Fabrication of Ni-decorated helical ribbon composite microstructure from self-assembled lipid tubule by electroless metallization

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Abstract Lipid molecules can self-assemble into a tubular structure, which is formed by tightly wound helical ribbons. Lipid tubules are utilized as a precursor to fabricate a novel Ni-decorated helical ribbon composite microstructure in a high yield by electroless deposition. The microstructure carries Ni nanoparticles on the flat face and wires at the edge of helical ribbon, in which the average size of nanoparticles is about 40—60 nm, and the wires are of a layered structure strongly correlated with a multi-bilayer structure in the lipid membrane. Compared with the tubular precursor, the Ni-decorated composite microstructure becomes short and irregular shapes due to the breakage in the deposition, and its formation is largely bound up with the tubular helical structure and the different catalytic process. Finally, the helical composite microstructure would have a potential application in the development of electric active materials.

Molecular self-assembly is a powerful approach for preparing new supermolecular architectures such as nanofibers and nanotubes[1]. Lipid molecules, due to their amphiphilic nature, can self-assemble to form a variety of microstructures, such as spherical liposome, tubules and helical ribbons[2]. Many lipid molecules can self-organize into the helical ribbon structures[3,4], for example, helical ribbons were self-assembled in a variety of multicomponent enantiomerically pure systems that contain mixed lipid substances[3]; the self-assembled nanotubules and ribbons were prepared from a phospholipid mixture by Spector[4]. Lipid tubules have also been extensively fabricated from a diacetylenic glycerophosphatidylcholine[5]. They are formed by a tightly wound ribbon, which is composed of a multi-bilayer lipid membrane.

On the other hand, because the molecular self-assembly is mediated by one or several weak, noncovalent bonds[6], the lipid helical ribbons and tubules are difficult to be used in practical engineering for their low strength. To increase their strength, a template-directed electroless plating has been conducted. For example, Schnur and Zabetakis *et al.* electrolessly deposited metal on the lipid tubules to form a metallic tubule[7,8]; authors in the paper fabricated a metallic microtubule with a helical pattern on the template of

lipid tubules by the electroless metallization[9]; Price *et al.* ever fabricated a nanoscale metallic spiral using a mixed phospholipid microtubule template[10].

Because the lipid tubular template is non-conductive, it is necessary to activate it to initiate plating before the electroless deposition. The conventionally employed catalyst was a colloidal Pd-Sn catalyst[7−9]. In the catalytic process, the Pd particles are adhered on the lipid template by excess $SnCl_2$ colloidal solution. In order to initiate metallization, we not only need to remove the outer shell of colloidal solution from Pd particles, but also try to avoid causing Pd particles to detach from the tubular wall in the meantime. Hence, the colloidal Pd-Sn catalytic method is rather complicated, and difficult to operate.

Price et al. developed a Sn-free Pd catalyst for the initiation of plating to fabricate the metallic spirals or helical nanostructures[10], and the Sn-free Pd catalyst has a simple procedure and selective deposition on template. In our paper, we also use the Sn-free Pd catalyst and conduct a different catalytic procedure to obtain a novel Ni-decorated helical ribbon composite microstructure after plating. The microstructure carries the Ni nanoparticles on the flat face and layered wires on the edge of helical ribbons, which is neither different from the helical gold wires, nor from the gold nanoparticles on lipid tubules in the literatures[11,12]. It is an assembled composite material with Ni nanoparticles and wires selectively deposited on the lipid helical ribbon. Furthermore, its microwave dielectric property is primarily investigated in order to potentially develop a novel electrical active composite.

1 Experiments and materials

Lipid material, diacetylenic glycero-phosphatidyl-choline (Fig. 1, called $DC_{8,9}PC$ for short), for the preparation of tubules, was purchased from Avanti Polar Lipid Co., and a thin layer chromatography (TLC) was used for its purity analysis and Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) analysis for its structure verification. Borane dimethylamine complex (DMAB) and sodium tetrachloride palladate (Na_2PdCl_4) were obtained from Fluka and used directly. Other reagents were all of analytical purity. Double distilled water was used in all experiments.

