



CHAPTER IV

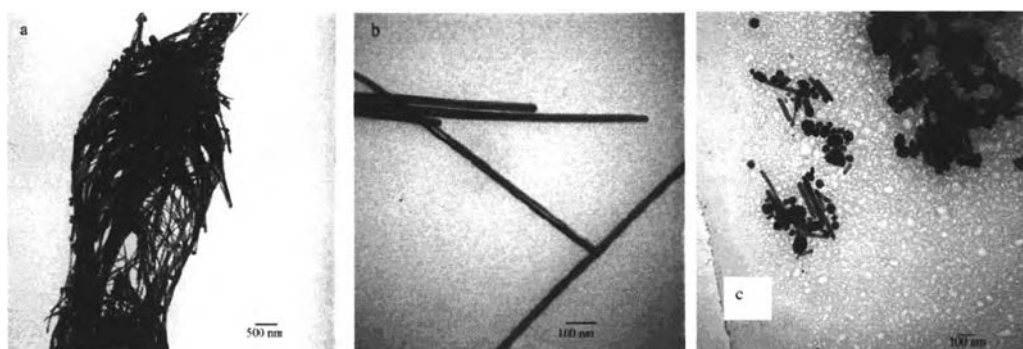
GREEN SYNTHESIS OF EXTRA-LONG SILVER FIBERS AND ITS APPLICATION AS A TEMPLATE FOR PLATINUM HOLLOW FIBERS FRABICATION

4.1 Introduction

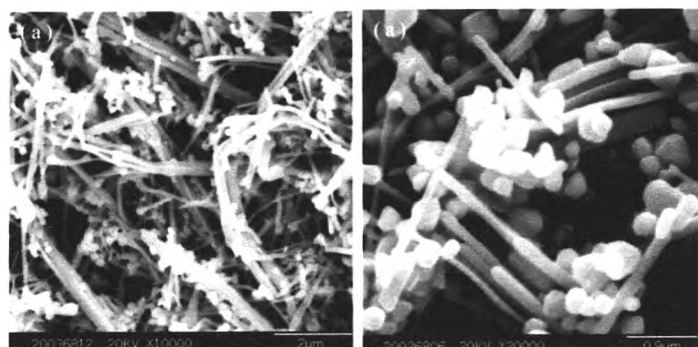
The synthesis of functional nanostructure by controlling synthesis method and modifying the growth condition in order to obtain functional nanostructure has been reported. For example, gold (Au) nanowire,[86] hierarchical platinum (Pt) nanostructure,[87] porous platinum nanotube,[88] palladium (Pd) and platinum nanoboxes,[89] copper (Cu) and silver (Ag) nanobelt.[90] There are much effort on creating complex nanostructure in order to tune its functionality, e.g., catalysts,[88] electrocatalyst,[91] surface enhanced Raman scattering,[87, 92] and electrical[93] because their properties are covered by size and shape of metal nanostructure. One of highlight material for nanostructure synthesis is silver because it expressed functionality based on size, shape and structure. For instance, the Ag@Pd/Ag nanocables showed a greatly improved mechanical strength. They used for hydrogen absorption and desorption of 50 cycles before breaking while pure palladium nanotubes were broken after 25 cycles.[94] The Ag nanodendrites showed the sensitivity for a glucose biosensor more than biosensor without using the Ag nanodendritic matrix.[95] Many synthetic routes were employed for creation of Ag structures, e.g., wet chemicals,[96] solvothermal,[97] seed mediation,[98] and template assisted.[99] However, these limit successes in commercialization of Ag nanostructures due to the using highly cost effective protocol and multi-step reaction. Moreover, surfactant or template was removes after the reaction. So its functionality may be diminished. In our approach, galvanic replacement technique with controlling environmental was used in order to create of silver microstructures (i.e., dendrite, pentagonal fiber, and hierarchical crystal structure). We must play attention has paid into fiber because of its potential application as electrode, template for creating a hollow structure for electronic, sensing application.

4.1.1 Literature reviews

Caswell K. K. et al. (2003) synthesized crystalline silver nanowire in the absence of a surfactant and without externally added seed crystallites. Silver salt (0.1 M AgNO_3) was reduced to silver metal by sodium citrate in the presence of NaOH at 100 °C. The concentration of hydroxide ion is a key parameter to generate nanowires which the length up to 12 micron. This method produced silver nanowires with high-yield while few spherical nanoparticles left as a by-product.[96]

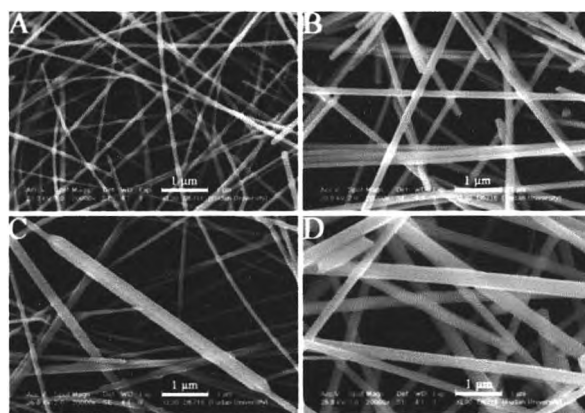


Wei, G. et al. (2003) prepared silver chainlike and dendritic nanostructures by a simple solvothermal method using poly(vinyl pyrrolidone) as an adsorption agent and architecture soft template. The reaction with appropriate amounts of ethylene glycol, silver nitrate, and poly(vinyl pyrrolidone) was performed in autoclave at 180 °C for 3, 4, 8, and 12 h. The dendritic nanostructure and silver nanowires with length of 15 μm and 20-100 nm in diameter were obtained.[97]

