Shape directed biomineralization of gold nanoparticles using self-assembled lipid structures

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Shape directed biomineralization of gold nanoparticles using self-assembled lipid structures

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As one of the building blocks of the cell membrane, lipids and their interaction with neighboring lipids and other molecules, as well as their ability to form different kinds of structures have garnered immense interest. By exploiting the effective shape and thermal-phase behavior of lipids, we have prepared lipid superstructures such as twisted ribbons, rectangular and hexagonal shaped lipidic nanostructures using curvature tuned prearation method. These lipidic superstructures were then used as nanoreactor templates for the inorganic synthesis of diverse shaped and sized gold nanostructures exploring different administration routes of reducing agent, citrate, and tetrachloroauric acid, which as a result formed different organizations of gold nanoparticles aligned and guided by the template structure. Tailor-designed metallic nanostructures can be obtained through a careful selection of lipids and conditions for lipid superstructure preparation and consequent use as a template nanoreactor. The diversely sized and shaped gold nano-structures obtained have great potential for catalysis and plasmonics.

1. Introduction

As one of the building blocks of cell membranes, lipids and their interaction with neighboring lipids and other molecules, as well as their ability to form different kinds of structures have garnered immense interest.[1] There are several structural factors and environmental conditions that affect the self-assembly of lipids into nano-sized structures, influencing the phase behavior and the curvature of the lipid. Lipid superstructures have been studied intensively over the last 30 years[2] with recent increasing interest in these nanostructured materials formed by self-organisation.[3] Vesicles, or liposomes, are the most widely known lipid based structures; however, lipids are also known to be able to self-assemble into several other structures, such as lipid tubes and rods,[4] lipid ribbons,[5,6] hexasomes[7] as well as cubosomes[8] and non-lamellar mesophase lipid aggregations.[9] Asides from being used as model systems to understand cell membrane nature,[6] these nano- and micro-structures are attractive as substrates for protein crystallization,[10] as templates for the synthesis of one-dimensional inorganic materials,[11,12] and as vectors for drug delivery.[4,13]

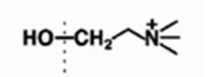
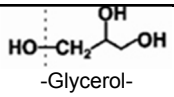
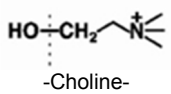
In parallel, there is enormous interest in the development of methods for the preparation of metallic nanoparticles of diverse sizes and shapes, particularly for application in catalysis, where structures such as cubes,[14] disks,[15] tubes,[16] stars,[17] and nanocages[18] provide crystal plane architectures that can be tailor-designed according to the specific application. Spherical nanoparticles are, to a large extent, synthesized by wet-state preparation methods such as the Turkewitch method (1951) [19] or the Schmid method (1981),[20] which is based on reduction/oxidation reactions. However, further control of the one and two-dimensional shapes of nanoparticles is still largely unaddressed. The seed mediated synthesis of rod-like structures exploiting the use of a growth-directing agent (hexadecyltrimethylammonium bromide (CTAB)),[21] as well as vapor-phase synthesis,[22] vapor-solid-liquid synthesis methods,[23] or patterning on a solid surface by etching or lithography methods[24] are some of the methods reported to achieve particle growth of specific shapes.[25] However, those methods often reveal nanoparticle populations with different sizes and shapes and requires strong reaction conditions, e.g. high temperature, high pressure, extreme pH or organic solvents.[26,27] As an alternative, template directed synthesis using self-assembled structures offer several advantages in comparison, not only because of the relative inexpensiveness of the technique and its simplicity and inherent applicability to scale-up, but also due to the unlimited potential combinations of biomaterials to form diverse template structures.[28–30,4,11]

