Spatial organization and patterning of gold nanoparticles on self-assembled biolipid tubular templates

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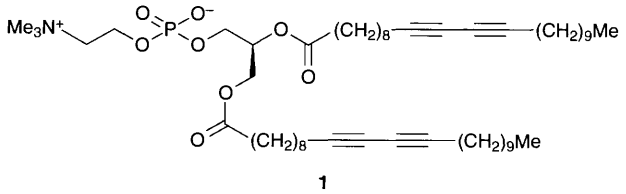
Helically-patterned arrays of gold particles are formed using lipid tubules as templates.

Biomineralization processes show a high degree of control over the morphology, orientation, and organization of inorganic materials to create remarkably complex patterns.[1] One significant feature of these systems is the use of organic supramolecular assemblies as templates for mineral nucleation and growth. Recently, biomimetic strategies have focused on the application of preorganized organic architectures in the synthesis of bioinorganic nanocomposites and shaped hybrid materials with microscale organization.[1–3] In particular,biolipid tubule structures, such as those formed by diacetylenic phospholipids or galactocerebrosides, have been used as substrates for the synthesis of high-axial ratio metal oxide or metallic organic–inorganic composites.[4–7] In these reactions, the lipid headgroups act as a template for inorganic nucleation and growth on the external surface of the preformed organic architecture.

Hollow tubules with diameters of 400–1000 nm, wall thicknesses of 2–10 bilayers (10–50 nm), and lengths of the order of 50–100 μm, are formed by the self-assembly of the synthetic lipid, diacetylenic phosphatidylcholine ($DC_{8,9}PC$; **1**).[8] These materials have an underlying helical structure and resemble wrapped ribbons by transmission electron microscopy.[8] The helical ribbon motif is a consequence of the rigid, diacetylene-containing lipid tails and the chiral lipid headgroup which give rise to packing anisotropy within lipid bilayer sheets forming in aqueous solution.[9,10] In previous syntheses involving the mineralization of $DC_{8,9}PC$ tubules with nickel,[5] copper,[5] alumina,[6] or silica,[7] the underlying helical feature was not revealed in the structures of the inorganic products. The present work describes the mineralization of $DC_{8,9}PC$ lipid tubules with gold nanoparticles formed by *in situ* reduction of $HAuCl_4$. Our goal was to exploit differences between the chemical reactivity of the lipid molecules residing at defect edge sites along the helical ribbon, and those sited within the lamellar bilayer sheets.



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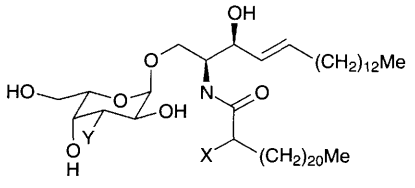

X = OH Y = OH **2**
X = H Y = OH **3**
X = OH, H Y = OSO_3^- **4**

In this way, the helical edges might serve as chemically patterned organic surfaces for the spatial organization of arrays of metal nanoparticles. For example, if these sites are capable of reducing Au^{III} to Au^0, then the helical pattern might be replicated by decoration with gold clusters.

Self-assembled helical tubular ribbons were synthesized by adding 1 ml water to a solution of 1 mg $DC_{8,9}PC$ (Avanti Polar Lipids, Alabaster, AL) in 1 ml ethanol (final lipid concentration of approx. 0.5 mmol dm^{-3}).[8] Precipitation of lipid tubules occurred overnight. Nanosized gold particles were deposited on preformed $DC_{8,9}PC$ tubules by adding 0.5 ml of 1 or 10 mmol dm^{-3} aqueous $HAuCl_4 \cdot 3H_2O$ (Aldrich) to 0.5 ml of the lipid tubule suspension in ethanol–water (0.5 mg ml^{-1}). Alternatively, for the simultaneous formation of colloidal gold and lipid tubules, 1 ml of aqueous $HAuCl_4$ (1 or 10 mmol dm^{-3}) was added to 1 mg $DC_{8,9}PC$ in 1 ml ethanol and left overnight. For the synthesis of $DC_{8,9}PC$ tubules in the presence of preformed colloidal gold, 1 ml aqueous, citrate-reduced colloidal gold[11] was used as the aqueous phase.

Transmission electron microscopy showed that specific decoration of the lipid tubules does not result when preformed gold colloid particles are used. In contrast, the lipid tubules are decorated with discrete gold particles formed from *in situ* reduction of $HAuCl_4$. The resulting patterns of the gold arrays differ depending on whether gold particle formation occurs simultaneously with or subsequent to $DC_{8,9}PC$ tubule assembly. When gold reduction and tubule formation occur simultaneously, the resulting tubules are decorated with gold particles, but no regular patterning is observed (Fig. 1). By contrast, when gold particles are synthesized on preformed tubules of $DC_{8,9}PC$, arrays of gold 'dots' follow the underlying helical ribbon structure of the tubules, as well as being organized along the longitudinal seam and circular ends of the tubules (Fig. 2). The gold particles associated with the preformed lipid tubules are fairly monodisperse, and the trend in particle size is correlated with the starting ratio of $HAuCl_4$ to lipid, *i.e.* helical arrays of smaller gold particles are formed when lower concentrations of the gold precursor are present (lipid/$HAuCl_4$ molar ratio = 1 or 5). However, at a constant concentration of gold precursor, the gold particles that decorate the preformed tubules are fewer and