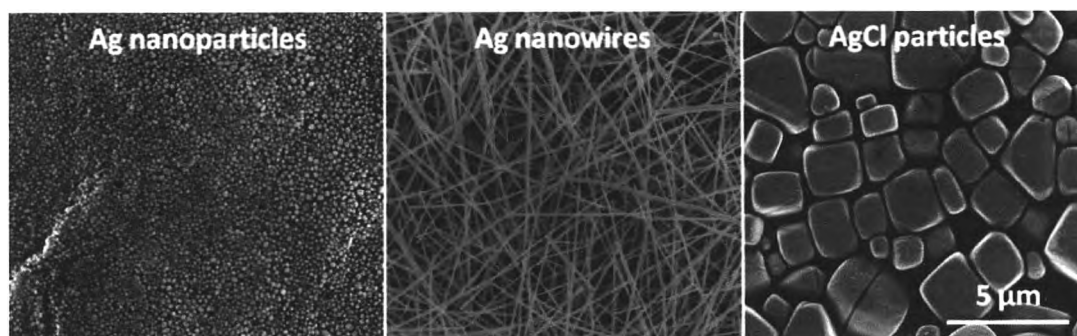


Zhang W. et al. (2008) prepared silver nanowires by a steel-assisted polyol method (SAP) at high silver nitrate concentrations up to 0.5 M. The reaction was performed with the following steps, silver nitrate solution (0.3 M in ethylene glycol), poly(vinyl pyrrolidone) solution (0.45 M in ethylene glycol), and several small pieces

of stainless steel grids (at least 0.5 g) were mixed together at 120 °C for 30 min. Then heat up to 140 °C and kept at this temperature for at least 1 h. After removing the stainless steel pieces, the separated product was rinsed with ethanol. By this method, the silver nanowires with high aspect ratios could be achieved and the diameter of silver nanowires could be adjusted in this method by changing the initial concentration of silver nitrate.[99]

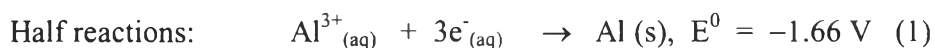


Coskun, S. et al. (2011) synthesized the silver nanowires using a polyol process. The reaction was performed with ethylene glycol solution of poly(vinyl pyrrolidone) (0.45 M) and NaCl (7 mg) at 170°C. In the meantime, silver nitrate (0.12 M) in ethylene glycol was added dropwise into poly(vinyl pyrrolidone) solution by an injection pump and stirred during the whole process. Upon the completion of dropwise addition, the nanowire solution was annealed for 30 min at 170°C. The results found that the process parameters such as temperature, injection and stirring molar rates, poly(vinyl pyrrolidone), silver nitrate ratio, and the amount of NaCl showed an influence for the synthesis of Ag nanowires by the polyol process.[100]



4.1.2 Galvanic displacement technique

The galvanic displacement compose of two half reactions, the first one is the oxidation/dissolution of a metals at the anode and the second one, the reduction/deposition of the ions of a second metal at the cathode.[101, 102] The reaction occurs if the electrochemical potential of the metal ions is higher than that of the solid metal. The relevant equations for a typical reaction between aluminum (Al) and silver (Ag) as follows:



The electrochemical potentials of some metals are shown in Table 4.1.

Table 4.1 Electrochemical potential of relevant species relative to standard hydrogen electrode.[102, 103]

Half reaction	E^0 (V)
$\text{Ag}^{+} + \text{e}^{-} \rightarrow \text{Ag}$	0.80
$\text{Au}^{3+} + 3\text{e}^{-} \rightarrow \text{Au}$	1.50
$\text{Au}^{+} + \text{e}^{-} \rightarrow \text{Au}$	1.69
$\text{Pd}^{2+} + 2\text{e}^{-} \rightarrow \text{Pd}$	0.95
$\text{Pt}^{2+} + 2\text{e}^{-} \rightarrow \text{Pt}$	1.18
$\text{PtCl}_6^{2-} + 4\text{e}^{-} \rightarrow \text{Pt} + 6\text{Cl}^{-}$	0.74

4.1.3 Applications of silver fibers

4.1.3.1 Template for fabrication of platinum hollow fibers

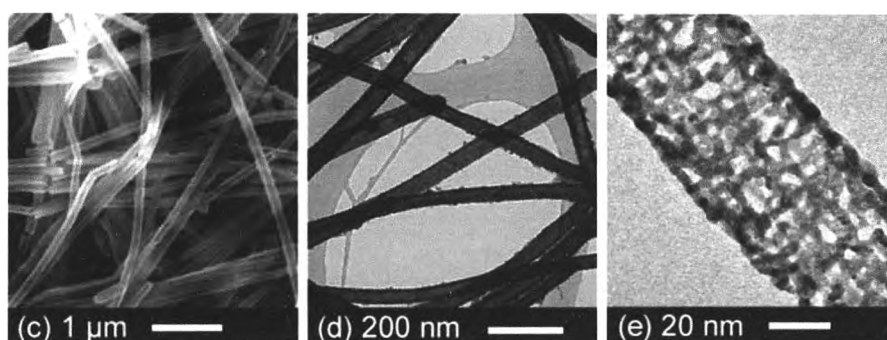
As mentioned in Chapter II that platinum played an important role in application for many industrial. Especially, it was employed in the catalytic and electrocatalytic applications. The activity of platinum in those applications depends on the morphology such as the surface area to volume ratio, composition, structure, as