1.1 Preparation of self-assembled lipid tubules

The self-assembled lipid tubules were prepared as follows[13]: add l0 mg $DC_{8,9}PC$ to a 10 mL hot solution mixture containing ethanol and water ($EtOH/H_2O$ 7:3 v/v), raise its temperature to 60℃ at a rate of 1℃/h, and incubate the sample for 1 h at 60℃, then cool the solution down to room temperature at a rate of 1℃/h. A large amount of white colloidal substance will be precipitated from the solution at 32℃−34℃. The excess ethanol in the lipid dispersion was removed by dialysis using a dialysis tube (its cut molecular weight 14000).

1.2 Catalysis of the lipid tubules

The Sn-free Pd catalyst was prepared by using Na_2PdCl_4 and excess sodium chloride, in which the excess sodium chloride will be helpful to stabilizing Pd complex ion[14]. An equal volume of the catalyst solution was added into the lipid dispersion. The mixture was stirred uniformly, and stayed for about 12 h. Then, the excess Pd solution was removed by dialysis, and the activated lipid dispersion stayed for about 3 months at room temperature, then for electroless metallization. In order to examine the deposition
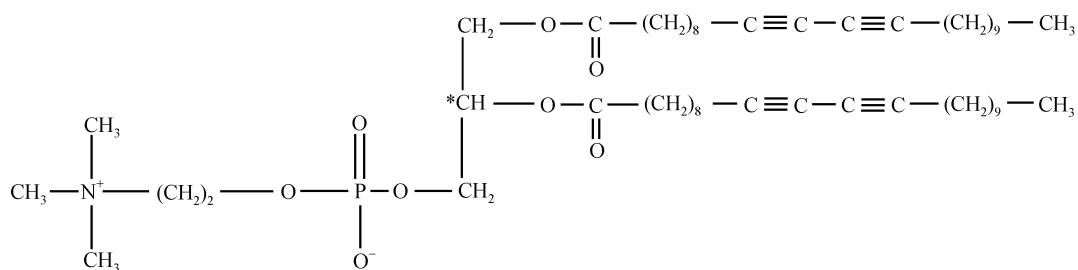

Fig. 1. Molecular structure of diacetylenic glycerophosphatidylcholine ($DC_{8,9}PC$). "*" means a chiral molecule.

feature of Pd particles on the lipid tubules, a small amount of activated lipid dispersion was treated by a diluted DMAB solution for about 3−5 min. The reduction reaction was quenched by a large amount of water, then the sample was washed with water and dried in air for a microscopic examination.

1.3 Fabrication of the composite microstructure

Electroless plating bath was mainly composed of $NiSO_4$, DMAB, EDTA·4Na etc., which was prepared according to the literature[15]. The electroless plating reaction could be expressed as

$$3Ni^{2+}+3(CH_3)_2NHBH_3+6H_2O \xrightarrow{Pd} 3Ni^0+B$$
$$+3(CH_3)_2NH_2^++2B(OH)_3+9/2H_2+3H^+$$
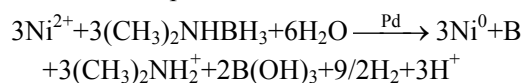
Take 10 mL of the plating bath to be diluted into 100 mL to obtain a 10% concentration solution for use. An equal volume of the 10% bath was added into the activated lipid suspensions and mixed gently. The mixture solution was incubated for several minutes, then, it started to bubble gas (H_2) and turned instantly black in color. The mixture system was continuously stirred till the gas was not released any more, and the metallized sample settled on the bottom. After centrifugation, the metallized sample was washed three times with water to remove residual plating salts. All samples were transferred on a film-coated Cu grid for the microscopic examination.

1.4 Microscopic examination and structure characterization

An optical examination was done by using an Olympus BH-2 type biological microscope. Scanning electronic microscope (SEM, JSM-5610LV) and transmission electronic microscope (TEM, JEM 2010) were used to perform further microscopic observation. The samples were coated with a thin layer of Pt to increase their conductivity for the SEM examination, and pipetted on a film-coated copper grid and air-dried at room temperature for the TEM observation. A composition analysis was conducted by using an energy dispersive X-ray spectrometer (EDS). X-ray diffraction (XRD) of the metallized samples was performed by using an X'pert diffractometer (Holland, Philips) with an accelerative voltage of 40 kV, an accelerative current of 40 mA, a CuKα radiation, and a graphite monochrometer at a scanning speed 2.4°/min. The sample for the diffraction measurement was prepared by spreading a thin slurry in water on a highly polished silicon wafer and subsequent air-drying.