A highly reported method that has been used for the preparation of nanoparticles is the so-called reverse micelle method. In this method, the inner core of the reverse micelles is considered as a nanoreactor,[25] within which controlled reactions leading to the formation of nanosized metallic and metal halide particles are carried out,[31] where the size of the micelle core is controlled by the molar ratio of water to surfactant/lipid molecules in solution. Typically, individual reverse micelle populations are prepared containing metallic precursors e.g. metallic salt and reducing agent, respectively. An exchange process occurs when the micelles collide due both to Brownian motion and attractive forces between the micelles, resulting in a fusion of the reverse micelles, an exchange of the contents within the cores, followed by a re-dispersion of the micelles.[32,33]As a result the reduction of the metal salt results in the growth of metallic nanoparticles within the core of the micelle. This method has found widespread application and has been used, for

example, for the synthesis of semi-conductor materials,[34] metallic nanoparticles[35] and nanoalloys.[36]

Phospholipids are naturally occurring amphipathic molecules that can form bilayer structures with high aqueous interior volume. Their capacity to encapsulate a wide range of molecules makes lipid based structures efficient nanoreactors for inorganic synthesis of metal nanostructures in milder and greener reaction conditions [37,38]. Moreover, the use of lipid based templates could overcome the problems faced with soft-template strategies; such as poor stability of the template during the synthesis and removal following particle synthesis, since they can be formulated to be stable in aqueous media and easily dissolved in organic solvents.[39] However, unlike micelle forming surfactants (e.g CTAB), lipids often prefer to self-assemble in spherical vesicles which limits their use in the synthesis of different shaped inorganic nanoparticles.[40] Recently, we reported on an ultra-rapid and environmentally friendly method for the preparation of highly stable liposomes using both charged and zwitterionic lipids, with different critical melting temperatures (T_M), exploiting a combination of a rapid pH change followed by a defined period of equilibration, resulting in monodisperse and stable liposome populations and also different shaped lipid mesostructure depending on the properties of lipids used.[41] In previous studies, those nanoliposomes were used to synthesize tiny gold and palladium nanoparticles with catalytic properties.[42,39] In the work described here, we exploit the curvature-tuned liposome preparation method for the formation of several lipidic nanostructures using different formulations of phospholipids leading to the self-assembly of the lipids into structures different from liposomes, such as twisted ribbons, rectangular and hexagonal shaped lipid nanostructures. Inspired from reverse-micelles, we proposed to use these nanostructures for the production of metallic nanoparticles with the size and shape of the resulting nanoparticle dictated by the lipid templates. Analysis of the lipid nanostructures and the metallic nanostructures formed was carried out using biological transmission electron microscope (TEM), scanning electron microscope (SEM), and X-ray diffraction analysis and the feasibility of the approach for the preparation of ribbon, hexagonal and cubical metallic nanostructures was clearly demonstrated.

Tablo 1: Properties of the phospholipids studied and conditions for the preparation of different shaped lipid templates.

Lipid (Tail Length)	Head Group	Molecule Charge	Final shape (Operation T_0*)
DPPC (18C) (1,2-dipalmitoyl-sn-glycero-3-phosphocholine)	 -Choline-	Neutral	Hexagonal (25 ^{0}C) / Rectangular (45 ^{0}C)
DMPG (14C) (1,2-dimyristoyl-sn-glycero-3-phospho-(1'-rac-glycerol))	 -Glycerol-	Negative	Twisted Ribbon (25 ^{0}C)
Lyso-PC (16C) (1-palmitoyl-2-hydroxy-sn-glycero-3-phosphocholine)	 -Choline-	Neutral	

*It should be noted that sample preparation method includes cooling step to the room temperature afterwards and all analysis were done at room temperature.

2. Experimental section

2.1 Materials

Phospholipids were supplied as a powder by Avanti Polar Lipids, Inc. and used without further purification. Sodium hydroxide, hydrochloric acid, di-sodium hydrogen phosphate (anhydrous, reagent grade), Na_2HPO_4), sodium dihydrogen phosphate (anhydrous), extra pure, (NaH_2PO_4) and glycerol 99.5%, reagent grade, were purchased from Scharlau Chemie SA. Sodium chloride was provided by Riedel-de Haën. Milli-Q water (1.82 MΩ.cm^{-1}) used to prepare buffers and liposomes were obtained using a Simplicity 185 Millipore-Water System.