well as the rearrangement of atom on the surface.[14] Therefore, the attractive structures of platinum are not only in zero-dimensional (e.g., spherical shape) but also one-dimensional, 1-D (e.g., rod and wires), two-dimensional, 2-D (e.g., plates), and three-dimension, 3-D (e.g., octahedron faceted).[14, 15] Particularly, one-dimensional platinum nanostructure displays its unique combination of dimensions at multiple length scale and nanometer-sized wall thickness leading to provide high surface area. Therefore, it can use as catalyst without the need of high-surface-area support.[16] Several techniques including impregnation method,[17] chemical reduction with a capping agent,[18] template directed electrodeposition,[19] and galvanic displacement have been used for synthesis of platinum nanostructures (1-D).[20] However, the limit in conventional chemical method is the use of highly cost effective protocol and multi-step reaction. Including, the product cleaning is required for a protecting agent removal. Moreover, surfactant or template must remove after the reaction. So its functionality may be diminished. However, the galvanic displacement is a simple and green efficient method to fabricating platinum nanostructures. Hence, it would become more effective method if the platinum hollow nanostructure (platinum nanotube or platinum hollow fiber) with a very high aspect ratio was constructed.

Chen Z. et al. (2007) synthesized platinum nanotube (Pt NTs) and platinum-palladium-alloy nanotubes (PtPd NTs) using a galvanic displacement reaction of silver nanowires (Ag NWs). Silver nanowires were synthesized by reducing silver nitrate with ethylene glycol in the presence of platinum seeds and poly(vinyl pyrrolidone). The platinum hollow structure product with diameter of nm, 5–20 nm long, and 4–7 nm wall thickness was obtained. Their activities were evaluated for oxygen-reduction reaction in proton exchange membrane fuel. They have the potential to possess high surface area, high utilization, high activity, and high durability.[16]

Alia S. M. et al. (2010) prepared porous platinum nanotubes (Pt NTs) with all thickness of 5 nm, an outer diameter of 60 nm, and a length of 5–20 μm by galvanic displacement with silver nanowires. The reduction reaction of silver nitrate used ethylene glycol as a reducing agent and refluxed at 170°C, the silver nanowires was obtained. Porous Pt NTs were tested for oxygen-reduction reaction (ORR) and

methanol oxidation reaction (MOR). Pt NTs exhibit specific ORR activity approaching that of bulk polycrystalline platinum (BP-Pt). In addition, Pt NTs show improving specific activity for MOR and chronoamperometry characteristics over carbon supported platinum nanoparticle (Pt/C) and BP-Pt catalysts.[88]



4.2 The goal of the research

1. To develop the silver nanostructures by galvanic displacement with well-defined the structures.
2. To apply the silver microstructures as a template for fabrication of platinum hollow structure.

4.3 Experimental section

4.3.1 Chemicals and materials

Commercial aluminum foil (Diamond[®] Foil) was purchased from Reynolds (United States). Sodium nitrate (NaNO_3), silver nitrate (AgNO_3), and nitric acid (HNO_3 , 65% w/v) were purchased from Merck[®] (Thailand). Hexachloroplatinic acid (H_2PtCl_6) was prepared as mentioned in section 2.3.2. All chemicals were analytical grade and were used without any additional purification. De-ionized water was used as a solvent. All glassware and magnetic bars were cleaned with detergent and rinsed with de-ionized water followed by aqua regia, and finally rinsed again with de-ionized water before use.

4.3.2 Synthesis of silver microstructures

The silver microstructures were synthesized galvanically by immersing a piece of (1.5 cm × 1.5 cm × 30 μm) commercial aluminum foil for food wrapping into a solution of

solution of AgNO_3 , (100 mL, 0.01–0.1 M). The cleaned and degreased foil was positioned at the bottom of a 150 mL beaker before filling with silver nitrate (AgNO_3) solution. An extra sodium nitrate (NaNO_3 , 1 M, 1.5 mL) was added into the solution. The solution was left undisturbed until harvesting for characterization (24–72 h). The silver microstructures galvanically grew from the topside of the foil. The bottom side facing the glass beaker did not show any development of silver microstructures. The silver microstructures were rinsed with de-ionized water and were dried before characterization.

4.3.3 Preparation of platinum hollow microstructures

The platinum hollow microstructures were synthesized by galvanic displacement of the silver microfibers which obtained from section 4.5.2 and platinum ions. Cleaned silver fibrous were immersed into the solution of hexachloroplatinic acid, H_2PtCl_6 (10 mL, 25 mM) at room temperature for 15 minutes under the atmosphere. The platinum hollow structure were removed from the solution and after rinsing with de-ionized water to remove the silver chloride precipitate, cleaned in nitric acid (2 M) for 1 h. Again rinsed with de-ionized water and were dried before characterization

4.3.4 Characterization

4.3.4.1 Scanning electron microscopy (SEM)

A galvanized silver fibers (or platinum hollow structure) were attached to a stainless steel stub through a carbon tape. Scanning electron microscopy (SEM) images were recorded with a JEOL JSM-6150 analytical electron microscope operated at 10-30 kV under high vacuum mode using a secondary-electron imaging (SEI). Elemental analysis was carried out using energy dispersive spectrometer (EDS) attached to the SEM.

4.3.4.2 X-ray diffraction spectroscopy (XRD)

Powder X-ray diffraction patterns were obtained with a Rigaku DMAX2000 X-ray diffractometer using $\text{Cu K}\alpha_1$ radiation ($\lambda = 0.154$ nm) and a power of 40 kV and 20 mA.

