Spatial organization and patterning of palladium nanoparticles on a self-assembled helical ribbon lipid

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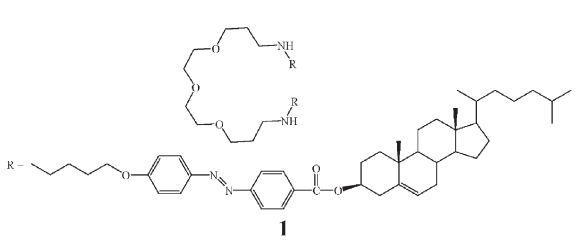
A cholesterol derivative 1 forms self-assembled helical ribbons in organic solvent, and treatment of this helical ribbon lipid as a template with $Pd(Ac)_2$ provides helically-patterned arrays of palladium nanoparticles followed by reduction.

There has been a growing interest in the fabrication of metal–organic nanocomposites consisting of naturally occurring biomaterials and metal nanoparticles for advanced materials applications.[1] One possible approach toward such nanostructures is to use biomolecular templates such as DNA,[2] the tobacco mosaic virus (TMV),[3] lipids[4] and protein microtubules.[5] Most of the inorganic materials obtained by metallization with nickel,[6] silver,[7] gold[8] and copper[9] have been obtained as linear wire or linearly-arrayed nanoparticle-type nanostructures. Although synthetic lipid tubes in artificial systems as well as DNA, and RNA in nature, self-assemble into fascinating highly ordered superstructures such as single-, double- and triple-helical structures, the underlying helical feature was not revealed in the structures of the inorganic products. Furthermore, relatively little work on the helical inorganic materials has been reported despite their utilization as asymmetric reaction catalysts,[8] helical sensors,[10] optical materials[11] and so forth.

The present work describes the template-directed spatial metallization on the surface of the self-assembled cholesterol-based helical ribbon with palladium nanoparticles formed by reduction of Pd^{II} to Pd^{0} with ascorbic acid. Our goal was to exploit differences in the binding strength between the lipid molecules residing at the edge sites along the helical ribbon and those sited within the lamellar-structured bilayer sheets. In this way, the helical edges might serve as a chemically patterned organic surface for the spatial organization of arrays of metal nanoparticles. If the molecules at the edge sites of the helical ribbon show higher affinity to Pd^{II} than those on the lamellar bilayer sheets, for example, then the helical pattern might be replicated by decoration with a Pd cluster.



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Compound **1**, a cholesterol in cooperating diaminoethylene glycol, was synthesized according to a similar method reported previously.[12] The diaminoethylene glycol moiety was introduced as a binding site of the transition-metal ions. The deposition of palladium nanoparticles on the self-assembled helical ribbon of **1** was carried out by two different methods (A and B). In method A, **1** was dissolved in acetic acid by heating for 30 min. The solution was maintained for 1 h at room temperature to form a stable supramolecular assembly. Then, 2.0 equivalents of an aqueous $Pd(Ac)_2$ solution was added to the preorganized helical ribbon solution. The reaction mixture was maintained overnight under nitrogen to complete the immobilization of Pd^{II} on the helical ribbons. This was followed by the addition of 1.5 equivalents of ascorbic acid as a reducing agent to mineralize the Pd nanocrystals on the helical ribbon. In method B, **1** was dissolved together with $Pd(Ac)_2$ in acetic acid by heating. In this procedure, monomeric molecule **1** may form a complex with Pd^{II}. Then, the complexed **1** grows to be a tubular structure. The reaction mixture was maintained at room temperature overnight for self-assembly, and reduced with ascorbic acid.

Fig. 1 shows TEM pictures of the helical ribbon **1** obtained from acetic acid. The helical ribbons are *ca.* 520 nm in width, 700–1700 nm in pitch and 50–100 μm in length. The helical ribbon might be induced with a suitable balance between the diaminoethylene glycol moiety as a polar head and chiral cholesterol tail groups which give rise to packing anisotropy within lipid bilayer sheets forming in the organic solvent.

TEM images and an EDX profile of the helical ribbon **1**after reduction of Pd^{II} are shown in Fig. 2. Interestingly, when tubule formation and reduction of Pd^{II} occur simultaneously, the resulting palladium particles of 3–5 nm are deposited onto the surface of the tubule (method B), but no regular patterning is observed (Fig. 2a). The Pd^{II} ion may disturb the balance between hydrophobility and hydrophilicity in **1**. This stabilizes the tubular or vesicular

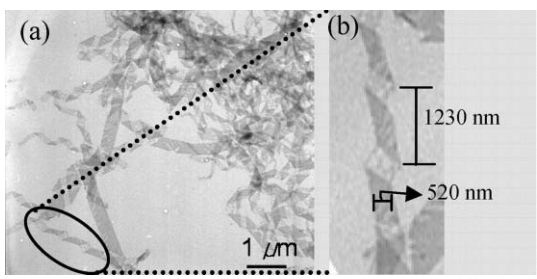

Fig. 1 EF-TEM pictures of the self-assembled **1** with a helical ribbon structure in acetic acid.