1.5 Determination of the microwave dielectric property

A reflection-transmission network parameter method was used to determine the dielectric properties of the composite, and the frequency used was in the range of 2−18 GHz. The coaxial samples for the determination were prepared as follows: The composite powder was uniformly dispersed in a melted paraffin wax, and cooled in a coaxial mold to prepare a hollow cylindrical sample with an inner diameter of 3 mm, outer diameter of 7 mm, and a height of 10 mm. The weight percentages of the composite in the coaxial samples are 10%, 20%, 40%, and 60% respectively. Reflection and transmission parameters S11 and S21 were determined with a vector network analyzer (transmission line model), and they were placed in eq. (1) to calculate the complex permittivity. The method can also be used to determine the complex magnetic conductivity of the composite. However, because the composite magnetic conductivity and magnetic loss values are very low in the high frequency, we will primarily discuss the changes in its permittivity.

To increase the accuracy, solid paraffin 100% was used to do a contrast experiment, and the bulk nickel powder was used for comparison with the composite. Parallel experiments were conducted for three times for each sample. In the experiment, keep the determined sample to tightly contact with the coaxial mold to eliminate the error.

With this determination technique, the error in real permittivity is less than 5%, and its imaginary error is strongly correlated with the dielectric loss value. If the loss value is more than 0.1, then its imaginary error is tolerated within 20%; however, if the dielectric loss is less than 0.1, the imaginary permittivity is not measured accurately. In this case, their data would be meaningless.

$$\varepsilon_r = \sqrt{\frac{y}{x}}, \qquad (1)$$

in which

$$x = \left(\frac{1+\Gamma}{1-\Gamma}\right)^2,$$

$$\Gamma = K \pm \sqrt{K^2 - 1},$$

$$K = \frac{[S_{11}^2 - S_{21}^2] + 1}{2S_{11}}, \qquad (2)$$

$$y = -\left[\frac{C}{2\pi f d}\ln\left(\frac{1}{T}\right)\right]^2,$$

$$T = \frac{S_{11} + S_{21} - \Gamma}{1 - [S_{11} + S_{21}]\Gamma}.$$

2 Results and discussion

2.1 Characterization of composite microstructure

Under an optical microscope, the prepared tubules are stacked disorderly just like a bird-nest or soda straw in a cylindrical shape (Fig. 2(a)). However, they exhibit helically wound patterns under TEM (the inset in Fig. 2(a)). The lipid tubules have a wide distribution of length (40−120 μm), and their average length is about 93 ± 10 μm (Fig. 2(b)). the average diameter of tubules ranges from 0.2 μm to 1.0 μm.

Lipid tubule is formed by one or several helical ribbons, which are composed of multi-bilayer membrane[16,17]. The formation mechanism of the lipid tubules would be based on the lipid molecular structure and its chiral interaction, and their formation process is presented in Fig. 2(c). Lipid molecule contains one chiral center in the 2-position carbon atom of glycerol bone, two long hydrophobic alkyl groups (tail groups), and one hydrophilic phosphatidylcholine group (head group)(Fig. 1). In water solution, the lipid molecules will spontaneously form a bilayer structure, and the lipid bilayers will be stacked to form a multi-bilayer membrane. The intrinsic driving force, originating from the molecular chiral interaction and the dominant orientation of molecular configuration caused by the rigid diacetylenic groups, will make the lipid bilayers be stacked with a tilt angle, not in a parallel pattern. Hence, it causes the lipid membrane to twist into a helical ribbon, driving the growth of lipid membrane to widen and eventually wrap into a stable tubule[18,19].