4.4 Results and discussion

4.4.1 The influence of silver ions concentration for fabrication of silver nanostructures

A galvanic reaction using 0.01 M AgNO_3 produced silver dendrites having characteristic light brown color (Figure 4.1A). Although there was no surfactant or capping agent employed, the fractal-like dendritic structure of silver microplates was obtained. [91] The dendritic structure continues growing until the scarified aluminum foil was exhausted. Similar to previous reports, this dendritic structure has shown potential applications in the field of SERS due to its high surface area-to-volume ratio, high density of hotspot, and ease of fabrication.[92]

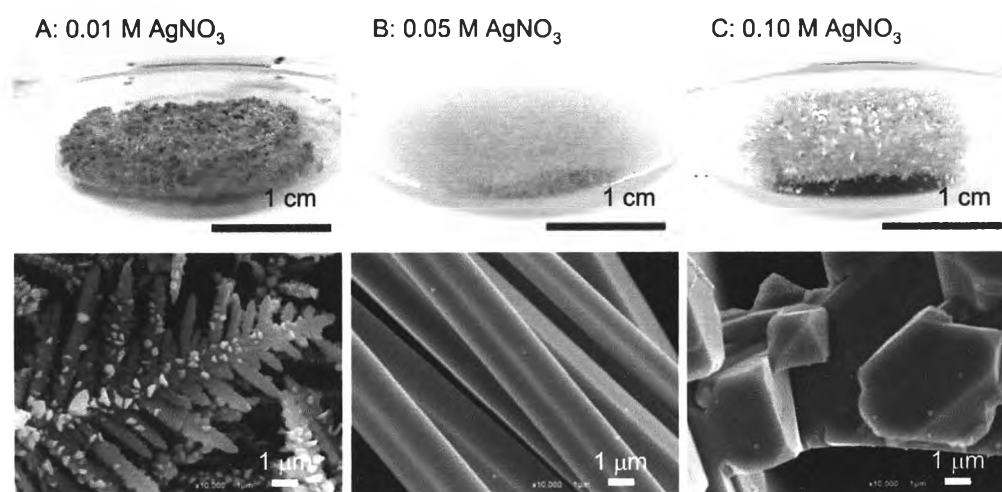


Figure 4.1 Digital images and the corresponding SEM micrographs of silver microstructures obtained after a 48 h galvanic reaction of aluminum foils ($1.5 \text{ cm} \times 1.5 \text{ cm} \times 30 \text{ }\mu\text{m}$) and AgNO_3 solutions: (A) dendrites, (B) microfibers (C) microcrystals. Scale bars: $1 \text{ }\mu\text{m}$ (SEM). Figure 4.2 shows additional SEM micrographs.

A higher AgNO_3 concentration of 0.05 M generated a tuft of five-fold twinned pentagonal silver microfibers with characteristic silver-white color (Figure 4.1B). When the solution was agitated, the delicate but tough microfibers extending out from the aluminum surface sway, yet does not break.