2.2 Preparation of lipid based nanostructures and template directed synthesis

Preparation of lipid nanostructures using curvature tuned preparation method.[41] Different lipid mixtures (50 mg) were directly hydrated in 4 mL of buffer (0.1 M PBS, pH 7.4), which had previously been heated to a pre-determined temperature, T_0 (Table 1). The temperature was kept constant by placing a glass flask (15 mL) in a water jacket connected to an UltraTerm 200 Model (P-Selecta) thermocycler. The mixture was vortexed in a 10 mL falcon tube (with glass beads) for 1-3 min and added to 6 mL of pre-heated and degassed buffer solution (0.1 M PBS, pH 7.4) in order to prepare empty lipid templates. In case of the encapsulating lipid nanostructures, the lipid mixture was mixed with 6 mL of pre-heated and degassed buffer solution (0.1 M PBS, pH 7.4) including either $HAuCl_4$ (20 mg) or sodium citrate (115 mg) and was left to stir for 15 min while the temperature was kept constant at T_0. As used in the nanoliposome preparation, lipid nanotemplates were prepared by use an immediate "pH jump" to produce a fast protonation and deprotonation induced lipid self-assembly.[41] For this, the pH was subsequently increased to pH 11 using NaOH and immediately re-adjusted to pH 7.4 using HCl. The resulting mixture was left to mix for a 25 min equilibration period under the same conditions. Finally, stirring and heating was stopped, and the solution was left to cool to room temperature for 25 min, and, subsequently, samples were stored at 4 ºC before use. All steps were conducted under Argon. Unless otherwise described, all lipid formulations consisted of phospholipid and lyso-PPC (88:12 molar ratio). The final lipid mass concentration was kept constant for all lipid formulations at 0.5% (w/v) (See Electronic Supplementary Information file for the formation of lipid nanotemplates).

Gold nanostructure synthesis patterned by lipid structures. In the case of the hexagonal and square shaped lipid structures, two individual populations of the lipid template either encapsulating citrate or tetrachloroauric acid were mixed, or, as a control, tetrachoroauric acid encapsulating lipid structures were immersed in PBS. In the case of the twisted ribbon shaped lipid templates, tetrachloroauric acid encapsulating lipids were immersed in PBS or citrate solution in PBS, or, alternatively were mixed with citrate encapsulating ribbons. In addition, citrate encapsulating lipid ribbons were immersed in tetrachloroauric acid solution in PBS. Mixtures were incubated at room temperature and samples were taken every 24 hours

and purified by centrifugation with methanol/ethanol (1:4 v/v) and kept in toluene at 4 °C until analyzed.

2.3 Characterization of structural changes and determination of size

Transmission electron microscopy (TEM) imaging via phosphotungstic acid hydrate staining. Encapsulating and empty lipid templates were analysed structurally usingtransmission electron microscope. Using a glass pipette, a drop of sample was added to a 200 mesh copper grid with a thin film of Formvar polymer and kept at room temperature for 1 min, followed by addition of a drop of 2 % v/v phosphotungstic acid hydrate (PA) (Panreac) solution (pH 7.2) in distilled water for 2 min. Subsequently, excess liquid was carefully dried using filter paper and the sample was left at room temperature until a dried film was obtained. Transmission Electron Microscopy (TEM) analyses were performed using a JEOL 1011 transmission electron microscope operated at 80 keV with an ultra-high-resolution pole piece providing a point resolution of 2 A°. Micrographs (1024 pixels x 1024 pixels) were acquired using a Megaview III multiscan-CCD camera. Images were analyzed with an iTEM image analysis platform, measuring the dimensions of particles from the photos captured at different parts of the grid and calculating the mean diameter from the series of experiments (n±3) conducted using the same parameters.

