DOI: 10.1002/ejic.200900698

Submicrosticks versus Submicrohelices by Sonication – Assembly of $PdCl_2$ Nanoparticles on Those Morphologies

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Keywords: Palladium / Sonication / Submicrohelix / Submicrostick / Surface chemistry

An unprecedented modulation of submicrohelix versus submicrostick morphologies by sonication has been systematically carried out on new propeller-type tri-*O*-isonicotinoylphloroglucinol. The formation and control of uniform submicrohelix and submicrostick morphologies show subtle external sonication media effects. The first control of submicrohelices versus submicrosticks by sonication without any additive or template seems to be a function of conformational isomers. The facile loading of $PdCl_2$ nanoparticles from K_2PdCl_4 on the morphologies is a conceptually advanced method of nanoparticle–submicromorphology interaction.

Introduction

The ability to manipulate submicroscopic morphology by means of an external stimulus is essential to the development of advanced task-specific materials such as photoelectronic devices, pigments, ion exchangers, desiccants, molecular recognizers, drug-delivery systems, biomimetics, and catalysts.[1–12] Strategies for controlling the submicroshapes of shape- and size-dependent materials include either modification of molecular building blocks or changes made to external conditions[13] such as capillary effects, electric and magnetic forces, permanent dipoles, van der Waals interaction, and the surfactant/precursor ratio.[14–21] In particular, research on the control of submicrohelical-based materials and their applications has become a hot topic.[22–26] A recent study has shown that submicrohelices can be induced from submicrobelts by UV radiation.[24] Additionally, a screw axial model has been proposed for some self-assembled helical submicrofibers.[27,28] Facile morphogenesis and control of submicrohelices without any additive, thus, is highly desirable. In this context, we present a method for the direct control of submicrohelices versus submicrosticks of tri-*O*-isonicotinoylphloroglucinol (L) by sonication along with direct loading[29,30] of $PdCl_2$ nanoparticles onto the surfaces of morphologies by means of a K_2PdCl_4 reagent. Our goal was to be able to simply and effectively interconvert morphologies by changes made to external conditions. The phloroglucinol derivatives have been known as bioactive materials.[31]

Results and Discussion

The addition of distilled water into an acetone solution of L (Scheme 1) efficiently produced uniform submicrohelices in high yield. The typical diameter of the helices fell within the range of 300–500 nm, and the length was more than 10 µm. The helical pitch ranged from 500 to 600 µm (Figure 1, top). The diameter and the thickness of the helices correlated with the concentration, solvent ratio, and precipitation time. Of course, the helices consisted of a mixture of right-handed and left-handed types. However, the same treatment with sonication afforded submicrosticks instead of submicrohelices. The average width of the sticks was within the 200–400 nm range, and the length varied from of 4 to 8 µm (Figure 1, bottom). The sticks were much shorter than the helices, presumably owing to mechanical fracture. Fortunately, the helical pitch could be roughly controlled by the sonication time during precipitation. That is, 10 min of sonication instead of 40 min resulted in an increase of the helical pitch (Figure 1, center).

The treatment of an aqueous suspension of the morphologies with an aqueous solution of K_2PdCl_4 resulted in direct loading of $PdCl_2$ nanoparticles onto the surfaces of the morphologies, as shown in Figure 2. The nanoparticles were uniformly distributed on the surface, indicating that the surface, consisting of N donors of pyridyl moieties, was $PdCl_2$-nanoparticle-philic. The sizes of the $PdCl_2$ nanoparticles ranged from 10 to 15 nm. Those on the surface were characterized by XPS and EDX in addition to SEM and TEM. The XPS spectrum of Pd (3d) at 336.54 eV was assigned to the $PdCl_2$ species (Figure 3 and Supporting Information). According to the EDX, K was not observed, indicating that the nanoparticles did not consist of K_2PdCl_4, but rather $PdCl_2$. Furthermore, the nanoparticles were insoluble in water, further supporting the conclusion that they

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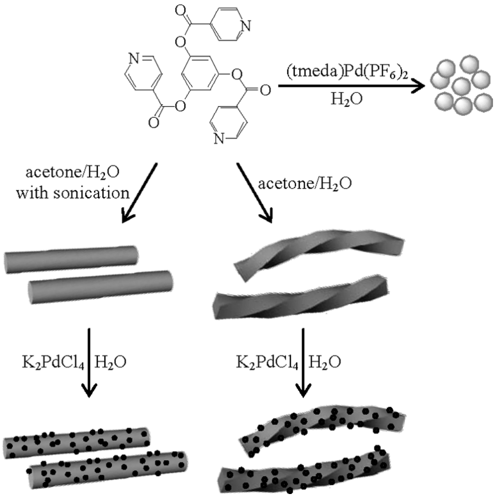
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.200900698.