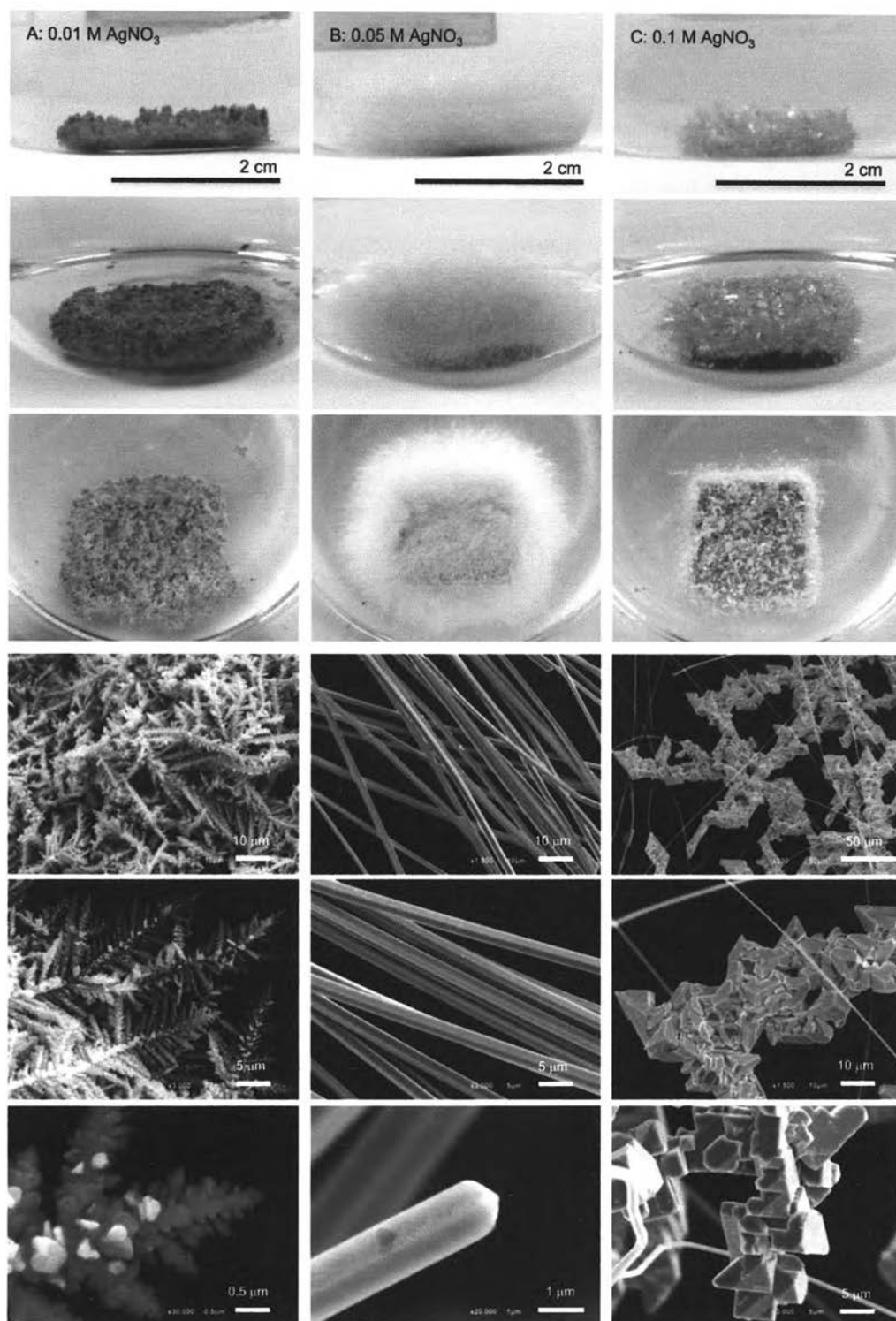


Figure 4.2 Digital images and the corresponding SEM micrographs of silver microstructures harvested after a 24 h galvanization: (A) dendrites, (B) pentagonal microfibers, and (C) microcrystals. The specimens are the same as those in Figure 1.

Although, the fiber has an average diameter of 2 μm , it was strong enough to withstand an applied tensile force exerted by a pair of tweezers while trying to pull a single fiber out of the silver wool. An average aspect ratio (Length/Diameter) of galvanically grown fibers for 48 h was 7500. A longer fiber can be obtained by increasing the galvanization time. Silver microfibers of 2 cm length were obtained with a 72 h galvanization.

However, a galvanization time longer than 72 h grew dendritic silver on the pentagonal microfibers (Figure 4.3). This development could be visually noticed by the appearance of a light brown color. This phenomenon suggests that after a prolonged galvanization time, silver ion concentration dropped to a level that could not sustain the thermodynamically controlled growth of pentagonal microfibers. The crystal growth was shifted to a new growth mechanism favoring a formation of dendritic structure at a low concentration of silver ion.

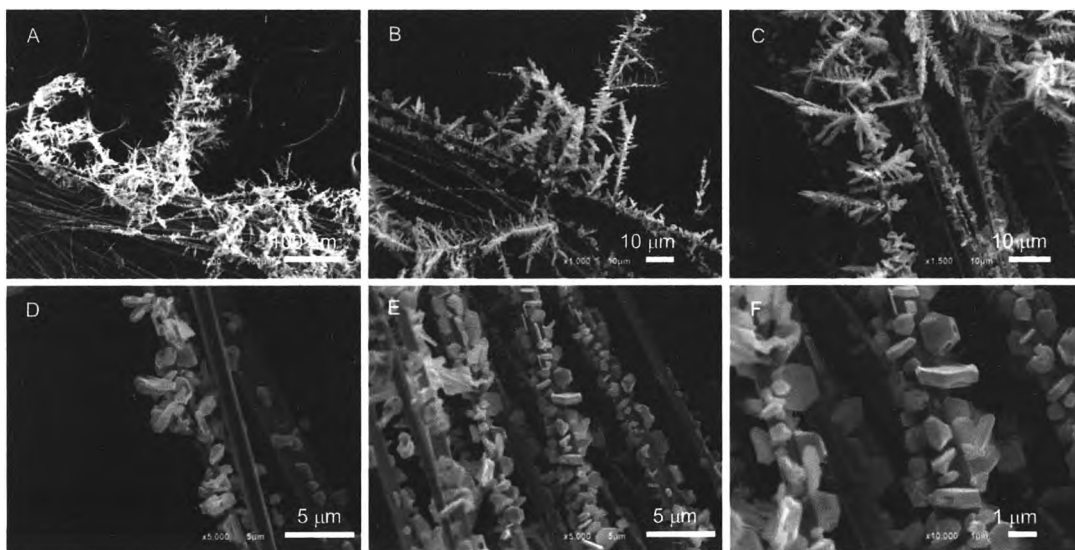


Figure 4.3 SEM micrograph of dendrite grown on pentagonal microfibers a later stage of a galvanic reaction with silver ion concentration (0.05 M AgNO_3 , Figure 1B).

At an even higher AgNO_3 concentration of 0.10 M, silver microcrystals with flat and shiny surfaces were obtained. Interestingly, small number of microfibers was also observed. A time dependent SEM observation indicated that the five-fold twinned pentagonal microfibers with $\sim 1 \mu\text{m}$ diameter, grew out of existing

microcrystals (Figure 4.4). The fast nucleation and growth kinetics at a high concentration put a time constrain on the formation of twin-defect, thereby the decahedral microcrystals and pentagonal rods were not the major seed particles produced. As a result, small amount of microfibers were obtained. Similar phenomena were observed in cases of silver nanowires synthesized via the polyol process, where nanowires were not the major products as the metal ion concentration was increased.

4.4.2 The investigation on the growth mechanism of silver fibers

Due to its potential applications as micro-electrodes, electrical conductors, radiation shielding, magnetic shielding, building block for functional materials, and SERS sub-strates,[104–107] we will focus our attention on the growth mechanism of microfibers. The time dependent SEM investigation (Figures 4.5) indicates that silver nanoparticles were spontaneously formed on the surface of sacrificed aluminum foil.