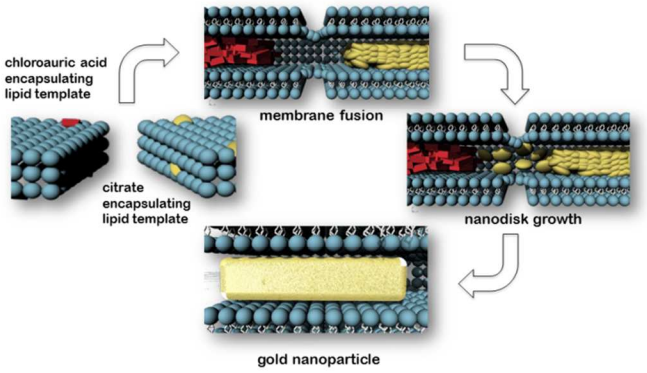
Determination of reaction yield of the gold nanoparticle synthesis. An ICP-OES instrument Spectro Arcos FHS16 was used to measure the mass fractions of Au in the nanostructures using calibration curves generated from standard solutions (0 - 40 ppm dilutions of transition metal mix 3 which was purchased from Sigma-Aldrich) with an R value of 0.999. The samples and standards were dissolved in 1% aqua regia ($3HCl:1HNO_3$). The analytical line used for the determination of Au was 242.795 nm. The synthetic yield for the different Au nanostructures was calculated as the difference between the Au mass determined by ICP-OES and the starting Au mass, corrected with the dilution factors and expressed in percentage (n=3). The formula used was X%=(C/Ci)x100 where C is the Au concentration (mg/L) measured by ICP in the samples containing the nanostructures and Ci is the starting concentration of Au (mg/L).

Scanning Electron Microscope (SEM). Scanning electron microscope studies were carried out using scanning electron microscope, SEM (Jeol JSM 6400, 40 kV). Spectrometric measurements were performed by spectrophotometer UV-Vis-NIR, Cary 500- Varian.

X-ray diffraction measurements. X-ray diffraction measurements were performed with a Rigaku X-ray diffractometer.

3. Results and Discussion

There have been a plethora of reports detailing the reverse micelle method,[25,31–35] where a clear correlation between template size, and the resulting nanoparticles formed, has been established. Reverse micelles are dynamic lipid clusters where they continuously fuse and re-disperse due to Brownian motion, exchanging their contents.[43] However, in the case of lipid bilayers, fusion is a more complex process where the membrane fluidity and hydrophobic interactions have been reported to be important factors for liposome membrane fusion, and is mostly an irreversible process.[44] Zwitterionic lipids fuse at temperatures below their critical melting temperature while fusion of charged lipids occurs at higher temperatures.[45] The mechanism of the 2D growth of rigid particles is proposed to be due to a shape patterned by a single template due to fusion of the two lipid structures encapsulating $HAuCl_4$ and citrate in their aqueous core, respectively. In the proposed model depicted in Scheme 1, electrostatic interaction occuring between $AuCl_4^-$ with a net negative charge and the zwitterionic –PC head with mobile positive-charge (Table 1) provides nucleation sites for the synthesis. Subsequent to the fusion of two lipid structures, citrate molecules slowly diffuse into the bilayer and reduce the Au(III) to Au(0) resulting in the formation of solid gold hexagonal and rectangular nanoparticles. However, possible transport of tetrachloroauric acid in the reverse direction should be taken into account as this would possibly result in amorphous aggregates as the reaction will occur faster in that direction.



Scheme 1: Proposed growth path of nanoparticle formation through membrane fusion of reactant encapsulating lipid structures.

To explore the proposed usage of the prepared lipid superstructures as template and nanoreactor for the preparation of metallic nanostructures of controlled size and shape, the afore mentioned lipid nanostructures were prepared from DPPC and DMPG lipids (Table 1) as described above, to form rectangular, hexagonal as well as ribbon shaped nano-architectures.