Scheme 1. General schematic diagram of morphology control along with the assembly of nanoparticles on the submicromorphologies.

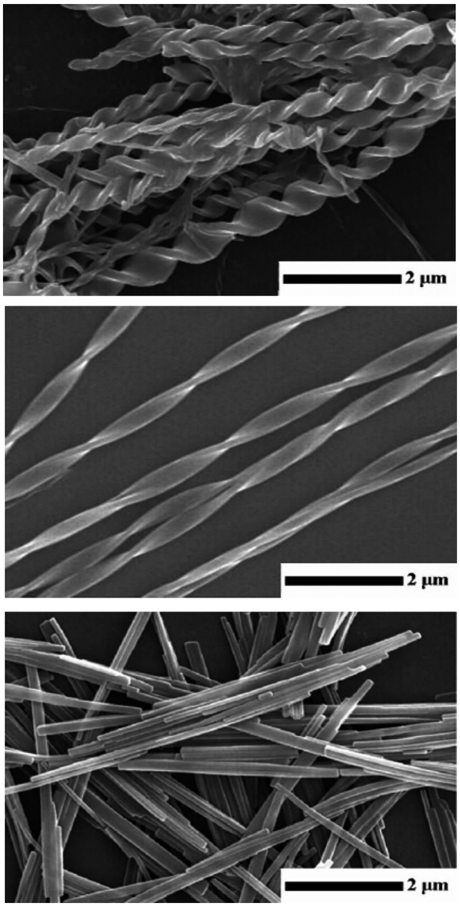


Figure 1. SEM images of short-pitch helices (top), long-pitch helices (center, 10 min sonication), and submicrosticks (bottom, 40 min soniation) of L.

were not K_2PdCl_4, but $PdCl_2$. A slight difference in the binding energy among the $PdCl_2$ nanoparticles on the surface and simple $PdCl_2$ (337.91 eV) was attributed to weak interactions between the surfaces of the submicromorphologies and the $PdCl_2$ nanoparticles (Scheme 2). The loading of $PdCl_2$ nanoparticles onto submicromorphologies is comparable to the formation of the complex [$PdCl_2$(N-N)] obtained from the coordination reaction of K_2PdCl_4 with amine ligands.[3] The $PdCl_2$ nanoparticles could not be easily loaded onto the surfaces of submicrospheres consisting of [$(Me_4en)Pd(L)]_2(PF_6)_4$. Such a result indicates that the weak interaction between nanoparticles and submicromorphologies plays an important role in assembly.[29,30] The loading of $PdCl_2$ nanoparticles is one of the useful methods of generating various hybrid materials. The specific case under consideration in this paper is an unprecedented method of loading $PdCl_2$ nanoparticles onto submicromorphologies by means of a K_2PdCl_4 reagent. When the hybrid $PdCl_2$-nanoparticles-loaded submicromorphologies were treated in chloroform, the submicrohelical or -stick morphologies were dissolved in chloroform, resulting in the aggregation of $PdCl_2$ nanoparticles. The electron diffraction pattern showed that the aggregated $PdCl_2$ nanoparticles were of polycrystalline structure (Figure 4). Such $PdCl_2$ hybrid materials might have applications in the following areas: hyperemic activity, catalysts, tuberculosis, corrosion-resistant materials of stainless steel, carbon monoxide detectors, toning solutions, electroplating of clocks and watch parts, and indelible ink.[32]

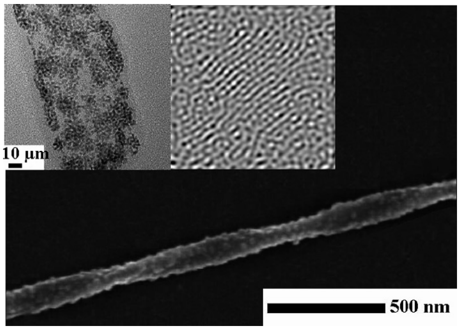


Figure 2. SEM images of an assembly of submicrohelix with $PdCl_2$ nanoparticles. TEM image (inset, left) and HRTEM image (inset, right) of $PdCl_2$ nanoparticles on the submicrohelix.

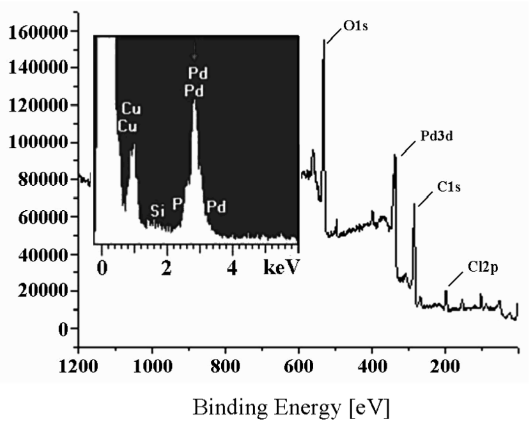
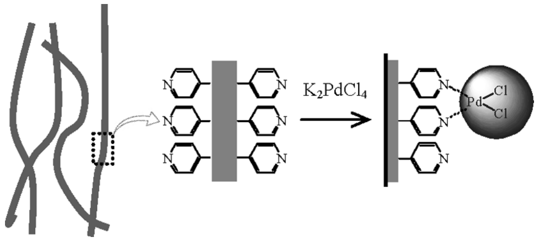


Figure 3. XPS and EDX (inset) diagrams of $PdCl_2$ nanoparticles on the submicrohelix.