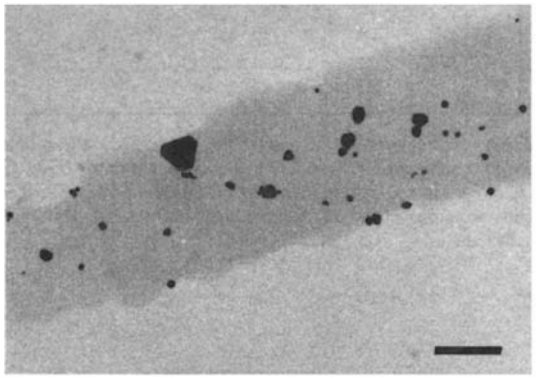

Fig. 1 Gold decoration of $DC_{8,9}PC$ tubules formed by *in situ* reduction of $HAuCl_4$ during organic self-assembly. Scale bar = 200 nm.

larger than those formed when tubule assembly and gold reduction occur simultaneously. This implies that fewer sites for gold nucleation are accessible when the lipids are assembled into tubules than when the lipid molecules are in solution, and thus that the helical patterns of gold particles on the preformed lipid tubules is integrally related to the architecture of the tubules.

These observations suggest that there are specific interactions between lipid molecules located at the exposed edges of the helical ribbon and the aqueous gold complex. These defect edges will deviate from the planar bilayer geometry of the ribbon surface such that the tails of the $DC_{8,9}PC$ molecules could be partially exposed. Thus, a redox reaction between $AuCl_4^-$ and the diacetylenic groups[12] might be responsible for the formation and specific patterning of the gold particles. The key step is the reduction of Au^{III} to Au^{I}, since the final reduction to Au^0 likely involves a disproportionation reaction (3 Au^{I} to 2 Au^0 + Au^{III}) which is fast in the presence of water.[13] Specific interactions between gold species and the defect edges of the lipid bilayer are also implicated by the observation that preformed gold colloid particles are not deposited specifically at the helical edges of preorganized tubules. Furthermore, this confirms that the helical edge decoration is not due to a drying artefact (*i.e.* staining of the tubules with colloidal gold) in preparing samples for TEM.

Tubular and helical structures of smaller diameter (85–100 nm) are formed by bovine brain α-hydroxyacyl galactocerebroside [HFA-Cer (Sigma); **2**], the non-hydroxyacyl galactocerebroside [NFA-Cer (Sigma); **3**], and mixtures with galactosylceramide I^3-sulfate [S-Cer (Lipid Products); **4**] by thermal cycling in ethylene glycol.[14,15] Reduction of $HAuCl_4$ in the presence of preformed NFA-Cer or NFA-Cer/S-Cer ribbons and tubules leads to the formation of discrete, relatively monodisperse, gold particles associated with the supramolecular assemblies, including along the twists of the helices (data not shown). However, some nucleation of gold crystallites in solution is also apparent. Deposition of gold on galactocerebroside tubules is not as specific or homogeneous as in the $DC_{8,9}PC$ system due to the wider variety of possible reducing centres for Au^{III} on the entire surface of the galactocerebroside tubules (*e.g.* sugar hydroxy,[16] alkene,[17] ether,[18] and carbonyl[11] groups) and in solution (ethylene glycol).[19] Patterns also arise simply by staining the lipid tubules with colloidal gold (data not shown).

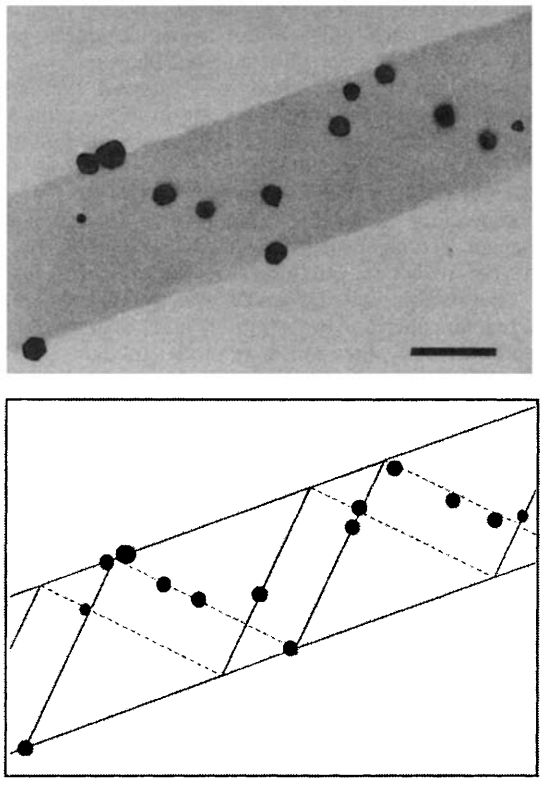

Fig. 2 Patterned decoration of preformed helical $DC_{8,9}PC$ tubules with discrete gold nanoparticles formed by *in situ* reduction of $HAuCl_4$ (lipid/$HAuCl_4$ molar ratio = 5) (top). Note the decoration of the helical edges of the tightly wound lipid ribbon, as illustrated schematically (bottom). Scale bar = 200 nm.

The formation of organized architectures of lipid/gold composites illustrates the potential for developing three-dimensional arrays of inorganic materials by pattern replication methods involving functionalized organic substrates. The results of our studies with $DC_{8,9}PC$ lipid tubules indicate 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. Indeed, the resulting organization is reminiscent of certain biological systems, such as the chains of nanometre magnetite particles formed within magnetotactic bacteria.[20] Although our investigations of gold decoration using preorganized $DC_{8,9}PC$ lipid tubules need to be refined further, we consider that a similar approach could be applied to a wide range of systems including liquid crystals, dendrimers and copolymers in which spatial patterns of reaction sites are organized by self-assembly processes.

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