{10–14} Thus, in order to quantify the effects of counter anions on the hydrophilicity of spherical surface, the contact angles of a water-droplet on the submicro spheres were measured. As shown in Figure 3, the spheres with PF_6^- showed higher contact angle than that of the spheres with NO_3^- or ClO_4^- . The contact angle of the sphere with ClO_4^- is higher than that of the spheres with NO_3^- . Thus, the results indicate that the order of $\text{NO}_3^- > \text{ClO}_4^- > \text{PF}_6^-$ favors water, which is consistent with a modified Hofmeister series.¹⁵ The wettability of the colloidal spheres is strongly dependent upon the hydrophilicity of the counter anions. That is, NO_3^- anion has strong hydrogen-bonding interactions with water molecules compared to ClO_4^- and PF_6^- . It is worth noting that this technique is useful for the determination of quantitative counter anion effects on hydrophilicity of submicro spheres. Such a modulation of surface

properties such as wettability, adhesion, and biocompatibility has important implications in both fundamental and technological advances.^{16–18}

In conclusion, assembly of ionic metal complexes in a mixture of solvents was proved to be an effective strategy for the preparation of monodisperse spherical colloids. This is the first case of the formation of the spherical morphology using the concept of ionic metal complexes. The surface wettability of the spheres could be extrapolated to the properties of counter anions. The structural modification via pliability of metal complexes will contribute to the development of micro-based functional morphology. Such colloidal spheres are easily soluble in water by an alkaline reagent, which is promising as pH-sensitive decomposable materials.

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- 19 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.