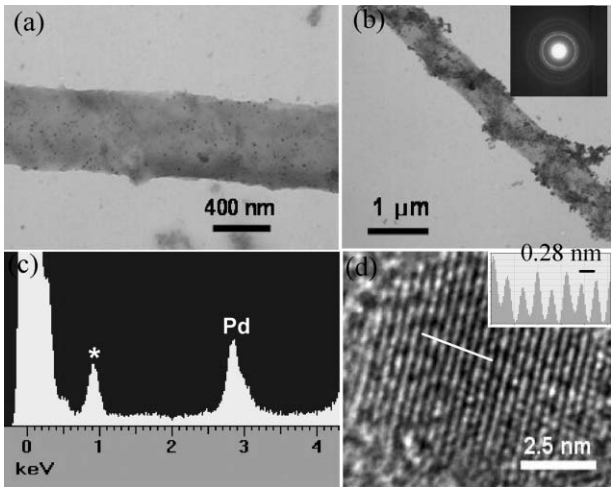

Fig. 2 TEM images of (a) deposition of palladium particles obtained from the self-assembled cholesterol-based tube and (b) decoration of the palladium particles with preorganized cholesterol-based helical ribbon. (c) EDX spectrum (* is the Cu element, which arises from the supporting grid) and (d) high resolution TEM image of (b) showing the presence of Pd.

structures but not the helical ribbon. In this case, the tubular structure was preformed. On the other hand, when Pd^{II} forms a complex with the preformed helical ribbon of **1**, arrays of the palladium 'dot' follow the underlying helical ribbon structure of the tubules, as well as being organized along the longitudinal seam and circular ends of the tubules (method A, Fig. 2b). Accordingly, the resulting patterns of the palladium arrays differ depending on whether palladium complexation occurs simultaneously with preorganized **1** or monomeric **1**. The palladium particles associated with the preformed lipid tubules have a narrow dispersion with diameters of 5–7 nm. These observations strongly suggest specific interactions between the lipid molecules at the exposed edges of the helical ribbon and Pd^{II}. We can carefully propose the following: these edges will deviate from the planar bilayer geometry of the ribbon surface such that the polar head of the cholesterol-based molecule **1** could be partially exposed. Also, the lamellar bilayer sheets of the helical ribbon are much more strongly solvated than that of the edge part of the helical ribbon. This would produce a local supersaturation of Pd^{II} ions around the edge of the helical ribbon, which may lead to deposition of the Pd particles localized at the edge. Furthermore, this confirms that the helical edge decoration is not an artifact of drying in preparing samples for TEM.

The distinctive signal of Pd is detected by the corresponding energy-dispersive X-ray (EDX) measurement (Fig. 2c). It is clear that Pd^0 is formed on helical ribbon **1**, followed by complete reduction from Pd^{II} to Pd^0 with ascorbic acid.

The electron diffraction pattern, shown in the inset of Fig. 2b, exhibits three diffused rings, which could be assigned to the (111), (220) and (311) reflections of face centered cubic (fcc) Pd. The X-ray powder diffraction pattern also confirmed the fcc structure of metallic Pd. In addition, a high-resolution TEM image of a single particle revealed an atomic lattice fringe with a distance of 0.28 nm, demonstrating the crystalline nature of the nanoparticles (Fig. 2d).

As a summary of the foregoing observations, we propose a mechanism for the deposition of the palladium particles along the lipid–palladium hybrid nanotubes as illustrated in Fig. 3. Generally, the Pd^{II} ion has a high affinity toward a nitrogen donor.[13] Thus we believe that the Pd^{II} ion can be positioned near the nitrogen donor atom in **1** (Fig. 3a; lower). The self-assembled morphology of **1** in the absence of Pd^{II} is clearly different from that in the presence of Pd^{II}; **1** in the absence of the palladium ion gave the helical ribbon structure (Fig. 3b; upper) whereas **1** in the presence of Pd^{II} gave the complete tubular structure (Fig. 3b; lower). The Pd^{II} ions are mainly adsorbed onto the edge sites of the helical ribbon of the self-assembled **1** by a difference of binding strength (Fig. 3c; upper). In contrast, when **1** was dissolved in acetic acid together with Pd^{II}, the Pd^{II} ions were homogeneously adsorbed onto the surface of the cholesterol-based tubes (Fig. 3b; lower). Then, the Pd^{II} ions were reduced with ascorbic acid. Accordingly, the spiral deposition of the palladium particles was induced by the helical ribbon structure of **1** as a template (Fig. 3d; upper). On the other hand, the tubular structure of **1** resulted in the irregular deposition of palladium particles (Fig. 3c; lower).

In conclusion, the present paper demonstrates the template-directed spatial deposition of palladium nanoparticles at the edges of a cholesterol-based helical ribbon by method A. This finding suggests that one possible approach to patterned three-dimensional inorganic arrays, such as helical assemblies, is to exploit the surface chemistry of reaction centres spatially organized within supramolecular assemblies.

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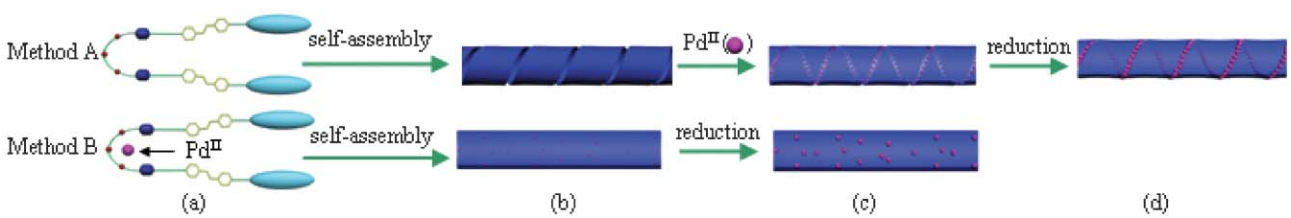

Fig. 3 Schematic illustration of the helical array of palladium particles using the cholesterol-based tube as a template. Upper: (a) **1**, (b) self-assembly, (c) adsorption with the Pd^{II} ion and (d) reduction with ascorbic acid. Lower: (a) **1** in the presence of the Pd^{II} ion (upper), (b) self-assembly and (c) reduction with ascorbic acid.

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