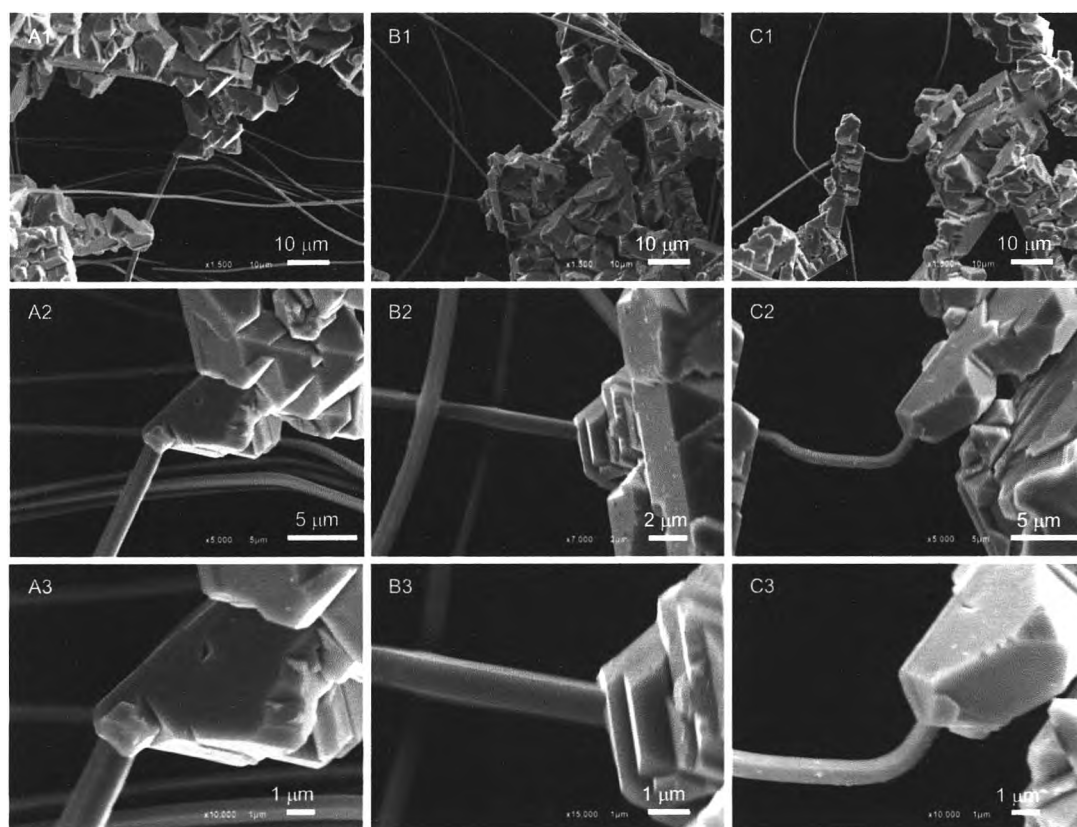


Figure 4.4 SEM micrograph of small pentagonal microfiber (~ 1 mm diameter) generated at a later stage of a galvanic reaction with high silver ion concentration (0.10 M AgNO_3 , Figure 1C). The fiber grew out of existing crystals.

Within 30 min, a large number of nanoparticles aggregated to form a cluster and underwent colloidal recrystallization before transforming into multiple-twinned particles (MTPs) decahedron microcrystals. It is well known that the most thermodynamically stable decahedron possesses the highest energy along the $\{111\}$ twinned planes.[15, 108, 109] Therefore, silver nanoparticles preferentially crystallize on the twinned defect planes in order to alleviate the high surface energy (Figure 2B). This thermodynamically driven crystal growth leads to an elongation along the $[100]$ direction as the decahedron microcrystal grew into a pentagonal rod bound by five $\{100\}$ facets. These observations confirm the previously proposed growth mechanism.[15, 108, 109]

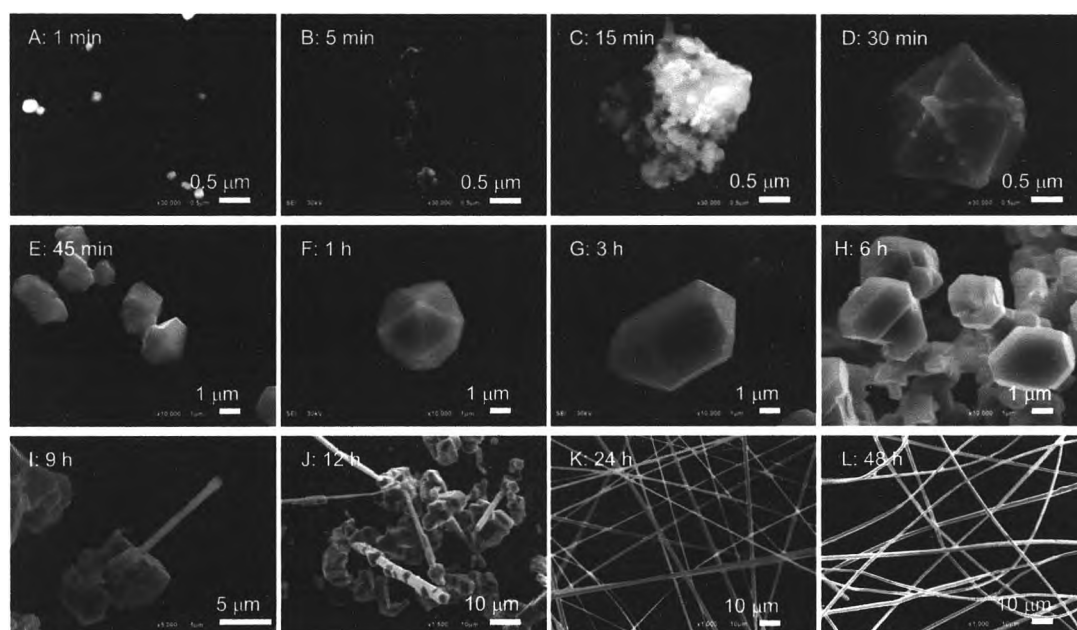


Figure 4.5 The time dependent SEM investigation on the growth mechanism of 0.05 M AgNO_3 by galvanically displacement with aluminum foil: (A) 1 min, (B) 5 min, (C) 15 min, (D) 30 min, (E) 45 min, (F) 1 h, (G) 3 h, (H) 6 h, (I) 9 h, (J) 12 h, (K) 24 h, (L) 48 h.