Rectangular-shaped lipid templates were prepared at an operating temperature of 45 °C from DPPC lipid and cooled down to RT before purification and analysis. The formed lipid structures were then used as templates (Figure 1a) afterwards. and nanoparticle synthesis was carried out by mixing $HAuCl_4$ encapsulating and citrate encapsulating lipid nanotemplates in a 1:1 ratio, and particle formation was monitored over 72 hours at room temperature. For control experiments, the citrate was replaced by PBS. Figure 1b shows the metallic nanoparticles formed within the lipid template and obtained following the lipid removal via centrifugation in a methanol/ethanol mixture. The metallic nanostructures prepared were disk like with 200±11 nm length and 80±7 nm width (aspect ratio between 1 and 1.5), which is 10-20 nm smaller (both length and width) than the average template size. As depicted in Figure 1c, a large proportion of the nanoparticles are oriented in the (111) crystal plane ((2Θ) at 38°) with relatively poor signal in (200) and (220) which is coherent with the crystal structure of the disk-

like metal nanoparticles.[46] The reaction yield of the gold nanoparticle synthesis was measured by inductively coupled plasma optical emission spectrometry (ICP-OES). After the sample was subjected to centrifugation, the AuNPs were effectively separated from the unreacted Au(III). Results showed a moderate turn-over with calculated yield of 25.6 %.

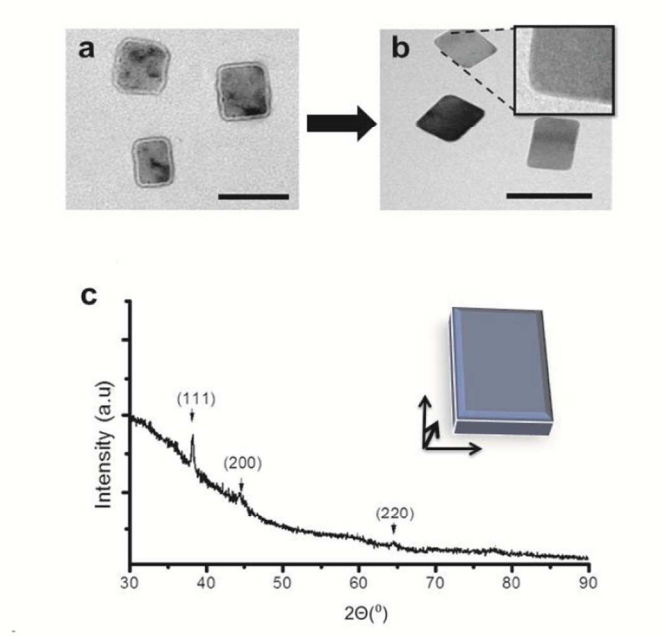


Figure 1. TEM images representing (a) the square shaped DPPC based lipid templates encapsulating $AuCl_4^-$ prepared at an operating temperature of 45 °C, (b) purified gold nanoparticles in toluene which were prepared after 72 hours of incubation at room temperature. Inset: magnified image highlighting the smooth edges of the gold nano-rectangle, and (c) their XRD pattern. Scale bars are 200 nm.

As with the rectangular shape lipids, lipidic hexagonal structures encapsulating tetrachloroauric acid and sodium citrate were prepared, respectively, from DPPC lipid at 25 °C. Again, a 1:1 molar ratio of each was mixed and monitored for over 72 hours and analysed by transmission electron microscope (TEM) and scanning electron microscope (SEM) before synthesis, during synthesis and following separation of the lipids from the formed gold nanostructures by centrifugation. Even though the yield was not very high (18.9%), a heterogeneous population, mostly of rectangular and hexagonal shaped gold nanoparticles, was obtained after 24 hours where the number of particles increased after 72 hours (Figure ESI1 and Figure ESI2). A better control over the template shape could reveal more homogenous distribution in particle shape and the size. In the absence of sodium citrate encapsulating liposomes, no nanoparticle structures were observed. The template size was measured as ca. 250 nm (Figure 2a), and the resulting particles were approximately 200-250 nm (Figure 2c and Figure ESI1). As can be seen from the inset of Figure 2b, a lipid bilayer surrounding the produced nanoparticle can be observed prior to purification. The particles produced had a tendency to grow in the (111) crystal plane (see Figure 2c) and with the (111), (200), (220), (311) and (222) planes, equal to that of a typical XRD pattern of the face-centered cubic (fcc) structure was obtained.[47,48] An SEM image of a single hexagon is depicted in Figure 2d.

