

RECENT RESEARCH PROGRESS ON PREPARATION OF SILVER NANOWIRES BY SOFT SOLUTION METHOD, PREPARATION OF GOLD NANOTUBES AND Pt NANOTUBES FROM RESULTANT SILVER NANOWIRES AND THEIR APPLICATIONS IN CONDUCTIVE ADHESIVE

Guangqing Yan, Li Wang, and Lei Zhang

State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

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Abstract. This review concentrates on the various chemical routes for synthesis of silver nanowires by soft solution methods, and also the production of gold nanotubes and Pt nanotubes from different templates. After a comprehensive comparison between the developed methods, it is concluded that the soft solution method has obvious advantages and is the most promising route for the mass production of silver nanowires. Herein its recent development is generalized into two groups: surfactant-assisted soft chemistry method and soft template method of which advantages and disadvantages will be discussed elaborately and separately. In addition, the synthesis of Au and Pt nanotubes from resultant silver nanowires, although less researched than other methods, is considered as the most convenient and facile route among the templated methods. Due to their high thermal and electrical conductivities, these metal nanomaterials are excellent candidates for the conductive filler in composite adhesive. Especially for one-dimensional metal nanostructures, they show great promise in the improvement of current conductive adhesive.

1. INTRODUCTION

Nanomaterials have shown plenty of speciality and superiority due to their small dimensions, and they have exhibited great applicable potential in the field of high-performance catalyst [1-3], magnetics [4], acoustics [5], optics [6] and electronics [7,8], attracting increasingly interests from the whole world. Metal nanowires and nanotubes, as one-dimensional (1D) nanostructures, have been extensively studied on their optical properties [9,10], and as well their potential use as conductive fillers to enhance the performance of the adhesives [11]. Due to the high electrical conductivity of bulk silver, gold and platinum, their nanowires and nanotubes are the most promising candidates to be used as conductive fillers of high-performance adhesives [12]. Hence, the

mass production of silver nanowires, gold and platinum nanotubes is necessary and of great significance.

For the synthesis of silver nanowires, plenty of chemical routes have been developed during these years. However, soft solution method has been widely considered as the most feasible route to large-scale production of silver nanowires. Xia et al. first proposed a PVP (polyvinylpyrrolidone)-assisted polyol process, which has become the most popular method nowadays [13]. Moreover, a variety of other surfactants (capping agent) have been developed to guide the anisotropic growth of silver nanowires later during these years [14-16], and the diversity of surfactants provides many choices to meet the various demands. Generally speaking, the

Corresponding author: Li Wang, e-mail: opl_wl@diel.zju.edu.cn

mass production by soft solution process is the most hopeful and feasible for its convenience and high efficiency compared with other methods. Besides, for the synthesis of gold and platinum nanotubes, the guidance of templates is almost indispensable. However, among the numerous applied templates, silver nanowires are the most convenient and excellent ones because of the perfect crystallographic match and no need for the additional procedures to remove the templates after completing the reaction [17,18].

Totally this article mainly reviews the recent research progress on synthesis of silver nanowires by soft solution method and fabrication of gold and platinum nanotubes from resultant silver nanowires. Furthermore, it also pays much attention on the feasibility and significance of applying these nanomaterials to the improvement of conductive coatings.

2. PREPARATION OF SILVER NANOWIRES BY SOFT SOLUTION METHOD

Nowadays, many non-chemical methods for fabricating nanowires have been developed out and some of them may have obvious advantages over preparation of peculiar morphological silver nanowires, but they are usually complicated, highly energy-consuming and sophisticated. Therefore, the chemical method has been the most promising way for the large-scale fabrication of silver nanowires in future. Among the various routes, the soft solution method is now the hottest point in the field of silver nanowires at present. Thousands of work has been devoted to the mechanical study, reactive condition exploration and application research during these years. Nowadays, some rapid progresses have already been made on understanding the detailed mechanism and relatively fine control also has been taken on morphology, size and aspect ratio of the product [19]. Hopefully, large-scaled production of silver nanowires through soft solution method can be realized in future.

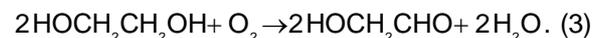
2.1. Preparation of silver nanowires by surfactant-assisted soft chemistry method

2.1.1. Mechanism

Among various soft solution methods, they are usually divided into two groups: surfactant-assisted soft chemistry method and soft template method, while their mechanisms are quite different from each other

and commonly are studied separately. For the surfactant-assisted soft chemistry method, plenty of surfactants have been used to guide the one-dimensional (1D) growth of silver nanowires. The anisotropic growth of these silver nanowires is partially ascribed to the selective adsorption of these surfactants onto the specific facet of the nanostructure and leaving the bare facet still active for the further deposition of silver atoms. Herein, we set the popular polyol method as the representative example to elaborately illuminate the recent research progress on the mechanism of the surfactant-assisted soft chemistry method.

For the polyol synthesis of silver nanowires, Xia et al. [13] had contributed a lot to the basic research and proposed many reasonable and important viewpoints on the mechanism, which had been widely adopted and accepted by other peer-researchers now. In most of the synthetic routes, AgNO_3 was usually adopted as the precursor and polyol always acted as both solvent and reducing reagent, while the capping reagent varies in abundance of candidates. After Xia et al. detected the presence of Glycolaldehyde (GA) in the polyol reactive system [20], the reaction formats were elucidated as follows:



They found that heating ethylene glycol (EG) in air resulted in its oxidative product (GA): a much stronger reductant than acetaldehyde. It was reported that, when temperature of the reactive system was above 150 °C, GA would become the predominant reductant in the presence of O_2 . So the reaction format (3) should be added into this reactive system. In addition, they also found the newly formed silver nanoparticles could catalyze the oxidation of EG to GA, which was defined as "autocatalytic effect" later. To some extent, this theory can explain the influence of temperature and O_2 on the final morphology of product, and this information may also enhance the reproducibility and scalability of this polyol synthesis of silver nanowires [21].

As we all know, the fabrication of nanowires in an isotropic solution would be quite easy and straightforward, when metal has an anisotropic crystalline lattice. But almost all the metals tend to crystallize into highly symmetric face-centered cubic lattices. Hence, we need the surfactant, namely the capping reagent, which not only protects nanowires

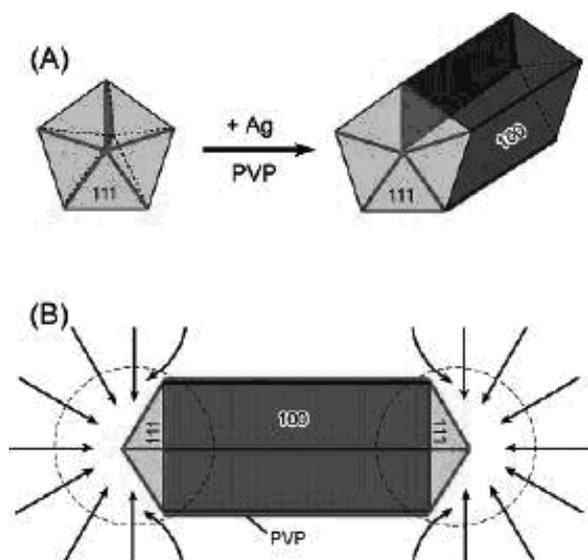


Fig. 1. Schematic illustration of the pentagonal model of silver nanowire and MTP, see [13] for more detail.

from aggregating into bundles, but also promote the anisotropic growth of the silver nanowires. So far a large number of capping agents have been used to control the anisotropic growth of silver seeds to obtain nanowires through soft solution reactions, such as PVP [13,22,23], CTAB [16], Sodium Dodecylsulfonate (SDS) [14,19], Vitamin B2 [24] and so on.