SEM micrograph (Figure 4.5 and 4.6) reveal a time-dependent development of silver microfiber. First, silver nanoparticles were rapidly and spontaneously generated on the surface of aluminum foil (Figure 4.5A). The particles undergo aggregation (Figures 4.5B, 4.5C) and colloidal recrystallization. Decahedron microcrystals were thermodynamically grown (Figure 4.5D) before developing to pentagonal rod (Figure

4.5E-4.5H). As the concentration of silver nitrate near the surface of the crystal decrease, the growth rate slowdown while the kinetically controlled growth imposed by the concentration gradient and the diffusion of metal ion across the concentration gradient triggered a development of silver microfibers on the existing pentagonal rods (Figure 4.5I). The microfibers continue growing in the growth solution without any agitation and become a centimeter long microfiber within 24 h (Figure 4.5K). A longer fiber could be obtained by a prolong galvanization. The fibers continue growing until the source of electron supply (the aluminum foil) was exhausted.

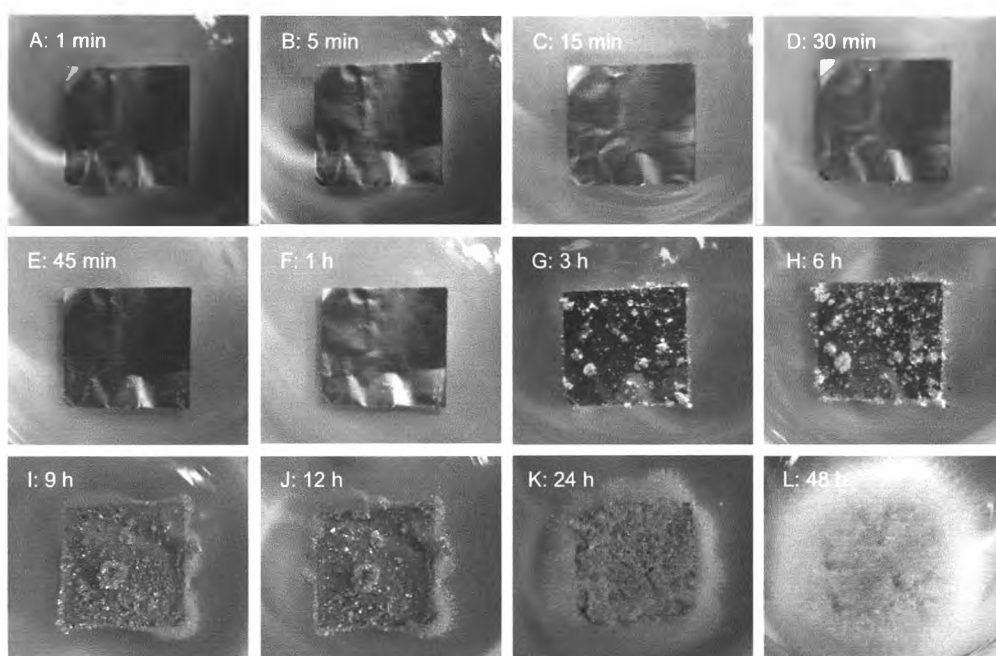


Figure 4.6 The time dependent digital image investigation on the growth mechanism of 0.05 M AgNO_3 by galvanically displacement with aluminum foil: (A) 1 min, (B) 5 min, (C) 15 min, (D) 30 min, (E) 45 min, (F) 1 h, (G) 3 h, (H) 6 h, (I) 9 h, (J) 12 h, (K) 24 h, (L) 48.

The change was triggered by a concentration gradient that developed slowly at the crystal/liquid interface as silver ions were consumed in the galvanic reaction. As silver ions near the interface depleted, the crystal grew with a limited supply. A pentagonal fiber with a smaller diameter starts growing from an existing pentagonal rod, as observed in the cases of nanorods.[15, 110] Note: the microfibers grew at the later stage have a smaller diameter ($\sim 500 \text{ nm} - 1 \mu\text{m}$), compared to those developed at

the early stage ($\sim 2 - 3 \mu\text{m}$). When the metal ion supply was sufficiently low (i.e., after a 72 h galvanization), silver plates start growing from $\{100\}$ facets of the existing pentagonal rods, Figure 4.3.

The observed phenomena indicated that decahedron microcrystals and pentagonal rods are pivotal structures for the development of microfibers. This conclusion is supported by the following observations: (1) there are no fibrous structures and pentagonal microcrystals observed in the dendritic structure (Figure 4.2A). The silver dendrites primarily consist of plate structures. According to crystal growth mechanism, the plated crystals originate from seed particles with stacking faults while the decahedron, pentagonal bars, and pentagonal wires initiate from those with multiple twins,¹³ (2) A fiber from the galvanically generated silver wool grows always from a pentagonal crystal (Figures 4.4 and 4.7), (3) A fiber with a smaller diameter developed at the later stage as an extension of the bigger pentagonal microfiber with the transition in diameter being abrupt (Figure 4.8).