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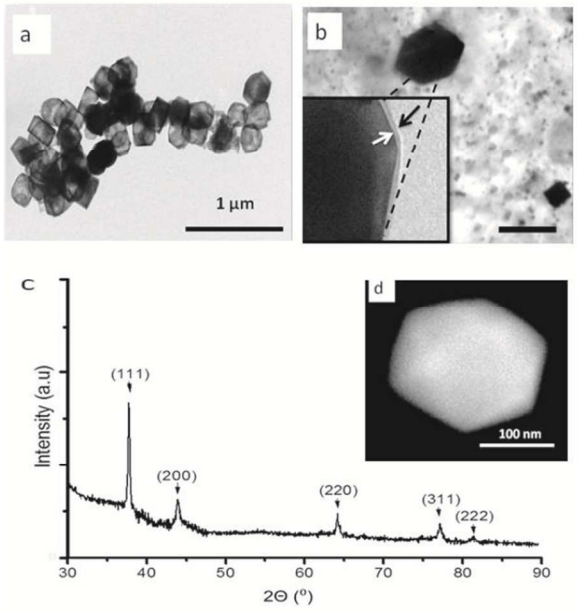

Figure 2. TEM images representing (a) the hexagonal shaped lipid templates formed from DPPC: lyso PPC prepared at an operating temperature of 25 °C, (b) a single hexagonal shaped gold nanoparticle before purification from lipids (inset is a magnified TEM image which the lipid layer on the particle is highlighted by the arrows), (c) XRD pattern and (d) SEM image of purified gold nanostructure demonstrating the (111) face of a single hexagonal gold nanoparticle.

Whilst there are many studies on the use of nanotubes [49,28] as templates for inorganic particle synthesis, there are very few studies on the use of ribbons as templates for ribbon shaped metal nanostructures. Jung et al, reported self-assembled helical lipid ribbons as templates for the synthesis of palladium nanoparticles using ascorbic acid as a reducing agent, where they observed either tiny nanoparticles embedded on the template surface or solid nanostructures depending on the patterning method used.[50] Jin et al, in another study, reported the preparation of silica nanostructures patterned from lipid structures including ribbons, hollow sphere and other chiral materials.[5]

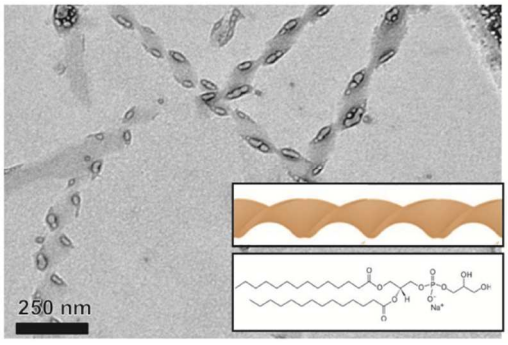

Figure 3. TEM images of twisted ribbon-shaped DMPG lipid self-assembly prepared at an operating temperature of 25 °C. Inset images are representative drawing of twisted ribbon shape and chemical structure of DMPG lipid.

In this study, we analyzed the template capacity of twisted ribbon-like lipid nanowires prepared from DMPG lipid (Figure 3, Table 1) for the biomineralization of metal salts as demonstrated with the rectangular and hexagonal lipid templates. However, due to the multiple fusion sites available

on the ribbons, which could lead to aggregation and collapse of the template, alternative routes were also considered and compared since the exchange of the lipidic contents would not occur by membrane fusion, but rather diffusion of the respective reagents across the lipid bilayer into the interior core of the ribbon-like structure.