After the plating, the most cylindrical samples become small irregularly spiral bodies (arrows, Fig.
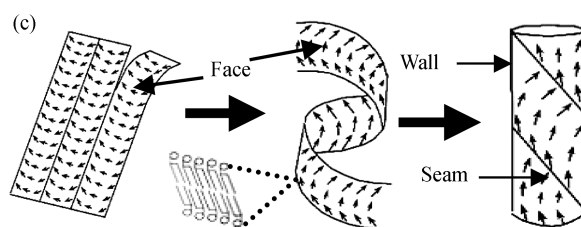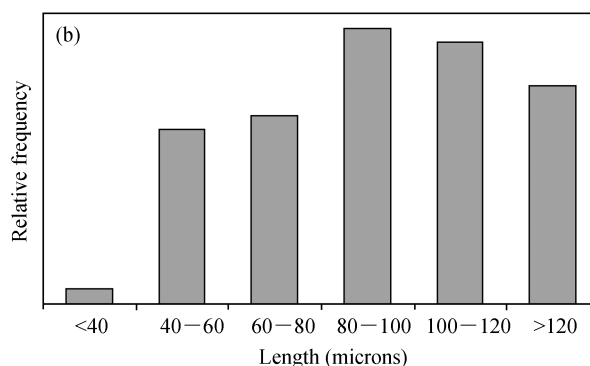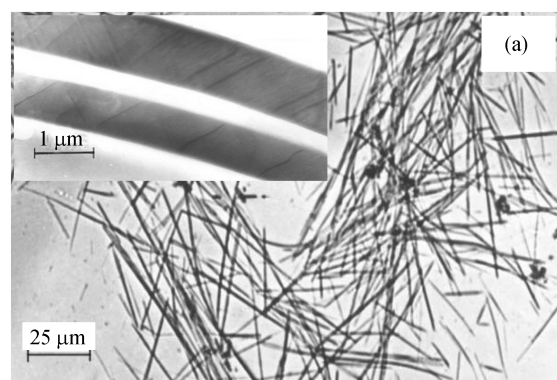

Fig. 2.   (a) Microscopic characteristics of lipid tubules under the optical microscopy and TEM (inset). (b) Histogram of the length of the lipid tubules. (c) The formation process of lipid tubule cited in refs. [18,19].

3(a)), and only a few still present the cylinder shape. The small spiral bodies have the different twisted shapes, either in a single loose shape, or a helix wrapped with the lipid tubules, or in a stack of many helixes. They have a length distribution in the range of 10−40 μm, and their average length is about 22 ± 5 μm, which is much shorter than that of the lipid tubules (Fig. 3(b)). The result based on 200 counts shows that the spiral bodies cover about 60%−70% in total, prepared with a high yield.

SEM examinations indicate that the small spiral bodies are of loosely helical ribbons with nickel deposited on them (arrows in Figs. 4(a) and (b)). From

(a)

2.5 μm

20 μm

(b)

Relative frequency

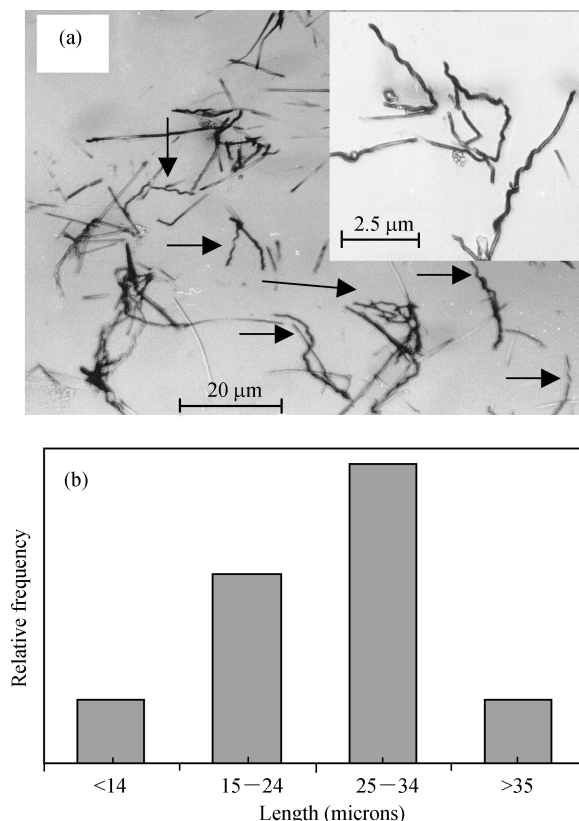<14   15－24   25－34   >35

Length (microns)

Fig. 3. (a) Small spiral bodies after electroless plating under the optical microscope (arrows and inset); (b) histogram of length of the small metallized spiral bodies.

the circle inset in Fig. 4(a), it can be seen that nickel at the edge has about 4－5 layers, between which there is a dislocation. The EDS analysis indicates that there are strong peaks of Ni, and the strong Cu and Pt peaks are attributed to the copper mesh and the conductive Pt film sputtered on the sample surface respectively (Fig. 4(b)). The metallized ribbon width is in the range of 0.4－1.0 μm, which is primarily consistent with that of helical ribbon in lipid tubules.