To date, the most popular capping agent is PVP in the synthesis of silver nanowires and its detailed mechanism hasn't yet been thoroughly studied out. It is believed that silver nanowires are derived from Multiply-Twinned Particles (MTPs), which are quite different from the ordinary nanoparticles and only can be generated under special situation [13]. As shown in Fig. 1, MTPs are covered by five $\{111\}$ facets at each end and the side surfaces of nanowires are bounded by five $\{100\}$ facets. The anisotropic growth is realized by selectively covering the facets $\{100\}$ with PVP as a result that $\{100\}$ facets are completely passivated, while $\{111\}$ facets are largely bare and still quite active. Hence the reduced silver atoms are preferentially deposited onto $\{111\}$ facets, leading to the anisotropic growth of silver nanowires [25]. Gao et al. [23] further proved that there was just a bed of Monolayer assembly (PVP) on the surface of silver nanowires. In addition, they further found that Ag^+ would immediately coordinate with the lone pair electrons of the oxygen atom on the carbonyl group of PVP, once PVP and silver nitrate were simultaneously added into the reaction. As a result, the chemical potential of Ag^+ would

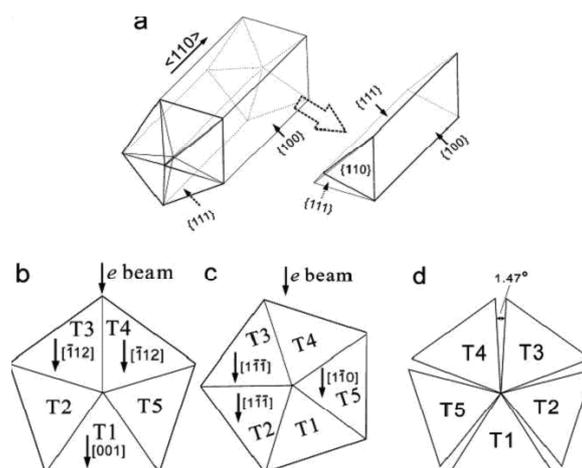


Fig. 2. Schematic model of the silver nanowires, data from [26].

decrease and the crystal seeds would be generated more easily during the nucleation period. Once the multiply-twinned particles formed, PVP would selectively adsorb onto the $\{100\}$ facets by the coordination and induce the 1D growth. Furthermore the molar ratio between the repeating units of PVP molecules and the external silver atoms of nanowires was calculated to be 1.5 through TGA and theoretical calculation.

However, Zhang et al. [26] proposed another mechanism later, in which they contributed the anisotropic growth to the effect of crystal strain rather than the selective adsorption of surfactant. As depicted in Fig. 2, the penta-twinned crystal with 5-fold axis, which was shared by two $\{111\}$ facets, was formed by the stacking fault, because the theoretical interfacial angle between two $\{111\}$ facets on the top surface was just $360^\circ/5 = 72^\circ$, while actually it was usually 70.53° for a perfect face-centered cubic (fcc) crystallite [27]. Thus, the angular mismatch indicated that there must be lattice distortion in the silver nanowires, and the atoms surrounding the radial direction had to offset the mismatch by crystal strain and dislocation so as to form seamless nanowires. It was obvious that crystal strain would augment with the diameter of nanowires increasing, and it would in return restrict the lateral growth of silver nanowires, and finally lead to the 1D growth.

Recently, through designing a series of unique experiments, Zhang et al. [28] proposed another mechanism, in which the synergy between crystal strain and surface energy was considered to be responsible for anisotropic growth of silver nanowires. It was reported that the crystal strain was not suffi-

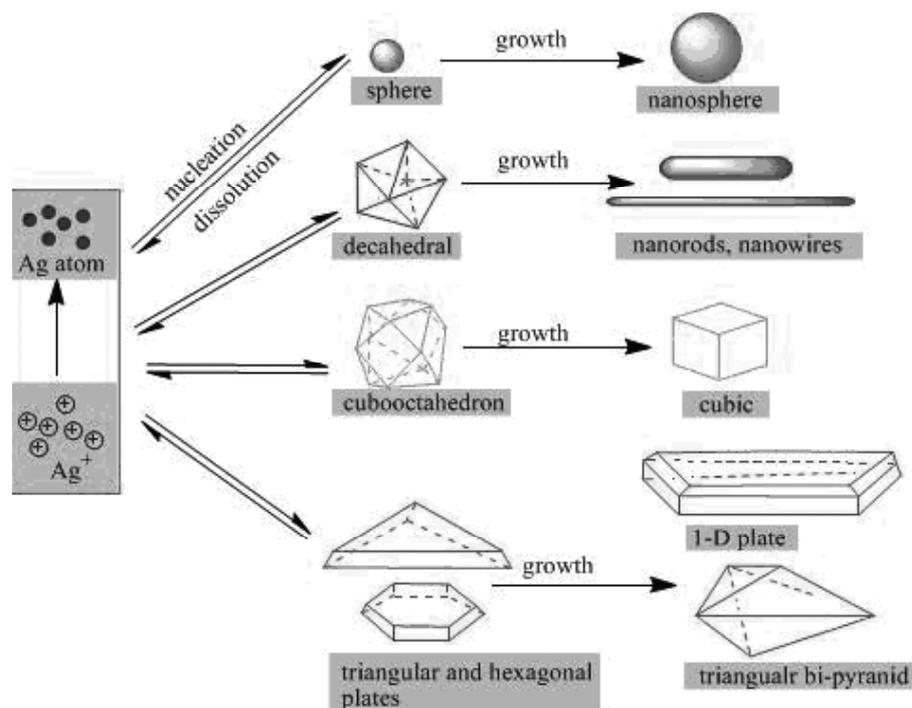


Fig. 3. Mechanism of shape selective oxidative etching and crystal growth of Ag nanostructures (modified), data from [31].

cient to provide enough restriction for 1D growth, and the surface-capping agent was indispensable for lowering surface energy difference between $\{100\}$ and $\{111\}$ facets to promote the growth of nanowires. Following this mechanism, Ag wires with tunable diameter and long length was obtained by controlling the lateral growth and the axial growth in two separate steps [28,29].