Scheme 2. Interaction between submicromorphology and $PdCl_2$ nanoparticles.

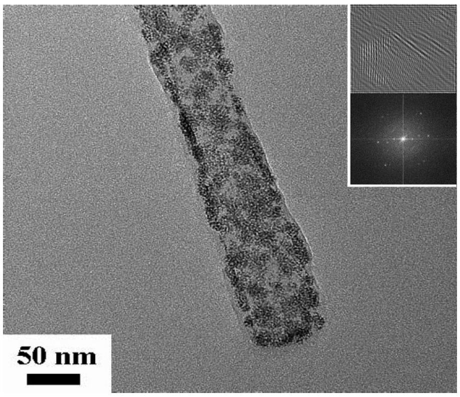


Figure 4. TEM image of $PdCl_2$-loaded submicrostick. Inset: HRTEM (top) and its FFT (bottom) images of $PdCl_2$ nanoparticles on the submicrosticks.

The reaction of $(Me_4en)Pd(PF_6)_2$ (Me_4en = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine) with L produces uniform submicrospheres (ca. 300 nm) as shown in Figure 5. The ^1H NMR spectroscopic data show that the two nitrogen donors of the ligand are coordinated with the Pd^{II} ion, whereas the one nitrogen donor is free. According to the ^1H NMR spectroscopic data, the structure is very similar to that of cyclodimeric [$PdCl_2$(triethanolamine triisonicotinate)].[2] The submicrospheres were characterized by elemental analysis, ^1H NMR, IR [$\nu(PF_6) = 843\ cm^{-1}$], and mass spectra ($m/z = 1763.1\ [M - PF_6]^+$, $1617.2\ [M + H^+ - 2\ PF_6]^+$; see Supporting Information) and SEM. They are insoluble in water, but are soluble in a mixture of water and acetone. Such amphiphilic solubility might be a driving force behind the formation of spherical morphologies.

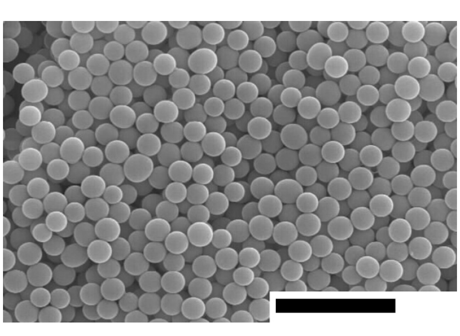


Figure 5. Submicrospheres of $[(tmeda)Pd(L)]_2(PF_6)_4$. Bar = 3 µm.

This system clearly shows the formation of different morphologies by sonication.[33–35] Simple precipitation in a mixture of acetone and water produces helices, but precipitation together with sonication affords sticks. The formation and manipulativeness of the two morphologies, submicrostick and submicrohelix, seems to be a function of the different molecular conformations imparted by sonication. The XRD powder pattern did not reveal the subtle differences between the morphologies (Supporting Information), but of course, the concentration of the acetone solution, the quantity of water, and the precipitation time all influence the morphology thickness. The formation of helical morphologies seems to be caused by the assembly of a stable propeller-type conformation (Supporting Information). The different types of conformation formed under sonication produces the stick morphology. The precise cause of the helical formation is not clear at this stage, though a delicate combination of stable conformation, π–π interaction between intermolecular pyridyl moieties and solvent effects might be the driving force behind the formation of submicromorphologies. In the present study, the *m*-pyridyl analogue did not yield a helical morphology (Supporting Information). The formation of a mixture of right-handed and left-handed helices could be attributable to the coexistence of propeller and reverse propeller conformational isomers. The helical diameter is dependent on the concentration of L and the precipitation time. The important feature is that during the formation of the helical pitch, the sonication time is an important factor. Morphological control by sonication without any additive is rare. Neither of the submicromorphologies are formed without water as a mediator. Detailed experiments on the various factors, including sonication time, concentrations, and precipitation time could yield information on the morphology size. In the case of $[(Me_4en)Pd(L)]_2(PF_6)_4$, the formation of submicrospheres seems to be determined by a combination of surface tension, conformation, and solvent effects. The growth kinetics of the spheres is determined by the interplay between the internal lattice structure and the external environment.