Of the four different approaches used, in **Method I**, tetrachloroauric acid encapsulating lipid templates were directly immersed in PBS buffer and monitored for over 72 hours of incubation at 25 ^{o}C as a control. Ribbon-like thin rods with slight appearance were spontaneously formed, even in the absence of reducing agent (Figure 4a) with no apparent signal in XRD measurements (results not shown). This is attributed to the ability of the DMPG to act as a capping agent on gold nanoparticles and -OH groups present on the glycerol head of the lipid might act as an initiator of the slow reduction of gold ions (Table 1) which took 72 hour to complete.[29,51]

However, when $HAuCl_4$ encapsulating twisted lipid ribbons were immersed in a solution containing sodium citrate (**Method II**), ribbon shaped nanostructures, with a more solid appearance and a stronger resemblance to the template were obtained (Figure 4b). The reaction yield of gold nanoribbons synthesized with this approach was calculated to be 30.5 %.

In the third approach (**Method III**), tetrachloroauric acid and citrate encapsulating lipid structures were mixed and small nanoparticles of 2 to 5 nm, arranged in a one-dimensional ribbon shape (Figure 4b inset) were observed after 24 hours of incubation at 25 ^{o}C. As depicted in the scheme represented in figure 4-III, when two twisted encapsulating lipid ribbons are mixed, the tetrachloroauric acid and citrate interact at the contact points, and particles form at these points due to the reduction of the Au(III) to Au(0), resulting in a nanoparticle chain which resembles the template.

The same type of one-dimensional particle alignment as obtained in Method III was observed when the citrate encapsulating lipid template was immersed in chloroauric acid solution in PBS (pH 7.4, 10 mM, 25 ^{o}C) (**Method IV**). The particles were around 15 nm (Figure 4d), and again arranged in nanoparticle chain type structure guided by the dimensions of the lipid template. These structures were formed due to the interaction between the tetrachloroauric acid and the citrate diffusing from the bilayer core. This facilitated rapid nucleation of particles on the diffusion cites of the template where they further aggregated to form chains aligned one after the other (Figure 4d). Both chain shaped and ribbon shaped gold nanostructures were stored at room temperature for a month. TEM studies showed no apparent aggregation during that period of time, demonstrating the stability of the resulting nanostructures.

When we analyzed the crystal properties of the metallic nanostructures obtained using the different methods, nanostructures obtained through the presence of lipid template (Method I) and by mixing lipid structures encapsulating citrate and tetrachloroauric acid (Method III) showed no apparent signal. On the other hand, the ribbon like structures obtained in Method II and nanochains in method IV showed a typical pattern of face centered cubic structure with higher and distinctive signal dominated at 2Θ of 38°- assigned to the (111) face- and also a distinctive peak at 2Θ of 44.5°- contributed to (200) face- (Figure 5). Twisted Au nanoribbons demonstrated a pattern of a two-fold symmetry with additional lattice spacing at (222). These results suggests that both samples mostly consist of one dimensional arrangement that were preferentially oriented with their (111) planes, therefore attributing to a significantly high (111) reflection intensity.