2.1.2. Synthesis of silver nanowires with different control agents

Up to now, many research groups have been devoted to exploring the synthetic conditions in the presence of PVP or other surfactants to promote the anisotropic growth of silver nanowires. Sun et al. [25] first proposed a polyol method to prepare silver nanowires for mass production, and they introduced PtCl_2 to form the platinum nanoparticles serving as seeds for the heterogeneous nucleation. These platinum nanoparticles would grow into silver nanowires in the solution after reducing AgNO_3 by ethylene glycol (EG). The product had uniform diameters in the range of 30-40 nm and lengths up to 50 μm .

As we all know, the polyol method traditionally needed two steps to synthesize the silver nanowires: seeding process and nanowires-growing process.

In the first step, AgNO_3 was reduced to form the nucleus seeds at a quite low concentration. Then the newly generated silver atom would selectively deposit onto the seeds to induce the 1D growth at a relatively high concentration in the second step. Therefore, without adding additional control agents, such synthesis of silver nanowires could not be achieved in one step. To simplify the procedure and improve the quality of the silver nanowires, plenty of control agents had been developed out and different species would show quite different functions. Commonly these agents are divided into three groups: inorganic anions, metal cations and organic molecules. They either form the colloids with the silver ions to serve as the initial nucleus, or change the rate of reduction and nucleation. Sometimes, these control agents also can protect the penta-twinned crystal from being etching by the oxidant. Anyway all of these functions are favorable for the formation of the silver nanowires.

Due to the much stronger oxidation ability of H_2PtCl_6 than AgNO_3 , H_2PtCl_6 is the ideal precursor to provide the seed for the growth of silver nanowires. Tsuji et al. [30] innovated to introduce the microwave to rapidly heat the reaction system in the presence of H_2PtCl_6 and a series of mixed one-dimensional nanomaterials was achieved within a few minutes. Through repeating centrifugal separation, the

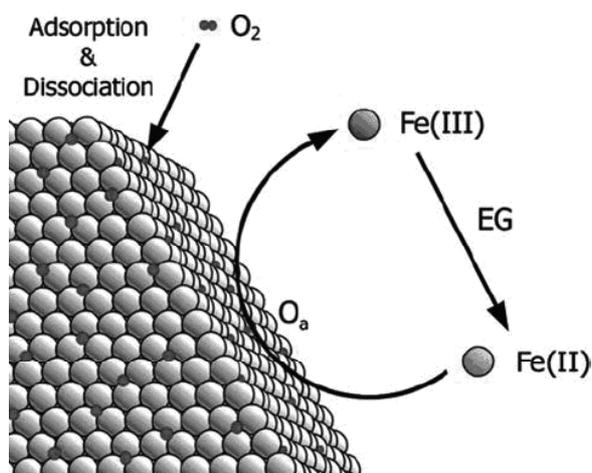


Fig. 4. Illustration of the role of Fe^{3+} and Fe^{2+} in the polyol synthesis of silver nanowires, see also [35].

one-dimensional products were easily separated from other three-dimensional particles and these separated particles would further act as seeds to grow into longer and thicker 1-D products through repeating this reaction. However, recently a novel viewpoint toward the roles of Pt seed and Chloride anions in this microwave-polyol method was proposed. They did not think that the preformed AgCl and Pt seeds were completely responsible for the nucleation and subsequent growth of the silver nanowires, and they realized the free Cl^- might also have a deep effect on the formation of the one-dimensional nanostructure and other silver nanoparticles. To the best of our knowledge, different morphological seeds would grow into different nanostructures (as shown in Fig. 3). They found that the free Cl^- would accelerate the re-dissolution of the formed nanoparticles and that was favorable for the growth of silver nanowires and other one-dimensional nanostructures [31].

It was reported that silver nanowires with adjustable diameters could be synthesized by adding different control agents [32]. The additive Haloid anions not only just provided initial nucleus, but also served for 'seed oxidative etching'. The detailed mechanism had been elucidated by Chipara et al. [33] in their article. The reaction of Cl^- with Ag^+ could act as a buffer decreasing the concentration of free Ag^+ as a result that the potential of the $\text{Ag}^{+/0}$ pair would be reduced and the rate of formation of silver atom would also decrease. Besides, the presence of Cl^- would accelerate the oxidative dissolution of silver nanoparticles in the ambient atmosphere. Therefore, these two factors both reduced the reac-

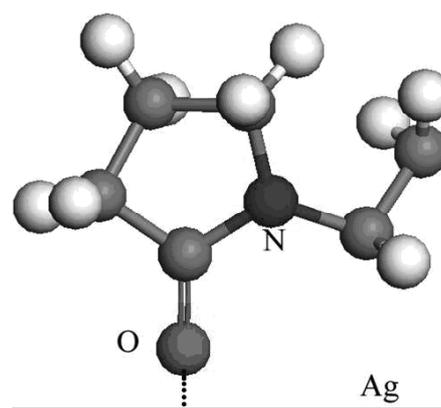


Fig. 5. Schematic illustration of PVP (polyvinylpyrrolidone) conformation on the surface of Ag nanowires, data from [23].

tion rate and it was known that the low reaction rate was favorable for the formation of silver nanowires. Despite of the Haloid anions, S^{2-} ions were also added as the control agent: the precursor of catalytic seed. It was reported that Na_2S could take a better control of the morphology of the product and obtained more uniform silver nanowires by the polyol method [32]. The authors also discovered that the lower concentration of Na_2S caused the formation of nanocubes, while the high concentration yielded silver nanowires. Depressingly, until now, the detailed mechanism was still not thoroughly disclosed [34].

Inorganic anions, which are applied to control the morphology of the silver nanostructure, have very obvious advantages for its convenience and relatively large-scaled fabrication. It really has great promising for the large-scaled fabrication of silver nanowires through this method. However, there also exists some defects on the products, such as the introduction of many impurities, relatively rough surface and severe distortion of nanowires.

Despite of the inorganic anions, the metal ions were also used to induce the growth of silver nanowires. It not only can provide the metal nucleus seeds, but sometimes also can make good use of its oxidative capability, which can consume the newly generated silver atoms to control the size of seed and decelerate the nucleation rate. Sun et al. [35] had succeeded in using Fe^{3+} and Fe^{2+} in the polyol method to synthesize nanowires (Fig. 4). They proposed that Fe^{2+} could react with the absorbed atomic oxygen on the surface of silver nanostructures, preventing multiply-twinned particles

from being oxidatively etched. In addition, the newly formed Fe^{3+} would, in return, be reduced into Fe^{2+} by ethylene Glycol (EG) again. It was also reported that, because of the oxidative etching by Fe^{3+} on the surface of the seed, the small silver nuclei would grow into nanowires with smaller diameter [32]. Similarly, Skrabalak et al. developed a rapid synthesis of silver nanowires through a CuCl or CuCl_2 mediated polyol process [36]. They made use of the reductive property of Cu^+ to scavenge the absorbed oxygen, which covered on the surface of the Ag seed preventing it from further Ag deposition. Moreover, the introduction of chloride ions also reduced the concentrations of initial free Ag^+ . Hence, both the cations and anions were added to enhance the accessibility to the silver nanowires.