Conclusions

We developed a simple approach to the formation and control of uniform helical and stick morphologies. These morphologies show subtle external media effects: the first control of submicrohelices versus submicrosticks by sonication in a mixture of solvents without any additives or organic solvents seems to be a function of conformational isomers. The present approach is a conceptually advanced method of metal-surface–donor interaction in loading $PdCl_2$ nanoparticles from K_2PdCl_4. The formation and manipulation of morphology can yield desirable materials applicable to sensors, transport, shape-memory materials, and drug-delivery systems in the human body.

Experimental Section

Tri-*O*-isonicotinoylphloroglucinol (L): Pyridine (19.41 mL, 0.24 mol) was added to a solution of isonicotinoyl chloride hydrochloride (21.36 g, 0.12 mol) in chloroform (150 mL) at room temperature. Subsequently, phloroglucinol (6.49 g, 0.04 mol) was added to the reaction solution, and the mixture was refluxed for 3 h. The chloroform layer was washed successively with 0.1 N NaOH solution and cold water. The chloroform solution was dried with magnesium sulfate and filtered. Removal of the solvent gave L (16.24 g, 92% yield); m.p. 175 °C (dec.). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.89 (d, J = 5.1 Hz, 6 H), 8.00 (d, J = 5.1 Hz, 6 H), 7.25 (s, 3 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 163.27, 151.38, 151.24, 136.24, 133.65, 123.40 ppm. IR (KBr): $\tilde{\nu}$ = 3037, 1753, 1617, 1460, 1410, 1261, 1140, 697 cm^{-1}. $C_{24}H_{15}N_3O_6$ (441.40): calcd. C 65.31, H 3.43, N 9.52; found C 65.21, H 3.66, N 9.74.

Submicrohelices: Distilled water (10 mL) was slowly added to an acetone solution (10 mL) of L (0.0022 g, 0.050 mmol); the mixture was left at room temperature for 3 d to afford a white suspension (0.0181 g, 83% yield).

Submicrosticks: Distilled water (10 mL) was added to an acetone solution (10 mL) of L with sonication for 1 h; the mixture left at room temperature for 3 d to afford a white suspension (0.0188 g, 85% yield).

Assembly of $PdCl_2$ Nanoparticles on Helices: K_2PdCl_4 (0.0020g) was added to an aqueous suspension (5 mL) of submicrosticks or submicrohelices (0.0011 g), after which the mixture was sonicated for 10 min. The mixture was then centrifuged to obtain the solid product, which was washed with water several times.

$[(Me_4en)Pd(L)]_2(PF_6)_4$: To a suspension of $(Me_4en)PdCl_2$ (0.059 g, 0.2 mmol) in H_2O (5 mL) was added $AgPF_6$ (0.101 g, 0.4 mmol) in H_2O (5 mL), after which the mixture was stirred at 70 °C for 1 h. After removal of the precipitated AgCl, L (0.088 g, 0.2 mmol) in acetone (10 mL) was added dropwise to the filtrate; the mixture was refluxed for 30 min, and the acetone was slowly evaporated to leave a white product (0.1303 g, 68% yield). ^{1}H NMR (300 MHz, [D$_6$]Me$_2$CO/D$_2$O): δ = 9.45 (d, J = 5.1 Hz, 4 H), 8.80 (d, J = 6.3 Hz, 2 H), 8.15 (d, J = 5.1 Hz, 4 H), 8.00 (d, J = 6.3 Hz, 2 H), 7.28 (m, 2 H), 7.00 (m, 1 H), 3.18 (s, 8 H), 2.77 (s, 24 H) ppm. IR (KBr): $\tilde{\nu}$ = 3115, 1755 (s, C=O), 1620, 1466, 1267, 1136, 843 (s, PF$_6$), 559 cm^{-1}. FAB MS: m/z = 1763.1 [M – PF$_6^-$]$^+$, 1617.2 [M + H$^+$ – 2 PF$_6^-$]$^+$. $C_{62}H_{64}F_{24}N_8O_{12}P_4Pd_2$ (1905.88): calcd. C 39.07, H 3.38, N 5.88; found C 39.50, H 3.30, N 5.59.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra, TGA curve, and energy-minimized CHEM 3D structure of L; TEM images, and XRD patterns of submicromorphologies; TEM image, XRD pattern, and EDX results of $PdCl_2$-loaded submicrohelices; TEM, HRTEM, and FFT images of $PdCl_2$ nanoparticles. ^{1}H NMR spectrum and MS data of $[(Me_4en)Pd(L)]_2(PF_6)_4$. ^{1}H NMR spectrum and SEM image of tri-*O*-nicotinoylphloroglucinol.

Acknowledgments

This work was supported by the Korea Research Foundation (KRF-2008-313-C00426) in Korea.

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Received: July 23, 2009