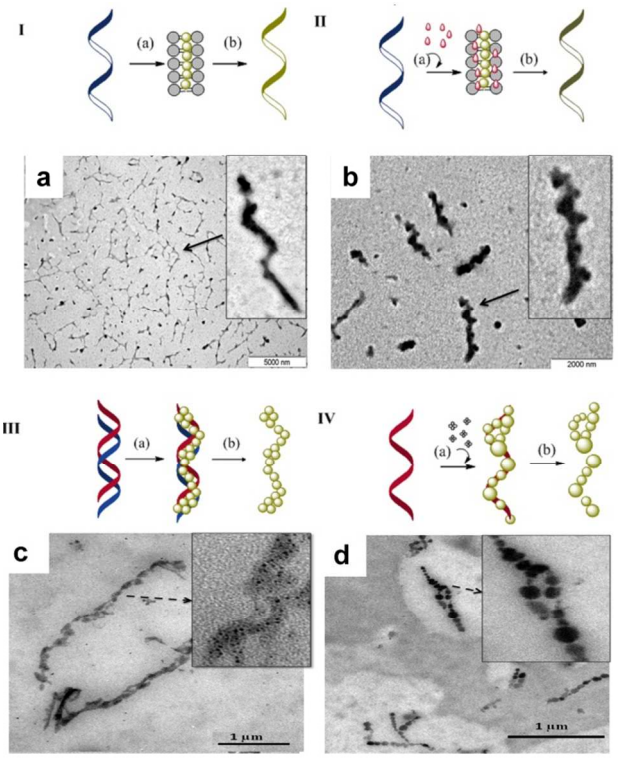

Figure 4. Schemes outlining the different strategies for the use of twisted ribbon shaped lipid templates for the preparation of ribbon-like gold nanostructures and TEM images of gold nanostructures formed as a result: (a) Method I: tetrachloroauric acid encapsulating lipid template alone after 72 hours, (b) Method II: tetrachloroauric acid encapsulating lipid template immersed in citrate solution, (c) Method III, tetrachloroauric acid encapsulating and citrate encapsulating lipid template mixed and left for 24 hours at room temperature, and (d) Method IV, citrate encapsulating lipid template was immersed directly into the tetrachloroauric acid solution.

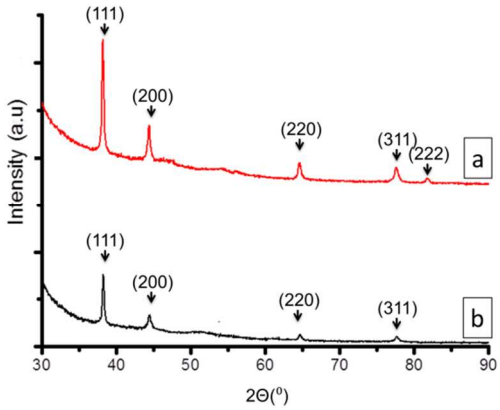

Figure 5. XRD patern of nanostructures synthesized. Both ribbon shaped gold nanostructures (a) and nanochains (b), prepared via Method II and Method IV, respectively, positioned dominantly in (111) crystal plane with more distinctive intensity at (111) and (200) faces in the case of gold nanoribbons.

Conclusions

The work reported here examines the potential of the lipid nanostructures as soft matter templates for metal biomineralization. Unusual lipid nanostructures including rectangular, hexagonal and twisted ribbons were formed via curvature tuned preparation method and used as templates for gold nanostructures. The resulting nanostructures' shape was mostly patterned by the template and the homogeneity of the particles formed was directly dependent on the homogeneity of the template shape. Ribbon shaped lipidic nanostructures resulted in diverse types of nanostructures where atomic alignment was strongly dependent on the biomineralization approach chosen and the direction was driven by the template shape (e.g ribbon and chain-like alignments). Resulting twisted gold nanoribbons showed a typical face centered cubic structure primarily dominated by [111] facets. In conclusion, self-assembled lipid based nanostructures were demonstrated to be promising tools for the synthesis of metal nanoparticles of controlled morphology and size. The possibility to prepare diversely shaped and sized nanoparticles in mild conditions should find a plethora of potential applications in catalysis, plasmonics and electronics.

Notes and references

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Electronic Supplementary Information (ESI) available: Chemical structure of the lipids used and broaden TEM images of particles prepared using hexagonal shaped lipid nanostructures as template. Discussion on the preparation of lipid nanotemplates. See DOI: 10.1039/b000000x/

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Table of contents entry

The potential of the lipid nanostructures including rectangular, hexagonal disks and twisted ribbons were used as soft matter templates for the biomineralization of gold.