Comparing with the inorganic control agents, the organic showed quite different and particular in the polyol solution and some of them maybe acted as the capping agent and surfactant for the anisotropic growth as well. These organic compounds usually tended to facilitate a much bigger radius of the product, such as ascorbic acid, which could promote the fabrication of silver nanowires with a mean diameter of ~ 190 nm [32]. Since the organic control agents usually act as surfactants or reducing agents in the reactive system, we do not make a separate discussion here, but will analyze it combining with capping agent later.

2.1.3. Synthesis of silver nanowires with different capping agent

Sometimes silver nanowires can be fabricated in the absence of additional capping agents, because some organic reactants can serve as both reducing agents and capping agents. As a result, it seems to be no capping agents. However, to obtain silver nanowires, the capping agents are almost indispensable, because we usually need to fabricate the nanowires of a highly anisotropic crystalline lattice in an isotropic solution and the silver nanowires can not be fabricated just by the restriction of crystal strain without selectively lowering the surface energy by capping agent. Most capping agents take advantage of the carbonyl group and amino group to selectively adsorb onto the specific facets of the silver nanowires inducing the 1D growth. The coordination (N-Ag, O-Ag) would properly passivate the adsorbent facets $\{100\}$. However, different capping agents have different conformation and would provide different steric repulsion. Therefore the silver nanowires with different morphology and different diameter would be obtainable.

Caswell et al. [37] had reported one seedless, surfactantless, wet chemical synthesis of silver nanowires in water. In this reactive system, the citrate not only strongly complexed the Ag^+ , but also performed as the reductant of silver ions and capping agent to silver nanomaterials. Moreover, hydroxide ions played very important roles in formation of silver nanowires, because it could complex with the silver ions as well. Nevertheless, due to no surfactant existing in the system, the product tended to grow into bundles and stuck to each other. Despite of the citrate, glucose, hypophosphite [26] and potassium tartaric [38] also can be used to synthesize the silver nanowires, but they only serve as capping agents without surfactants providing good dispersity. As a result, it was inevitable to cluster into bundles.

To obtain the product of good dispersity, some surfactants were added into the reaction, and they can serve as capping agent to guide the anisotropic growth as well. For instance, PVP's lone pair of the oxygen on the carbonyl group can strongly coordinate with silver atoms on the side surface while leaving the end surface of nanowires uncovered for silver deposition [23,39]. PVP used as inducing agent has been intensively studied during these years and the correlative theories become more and more sophisticated. However, polyvinyl alcohol (PVA) and polyethylene glycol with oxygen of lone pair tend to coil into agglomerate, which is unfavorable for the formation of one-dimensional structure.

Except for PVP, the Gemini surfactant was also used to direct the growth of silver nanowires. Xu et al. [40] had used the methenamine as the reducing agent to synthesize the silver nanowires of high aspect ratios with an average diameter of ~ 30 nm. In this reactive system, the Gemini provided Br as control agent and methenamine degraded to generate HCHO and NH_3 . Then NH_3 can complex with the Ag^+ and HCHO would act as the reducing agent. Finally, both the slow reaction rate and the Capping effect of Gemini surfactant contributed to the anisotropic growth of silver nanowires. This synthetic route is quite advantageous, because it not only simplifies the procedure, but also takes place in aqueous solution at a relatively low temperature.

Cetyltrimethylammonium bromide (CTAB) is another good choice for guiding the anisotropic growth of silver nanowire and nanorod. Unlike PVP, CTAB tends to selectively adsorb onto the side surface of silver nanostructures through the coordination between N on the amino group and silver atom. It was evidenced that CTAB formed the bilayer on the metal surface to hinder the lateral growth of

nanowires or nanorods and its mechanism was the same as PVP's [41,42].

In the assistance of some special capping agents, silver nanowires of different morphology may be synthesized for some special use, such as zigzag morphology. He et al. [43] successfully fabricated the silver nanowires of zigzag morphology using N,N-dimethylformamide as the reducing agent in the presence of tetrabutyl titanate (TBT) and acetylacetone (AcAc). It was reported that TBT and AcAc could guide the silver nanoparticles selectively aggregation along the preferred crystallographic axes to form short nanorods, while the zigzag morphology should be contributed to the simultaneously adsorbing one nanoparticle by two different nanorods. In another synthetic system, tetrabutylammonium bromide (TBAB) was used to guide the anisotropic growth of silver nanowires through the reduction of the hydrazine in the presence of decanoic acid and dodecylamine. The role of TBAB is similar to PVP, which can selectively cover the {110} and {100} planes. The aspect ratio of the product can be controlled ranging from 1-70 by varying the reaction time and concentration [44]. Recently, a novel and interesting mechanism was proposed for these situations [45], which was quite different from the previous one. They supposed that the formation of silver nanowires based on the aggregation-based mechanism. It was reported that the silver aggregation of nanoparticles would form in the initial stage of the experiment, and it aggregated via the ion bonding between the cysteine molecules on the surface of silver nanoparticles. So the pH value was quite crucial for the formation of silver nanowire. However, in this system, the product tended to be needle-like, had low aspect ratio and extended along different directions.

Generally speaking, the capping agents are usually indispensable for the synthesis of uniform, regular and mono-disperse silver nanowires. Their concentration can make a good control over the morphology, size and aspect ratio of silver nanowires in the soft solution method. Furthermore different capping agents will induce the formation of different silver nanowires, which would meet the different demands.

Except for the control agents and capping agents mentioned above, there are still many other influencing factors which should be considered carefully. As we all know, the multiply-twinned particles (MTPS) are responsible for the formation of silver nanowires, while some byproducts may have profound effect on them. For example, the generated HNO_3 can consume the newly formed MTPS, espe-

cially when the preparation is in a relatively high concentration. Recently, Zhang et al. [29] proposed a route by adding stainless steel to restrain in situ nitric acidic etching. The stainless steel consumed HNO_3 in advance, efficiently protecting the MTPS from being dissolved. This mechanism may have great significance on the large-scale fabrication of silver nanowires, because the etching power of HNO_3 is quite strong even at a low concentration. Besides, the generated H_2O and organic byproduct may also have significant effect on the morphology of the nanomaterials. Unfortunately, there still needs much work to do on this aspect. Moreover, the shielding gas not only greatly influences the reproducibility of the experiment, but also has obvious effect on the morphology of the product [21]. It was said that the inert gases were quite favorable for the repeatability of the experiment, while the existence of O_2 would promote the formation of silver nanowires. Hence, the synthesis of the silver nanowires extremely needs us to take good control of all the factors, and consequently, we have to make a deeper insight into this field.