TEM examination indicates that Ni nanoparticles are formed on the flat face and wire-like structure (called wire for short) at the edge of helical ribbon (Fig. 4(c)). Ni nanoparticles have a uniform distribution on the face, and their average size is in the range of 40－60 nm. As shown by the arrow in Fig. 4(c), Ni wire breaks apart at the turning point of helical ribbon due to the inner stress in itself. Fig. 4(d) shows one Ni wire in a destroyed ribbon, and it has a double-layer structure (arrow), in which the thickness of each layer is about 6－8 nm, comparable to the thickness of one

lipid bilayer, 6.6 nm[16]. The diameter of one Ni wire is in the range of 15－30 nm (Fig. 4(d)).

XRD result shows that there are two broad peaks of Ni (Fig. 5), which indicates that the as-deposited Ni would be of an amorphous structure. The amorphous structure would be caused by the presence of a small amount of element B[20], and the element of B originates from the reducing agent DMAB in the plating bath.

2.2 Analysis of the formation mechanism of the Ni-decorated helical ribbon

A comparison experiment indicates that there is no difference in the shape between the original and the activated tubules (stayed after 3 mon). Therefore, the formation of the Ni-decorated helical ribbon should occur in the plating process. But when the lipid tubule is in contact with the catalytic solution for a short time, there is no Ni-decorated helical ribbon observed after plating. Hence, the reason for its formation would primarily lie in the catalytic process. In this work, an important factor, that is the long-time stay of activated lipid tubules in the catalytic process, would play a certain role.

In the Sn-free Pd catalyst solution, Pd complex ions are of negative charge[14]. In the self-assembly process of lipid molecules into bilayer, the hydrophobic tail groups will spontaneously be oriented towards the inner side; while the hydrophilic head groups towards the outer side, in which the choline group is of a positive charge, being beneficial to the electrostatic adsorption of Pd complex ions.