2.2. Preparation of silver nanowires by soft template methods

2.2.1. Mechanism

For 1D nanostructure, mesophases structures, which are usually self-assembled from surfactants, provide a group of useful and soft templates for the anisotropic growth of silver nanowires and nanorods in relatively large quantities. It is well known that some surfactants tend to self-assemble into rod-shaped micelles at its critical micellar concentration (CMC). Therefore, the surfactants are commonly adopted to form the micelles and emulsion in the soft template method, and then these mesophases structures provide the micropores for the growth of silver nanowires as shown in Fig. 6. Quite different from the surfactant-assisted soft chemistry method, soft template method depends on the restriction of the micelles and emulsion to guide the 1D growth of silver nanowires and nanorods but not the selective adsorption of the surfactants to mediate the surface energy. It was reported that the surfactants could initially induce the one-dimensional growth, and the rod-like micelles would further promote the formation of silver nanowires [46,47]. Generally speaking, the interface restriction from the surfactant molecules contributes to the growth of nanowire, while the aspect ratios of silver nanowires are dominantly decided by the morphology and sizes of the micelles and micro-emulsion. The concentration of

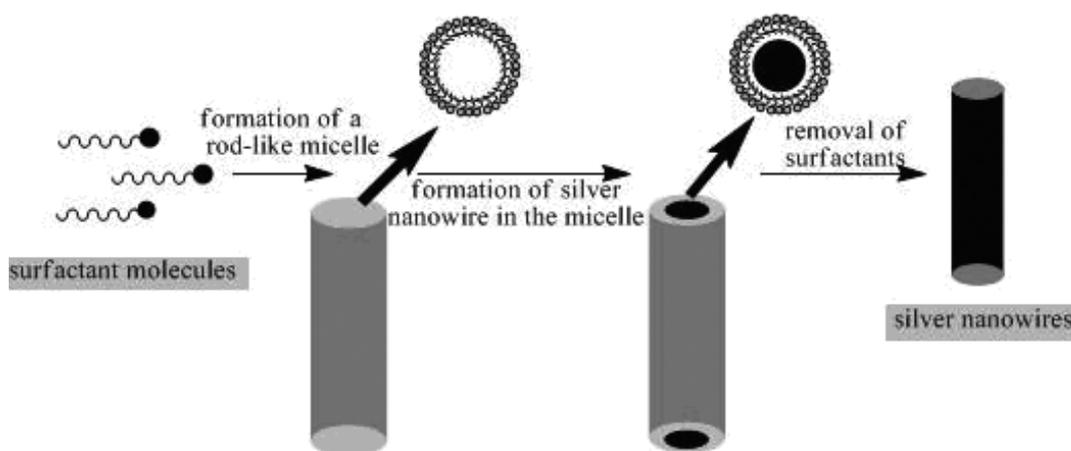


Fig. 6. Schematic illustration of typical soft template method for the synthesis of silver nanowires (modified), see [46] for more details.

precursors and surfactants also plays an important role in these aspects of the products.

2.2.2. Preparation of silver nanowires by different soft templates

Block copolymers formed by several immiscible segments can be exploited as the soft templates for the synthesis of silver nanowires. It was reported that some regular cylinders would formed in the presence of block copolymer under appropriate conditions, which are very similar to the micelles and emulsion inducing the 1D growth [46,48].

In the presence of AgNO_3 , Vitamin C and sodium dodecyl sulfate (SDS), Liu et al. [14] had synthesized the silver wires with high aspect ratio in the ethanol solution. It was proposed that the micelles of SDS in the ethanol solution led to the aggregation of the silver clusters and the anisotropic growth of the silver nanowires. It is well known that the micelles in different surfactant concentration display different shapes, such as spherical, lay-like and rod-like. However, just the rod-like soft template would guide the anisotropic growth of the silver nanowires. Besides, the reducing rate of the precursor is key to the formation of nanowires and the detailed mechanism of this method still needs us to further study it. When the Vitamin C was replaced by a stronger reducing agent: tri-sodium citrate, the reaction speed should be under better control. The concentration of tri-sodium citrate became more determinative and sensitive to the morphology and sizes of the product [19]. Besides, the anionic surfactant dodecyl benzene sulfonic acid sodium (DBS) was also reported to be used as the soft template

for the silver nanowires. Particularly experimental results showed that the concentrations of the reactant AgNO_3 and tri-sodium citrate were interdependent in the fabrication of the silver nanorods and nanowires [15]. In addition, it was reported that silver nanorods and nanowires were obtained by a seed-mediated growth approach in the rod-like micellar media. The micellar media was formed in a AgNO_3 /ascorbic acid/CTAB/NaOH solution. The synthesized silver nanorods had 40nm long with aspect ratio 2.5-15, and the silver nanowires even had 1-4 μm long with aspect ratio 50-350. The only difference between the preparations of silver nanorods and silver nanowires was the relative concentration of NaOH in the solution [47]. Recently, a novel soft template method of silver nanowires was achieved in a reverse micellar solution, while it was obviously distinct from the previous ones. Initially, silver nanotubes were formed through the self-assembly of silver nanoparticles by the interaction of the coating surfactants, and then as-synthesized nanotubes were further sintered in air at 500 $^\circ\text{C}$ to obtain the silver nanowires. This method mainly took advantages of the self-assembly of octanoic acid into nanotubes and depended on these tubular templates to fabricate the silver nanowires [49]. In addition, the mixture of polyethylene and ethylene glycol was also reported to provide the micro-emulsion, which guided the one-dimensional growth of silver nanowires [50].

Until now, even if various surfactants have been exploited as the soft templates to synthesize the silver nanowires, but their mechanism is still largely unclear. The soft template method is mainly dependent on the micropores of the rod-like micelles and

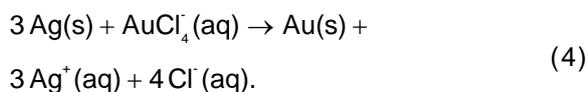
micro-emulsion to restrict the lateral growth of silver nanowires and nanorods. However, it is usually very difficult to prepare the micellar phase and of low reproducibility, so still needs us to devote more efforts to improve these methods.

3. PREPARATION OF GOLD NANOTUBES FROM RESULTANT SILVER NANOWIRES

Traditionally gold nanotubes are prepared by depositing the newly generated gold atoms onto the surface of the templates, such as goethite rods [51], silica wires [52] and polymer latexes [53], and then the template cores need to be selectively removed. However, using the silver nanowires as the templates may have some intrinsic advantages in fabrication of gold nanotubes, because it need not selectively etch the cores after deposition and quite uniform nanostructures will be obtained after the galvanic replacement reaction due to the perfect crystallographic match between silver and gold. Furthermore, the mechanism in this field has been studied and explored for a relatively long period. It is the most popular method for fabricating gold nanotubes in the laboratory now.

3.1. Mechanism

Xia et al. [54] first proposed the galvanic replacement method for the synthesis of gold nanoshell. The gold shell was normally obtained by adding HAuCl_4 to the dispersion of silver nanostructures at a quite mild temperature. Then silver nanostructures would be oxidized by HAuCl_4 according to the following reaction equation.



The gold atoms generated in this system were confined to the vicinity of the template surface and then adsorbed onto it. After their nucleation and growth into nanoparticles, they would form a thin shell around the templates. Meanwhile the templates: silver nanostructures were oxidized into Ag^+ and then diffused into the bulk solution. Moreover the gold nanoshell would retain the morphological feature of the silver templates. In other words, silver nanospheres templated the growth of spheric gold nanoshell; silver nanowires induced the fabrication of gold nanotubes and so on.

Generally, the template-engaged replacement reaction includes two distinctive steps. In the first

step, silver nanowires are oxidized to generate the gold atoms, which are deposited epitaxially on the surface of the templates, and the internal silver atoms also diffuse into the newly formed gold shell to form the seamless surface of Au-Ag alloys. The second step is dealloying process, in which the silver atoms are selectively removed from the uniform alloyed wall and the concomitant morphological reconstruction leads to the formation of pinholes in the walls of the gold nanoshell [18,55,56]. The silver nanostructures are utilized to be templates of the fabrication of gold nanotubes basically because of the good matching between the crystalline structures of gold and silver.

When HAuCl_4 solution is added into the reaction system, some interior cavities are concomitantly developed in each silver nanowire. With the reaction continuing, consecutive hollow inside may form finally in the nanowires and the outside shell is comprised by Ag-Au alloy. Meanwhile, some generated openings on the surface of nanotubes are favorable for the diffusion of AuCl_4^- , Ag^+ , Cl^- and Au. The various mass diffusion of gold and silver atoms proceeds on the outer surface of template to result in the formation of smooth Ag-Au alloyed layer. After that, if HAuCl_4 continues to be added into the system, the silver atoms in the alloy layer would start to be consumed. According to the stoichiometric relationship in the reaction formation, the expense of three silver atoms only generates one gold atom, which forms numerous lattice vacancies. To release these lattice vacancies, the nanowires will reconstruct its morphology via Ostwald ripening. Finally, the nanostructures tend to coalesce and collapse into small fragments of pure gold [18,54,55]. The typical morphological evolution without the inducing agents is just as Fig. 7 shows.

It was reported that the template-engaged replacement reaction in the presence of CTAB or PVP was quite different from the previous one on the morphological evolution. After HAuCl_4 was added into the reactive system containing CTAB or PVP, some small holes would immediately form on the side surfaces of silver nanowires. As the reaction proceeded, the small holes would transform into one uniform and regular channel along the axis in each facet. Meanwhile, the gold deposition started to cover the nanowires from the edges to the midsection [57]. CTAB not only served as a stable agent, but also acted as the inducing agent for the anisotropic growth of gold nanotubes. These gold nanotubes protected by CTAB possessed perfect structures, smooth surfaces, highly crystalline walls, and similar cross-sections to that of the silver tem-

plate Unfortunately, until now, some detailed mechanism is still under investigation.

It was said that temperature played a quite important role in this system, because the diffusion rates of silver and gold atoms had high impact on the morphology of final product. For example, at room temperature, the precipitate of AgCl would hinder epitaxial deposition of the newly formed gold atoms and the slow diffusion of Ag and gold would also induce the product with rough surfaces [18]. Hence the replacement reaction was commonly manipulated at 100 °C.

The templated-engaged replacement reaction was not only suitable for the aqueous system, but also fit for the organic medium. Xia et al. [56] had studied the replacement reaction between silver particles and HAuCl_4 in chloroform. They found the details of reaction were quite different from previous study and the addition of oleylamine was quite critical for the formation of uniform nanoshell free of AgCl contamination due to the complex between AgCl and Oleylamine.

3.2. Advantages and disadvantages of silver-nanowires template on synthesis of gold nanotubes

It is obvious that synthesis of gold nanotubes from the silver-nanowires template is of prominent and attractive advantages. The tubular structure can be achieved directly and there is no need for the additional operations to remove the template cores. The as-synthesized gold nanotubes have a relatively high purity and almost no impurity is introduced into the nanotubes from the templates. The produced nanotubes can completely retain the morphological feature from the silver-nanowires templates and keep a quite uniform structure. The galvanic replacement reaction is performed at a mild temperature and in the aqueous solution. Therefore fabrication of gold nanotubes from silver-nanowires templates is low energy-consuming and environmentally friendly to some extent. However, the morphology of the as-synthesized nanotubes is quite sensitive to the amount of added HAuCl_4 . Different molar ratio of the precursor to silver-nanowires template will result in completely different gold nanotubes. Hence this method is of relatively low reproducibility, but the introduction of some surfactants will improve this situation and fabricate the product with higher quality. For instance, in the presence of CTAB, the synthetic gold nanotubes would become quite uniform, smooth and well-dispersive, while they tend to bundle together if replacing the CTAB by PVP [57]. In addition,

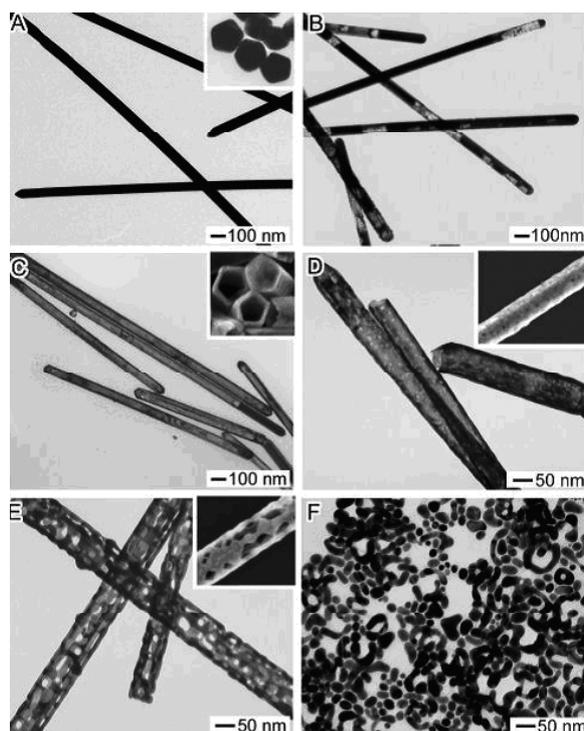


Fig. 7. TEM images taken from silver nanowires (A) before and (B-F) after they had reacted with different volumes of 1 mM HAuCl_4 solution [18].

tion, this method only can proceed at a quite low concentration if we want to avoid the contamination from the precipitate, because AgCl has an extremely low solubility even at 100 !.

Except for the silver nanowires, there are plenty of other nanostructures applied as the templates for the synthesis of gold nanotubes. Spuch-Calvar et al. [51] utilized the Goethite rods as the sacrificial templates to obtain submicrometer gold nanotubes using the formaldehyde as reducing agent. The product had a length of a few hundreds nanometers, while only had an aspect ratio between 3 and 4. The thickness and surface roughness can be adjusted by varying the concentration ratio between modified goethite rods and HAuCl_4 . Besides, the SiO_x and silica nanowires was also reported to be applied to fabricate the gold nanotubes [52,58], however their fabrications by these kinds of templates are quite complicated because it needs to remove template cores after galvanic replacement reaction.