In the catalytic process, the long immersion of lipid tubules in Pd solution and long-stay of activated tubules would make the Pd complex ions have enough time to diffuse into the interlayer zone in the tubular walls along the seams of wrapped ribbon and adsorb on the flat face of lipid membrane (seen in Fig. 2(c)). Since the bend of ribbon will cause the thickness difference of the membrane, as well as less steric hindrance and the greater polarity at the edge[10,21], it will cause a greater adsorption of Pd ions than that on the flat face. The deposition feature of Pd indicates that Pd deposition at the seams occurs in a greater degree, so that they form a dark helical line (arrows in Fig. 6(a)), and there is a multi-layer deposition pattern at the
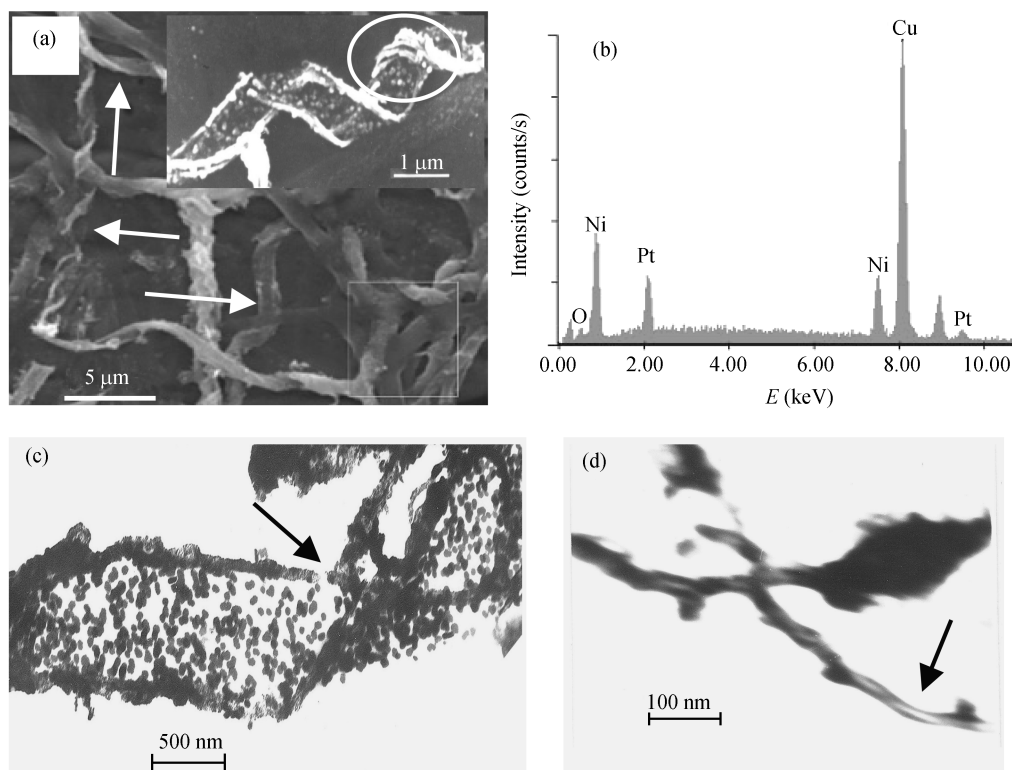
Fig. 4.   (a) SEM images of the composite microstructures (arrows), and the circle inset shows the dislocation between nickel layers at the ribbon edge; (b) EDS composition analysis in the square frame in (a); (c) TEM image of Ni-decorated helical ribbon composite microstructure (the arrow indicates the breakage of nickel wire at the turning point); (d) a single nickel wire with a double-layered structure (arrow).
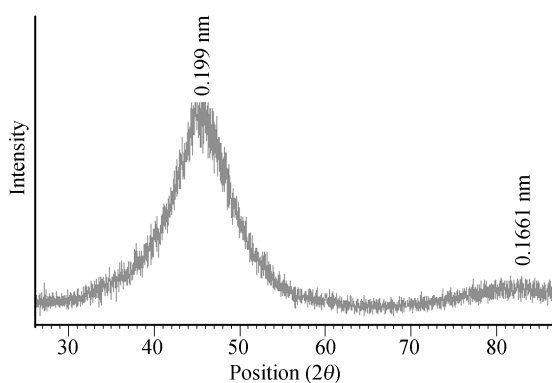

Fig. 5.   XRD pattern of the composite microstructure.

seams of ribbon (arrow, Fig. 6(b))[22].

In the plating process, nickel ion was reduced into metal by reducing agent DMAB, in the meantime, a large amount of hydrogen gas was released in reaction. At the seams of ribbons, the higher density of Pd and the more contact with the plating bath would initiate a greater degree of nickel deposition to form the continuous wire; however, on the flat face, particularly on the inner face of membrane in the tubular wall, the lower density of Pd and the less contact with plating bath would initiate a smaller degree of deposition to form the discrete nickel nanoparticles. Meanwhile, the swiftly released hydrogen in the plating reaction would not only cause the tightly wound ribbons to loosen, but also cause lipid tubules or helical ribbons to break, eventually resulting in the formation of the Ni-decorated composite microstructure being short and in different spiral shapes.

However, a question arises: why did Price *et al.* fabricate a nanoscale metallic spiral, but not the metal-decorated composite microstructure by using the same Sn-free catalyst[10]? On one hand, the reason would both rely on the use of a negatively charged lipid analogue in the self-assembled system of DC$_{8,9}$PC, and on the tubular surface modification by the alternatively adsorbed polyelectrolytes. Their preferential adsorption of the charged lipid and polyelectrolytes at the seams of helical ribbon will create and amplify the ligand sites as required for binding a negatively charged Pd catalyst and for the electroless metalliza-
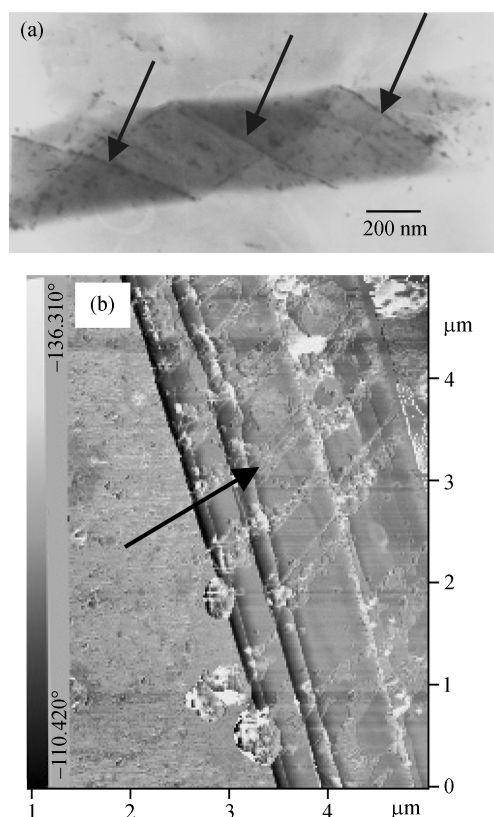
Fig. 6. TEM (a) and AFM (b) images of deposition features of Pd nanoparticles on the lipid tubules. Arrows in both (a) and (b) indicate there is higher density of Pd at the seams of wrapped ribbon than that on the flat face. As indicated by the arrow in (b), there is a multi-layer pattern at the seams of ribbon[22].