Despite the nanowires, sometimes nanoparticles would also be utilized as the sacrificial templates. Schwartzberg et al. [59] had reported that gold nanotubes were synthesized via magnetic

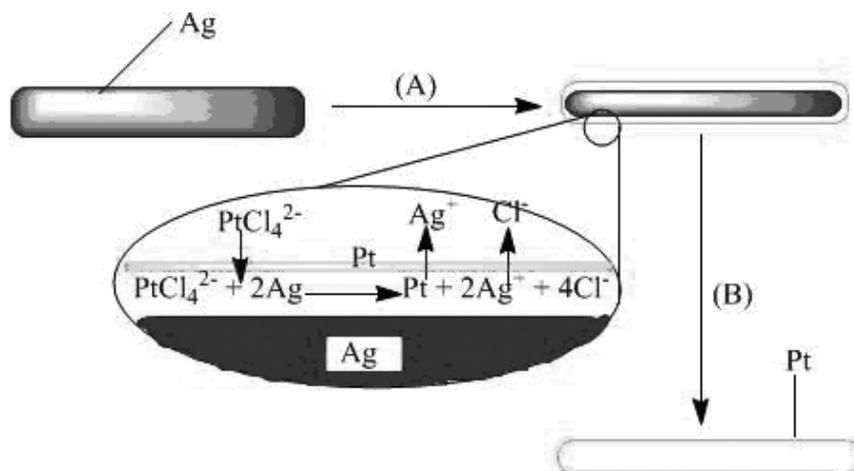


Fig. 8. Schematic illustration of the experimental procedure that generates Pt nanotube from silver nanowires(modified), see [54] for more detail.

alignment of Cobalt Nanoparticles. When the external magnetic field was strong enough, the cobalt nanoparticles would align into chains along the magnetic field vector. As long as appropriate quantity of sodium citrate was added into the precursor, the consecutive gold nanotubes would be generated. Due to the existence of Cobalt, the alignment of gold nanotubes can be easily controlled by magnetic field. But the product was not so uniform and their surface was uneven. Besides the cobalt nanoparticles was also difficult to be removed without destruction to the nanotubes.

The templated-engaged method seems to be the only way for the fabrication of gold nanotubes. Compared with the other used templates, silver nanowires are considered as the most promising templates for the mass product of uniform gold nanotubes due to avoidance of template-removal process and facile reaction operation. However, it still needs us to devote more time and energy to exploring and discovering the underlying mechanism and optimizing reaction conditions to perfect this synthesis route.

4. PREPARATION OF PLATINUM NANOTUBES FROM RESULTANT SILVER NANOWIRES

4.1. Mechanism

Comparing with gold nanotubes, the articles on Pt nanotubes are relatively less reported. However, as one kind of excellent metallic catalyst for many organic reactions, the fabrication of Pt nanotubes is

attracting more and more attentions from all over the world. Except for gold, the silver-engaged template replacement reaction, in principle, is applicable to many other metals, if only their standard reduction potentials are higher than that of Ag⁺/Ag. Therefore the fabrication of Pt nanotubes from silver-nanowires templates is feasible and of great significance.

Generally speaking, the mechanism of this process synthesizing Pt nanotubes from silver nanowires is largely similar with that of gold nanotubes. Xia et al. [54] first mentioned this template method for Pt nanotubes and they proposed that Pt(CH₃COO)₂ was reacted with silver template to induce the selective deposition of Pt atoms, and the as-synthesized Pt nanotubes exhibited the similar morphology with the gold nanotubes. However, after further study, they found that the surface of Pt nanotubes appeared rougher and was commonly of discrete nanoparticles. Finally, this phenomenon was attributed to relatively higher melting point of Pt and the wall of Pt nanotubes could not be effectively reconstructed through the Ostwald ripening process at 100 °C in aqueous solution. Consequently, to solve this problem, another suitable solvent with a higher boiling point should be selected [17]. In addition, H₂PtCl₆ was also used as the precursor of metallic Pt in this galvanic replacement reaction [2] (Fig. 8). However, the wall of the tubes was polycrystalline and the surface was quite rough as well, but it inherited the morphological characters of the silver-nanowires template as well.

4.2. Advantages and disadvantages of silver-nanowires template on synthesis of platinum nanotubes

Except for silver nanowires, there were a variety of other templates, which could be used to synthesize Pt nanotubes. Shaislamov et al. [60] utilized porous alumina templates wetted into the precursor solutions containing polymeric source and obtained Pt nanotubes. However, the synthetic procedure was largely trivialized by the removal of alumina template. Some tubular polymer was also reported to be applicable for the fabrication of Pt nanotubes. Yu et al. [61] attempted using sequenced peptide-functionalized nanotubes as templates and controlled the morphology of Pt coating by adjusting the pH to switch Pt nucleation sites among the amino acids. In addition, Kumara et al. also illustrated the possibility that used flagella nanotubes as templates [62]. However all of these templates were quite difficult to be separated from the Pt nanotubes and most of the nanotubes were assembled by the small Pt nanocrystal. Therefore these Pt nanotubes were synthesized without smooth and consecutive surface and commonly concomitant with the organic impurities. Recently, the dual templates were utilized to fabricate the mesoporous Pt nanotubes [63]. A reduced pressure procedure was contained in this system with the combination of hard templates and soft templates. The nanotubes were proved to be the assembly of Pt nanoparticles with a size ca.3 nm. Actually this method was quite low-efficiency and the operation were usually performed trivially. Recently another novel and attractive method had been reported to fabricate silver nanotubes and the synthesis of the final nanowires was achieved through sintering the prefabricated silver nanotubes. Unlike the previous methods, these silver nanotubes were fabricated without additional templates, while they were obtained through the self-assembly of nanoparticles in a reverse micellar solution. Although, this method was reported for the fabrication of silver nanotubes, but the possibility of applying it to the fabrication of Pt nanotubes was stated by the author as well [49].

So far, silver nanowires have been the most ideal and prominent candidate to template the growth of Pt nanotubes among the above mentioned templates. It was proved that the nanotubes would inherit the morphological characters of the silver-nanowires template faithfully as a result that the morphology of the product was in a good control. Due to the good crystallographic match between Ag and Pt, Pt nanotubes are usually of the good

crystallinity and uniform structure. The high purity of the product allows it wide-range application with less limitation. However, fabricating Pt nanotubes by the silver-nanowires method still encounters some problems, such as rough and porous surface, low-efficiency. There is still a lot of work needs to be done before the mass production is feasible and economical.

5. CONDUCTIVE COATINGS

Nanocomposite has been a hot field for a long time and its application in the coatings would bring dramatic change in the performances, such as physical and mechanical properties, anti-corrosion performance and so on. Most researches in this field mainly focus on using inorganic nanomaterial for the betterment of ordinary coatings. Some of them have been already commercialized, such as SiO₂, ZnO, and TiO₂.

In the past, silver nanomaterials were added into the adhesive just for the antibacterial property. However, recently silver was introduced into adhesive for the enhancement of its conductivity. As a kind of noble metal, the amount of bulk silver added into the adhesive was expected to be reduced so as to cut costs and improve adhesive strength.

In most researches, it commonly exploited resin as the polymer matrix, such as epoxy resin [64,65], acrylic resin [66], and so on. The silver conductive filler might have different size, morphology and content as a result that the ECA correspondingly showed different characteristics and properties [67]. Traditional silver ECA usually was filled with micro-sized particles and expected to be applied for the microelectrical packaging. Comparing with Sn/Pb solder, traditional ECA indeed had some prominent advantages. It can improve linear distinguishing ability and lower processing temperature, while it also had some limitations and deficiencies, such as poor joint performance, unstable contact resistance and lower conductivity. To perfect its performance, Ye et al. [68] firstly introduced silver nanoparticles into the filler and studied the conductivity change of the coatings. They suggested that the resistance between two particles was composed of constriction resistance (from direct contact) and the tunnelling resistance (from nanogap), while the nanoparticle-containing adhesives were controlled by tunnelling effect. Furthermore, Lee et al. [69] found that the addition of doped silver particles (doping the nanoparticles into the microparticles) could effectively reduce the resistivity of ECA, when the total content of silver in the ECA was near a percolation

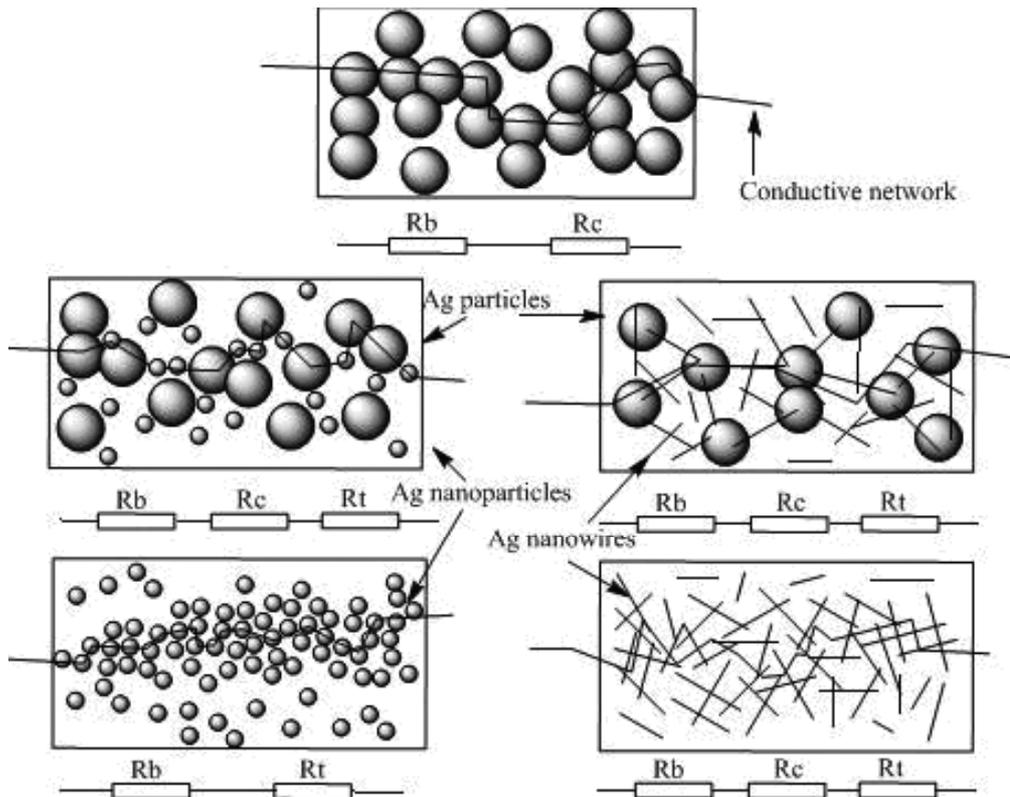


Fig. 9. Conductive scheme of ECA filled with Ag micro-particles, nanowires or nanoparticles (modified) [according to Refs. 12 and 71].

threshold. They proposed a reasonable mechanism to illuminate this phenomenon. Near the percolation threshold, the silver microparticles still could not completely contact with each other and the addition of silver nanoparticles could help to form the continuous conductive network so as to lower the resistivity of ECA. Due to the small dimension, for a fixed amount of silver, the nano-sized silver contained more particles than the micro-sized did. The larger number of particles would be beneficial for the interconnection between micro-sized ones. Certainly it would increase the contact resistance, but the tunnelling effect between the nanogap would reduce the bulk resistance of conductive adhesives.

In most occasions, high conductance and good bonding strength of such ECA seem to always conflict with each other. Because conductance is contributed by silver filler and the bonding strength is mainly derived from resin matrix. So if we want to obtain ECA of both high conductance and good bonding strength, we can manage to change the filler's morphology and contact form to improve ECA's conductance rather than increase silver quantity. It was reported that the doped nanowires were favorable for perfecting linkage among particles and made the

probability of contact and contact area much more than the undoped cases [70]. Wu et al had proved that ECA filled with silver nanowires (mass fraction 56%) had intrinsic resistivity 6 times lower than that filled with silver particles (mass fraction 75%). Moreover, it also showed higher shear strength (17.6 MPa on Al substrate) due to the reduced amount of the conductive filler [71]. They explained these phenomena just as shown in Fig. 9. Firstly the fibroid shape of nanowires made them have larger contact area and fewer contact points compared with Ag particles or dendritic, when they were filled into the polymer matrix. Secondly, the contact points were more stable and the conductive network was more easily formed. Thirdly, due to the existence of silver nanoparticles in the nanowires system, the tunnelling effect of these particles would lead to the formation of a more stable conductive network. As shown in Fig. 9, the total resistance of ECA filled with silver nanowires was $R_c + R_b + R_t$ (R_c was contact resistance, R_b was intrinsic resistance and R_t was tunnelling resistance), and the total resistance of ECA filled with silver particles was $R_c + R_b$. For silver, its intrinsic resistance R_b was quite negligible and through theoretical calculation, R_t was also

very small. Hence, the total resistance was mainly determined by R_c . As we known, for the ECA filled with nano-sized particles, the contact points were much more but the contact area was much smaller than those for the system filled with nanowires. Hence, R_c for the system doped nanowires was much lower than that for the system doped particles. Generally speaking, the doping of silver nanowires into the ECA would greatly enhance the conductivity of adhesives, while still keeping the good bonding strength of the resin.

6. CONCLUSION

The synthesis of silver nanowires from soft solution method is the most promising and feasible route for its convenience and high efficiency. Moreover, Au and Pt nanotubes from resultant silver nanowires are of relatively high uniformity and fine quality. Especially, the avoidance of procedure to remove the templates after completing reaction makes this route of great advantages over the other template methods. To some extent, the addition of silver nanowires can efficiently reduce the usage of bulk silver in ECA so as to enhance the bonding strength of the coatings [70]. Therefore, large-scaled production of silver nanowires is necessary and of great significance at present. Nowadays, there are still no silver nanowires commercialized, because almost all the routes can't meet the demand of mass production and need to be further studied. Since the soft solution method is operated under mild reaction conditions, results in high-quality product and only needs simple follow-up treatment, it is a feasible and promising route for the mass production of silver nanowires to improve the silver ECA in the future. Besides, the other nano-sized metals, such as gold nanotubes and Pt nanotubes, are also expected to be exploited in the improvement of the ECA.

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