tion at the naturally occurring seams present in the lipid tubules. However, on the other hand, the short catalytic time of lipid tubules would make it hard for Pd complex ions to diffuse into the interlayer zone of the membrane in the tightly wound ribbon face, resulting in the difficulty in the electroless metallization. These factors could be presumed to make the deposition mainly occur at the seam site to obtain the metallic spirals, not the Ni-decorated composite microstructure.

Lipid membrane has a multi-bilayer structure[17]. Research has shown that when the diameter of the metal nanoparticles is smaller than the thickness of one lipid bilayer, they will present a layered deposition pattern at the edge of helical ribbon[17]. The thickness of one lipid bilayer is about 6.8 nm[16]; while from Fig. 4(c), the thickness of one single layer in the Ni nanowire is just in the range of 6−8 nm. Hence, it could be presumed that each layer in Ni wire will in-

dicate one bilayer of lipid membrane, and the two-layer Ni indicates that the lipid membrane in helical ribbon is composed of two bilayers.

Therefore, it could be concluded that the formation of the Ni-decorated helical ribbon composite microstructure is strongly correlated with the helical feature in the self-assembled lipid tubules and the different catalytic process.

2.3 Analysis of the microwave dielectric property of of the Ni-decorated helical ribbon

The result of 100% paraffin samples shows that their real permittivity is 2.2, and the imaginary value or loss is zero, and they do not change with frequency, therefore, the permittivity change in the experiment is primarily attributed to the composite microstructure itself. Because the dielectric loss values of the composite and bulk Ni powder are less than 0.1, and their imaginary values are not accurate, the discussion is focused on the change of their real permittivity. Their average values are calculated from the summation in the applied frequency (2−18 GHz), as presented in Table 1.

Table 1 Average values of the real permittivity of different weight percentages for the samples with an applied frequency of 2−18 GHz (Their average values were obtained from the summation in the range of frequency)

Samples	10%	20%	40%	60%
Composite microstructure	2.55	2.61	7.28	9.5
Bulk Ni powder	2.33	2.60	3.61	6.24

Table 1 shows that their average values increase with an increase in the weight percentage, and at the higher percentages (40% and 60%), they increase in a greater degree. It also indicates that the values of the composite microstructure are higher than that of the bulk Ni powder, and at the higher percentages, there is a larger difference. The difference between the composite microstructure and bulk Ni powder would primarily be attributed to the amorphous structure of the as-plated Ni on template. The amorphous structure makes the decorated Ni have the great lattice strain[23], and in Ni nanoparticles and wires, there would exist a great amount of different defects in their interfaces. Under an applied electric field, electric charges could accumulate in the interfacial defects to form a dipole moment, which is called interface polarization or

space charge polarization, resulting in a higher permittivity[24]. Hence, higher percentages will cause a greater interface polarization and higher permittivity for the composite microstructure. However, the bulk Ni is of a crystal structure, and there is no interface polarization, which results in a lower value.

3　Conclusions

A novel Ni-decorated helical ribbon composite microstructure is prepared in a high yield by electroless plating, in which the lipid tubules are utilized as a precursor. It is a composite material with Ni nanoparticles and wire selectively deposited on the helical ribbon. The composite microstructure would have the potential to be utilized to design a novel electric active material by tuning its Ni crystal structure.

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