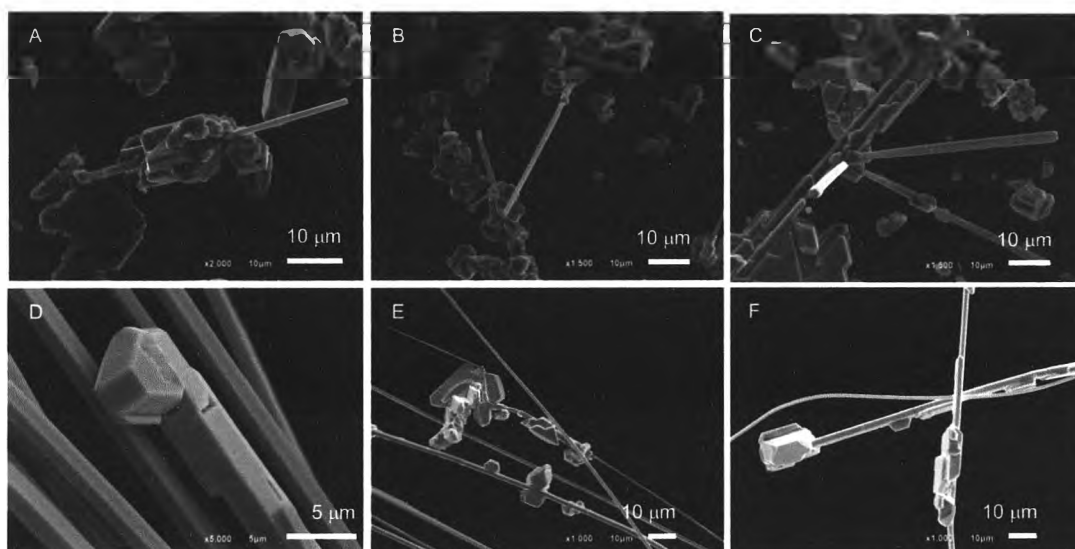


Figure 4.7 SEM micrographs reveal the fiber pulled out from a pentagonal crystal.

The XRD patterns indicate that the dendritic and fiber structures are dominated by (111) facet (Figure 4.9a and b) while the microcrystals are dominated by (111) and (200) facets. The intensity ratio between (111) and (200) facets is approximately 3:1,

which further confirms the fact that a large fraction of the crystalline plane in the silver microfibers is $\{111\}$ facet.

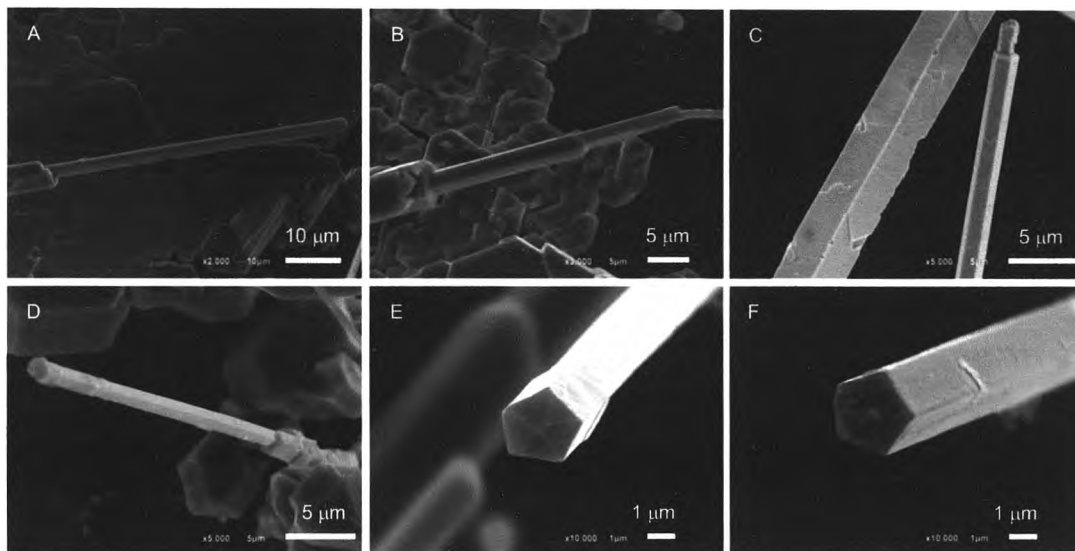


Figure 4.8 SEM micrographs reveal small fiber developed at the later stage of the fiber growth.

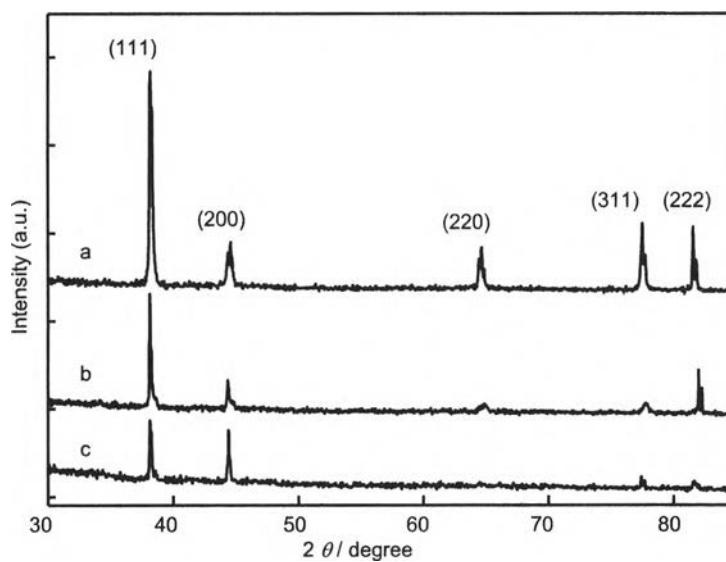


Figure 4.9 XRD patterns of silver microstructures synthesized by a galvanic replacement reaction between an aluminum foil ($1.5 \text{ cm} \times 1.5 \text{ cm} \times 30 \text{ }\mu\text{m}$) and 100 mL silver nitrate solutions: (A) 0.01, (B) 0.05, and (C) 0.10 M AgNO_3 . The obtained microstructures are (A) dendrites, (B) pentagonal microfibers, and (C) microcrystals, respectively. The silver microstructures were harvested after a 24 h galvanization.

4.4.3 The influence of nitrate ions for the development and growth of silver microfibers

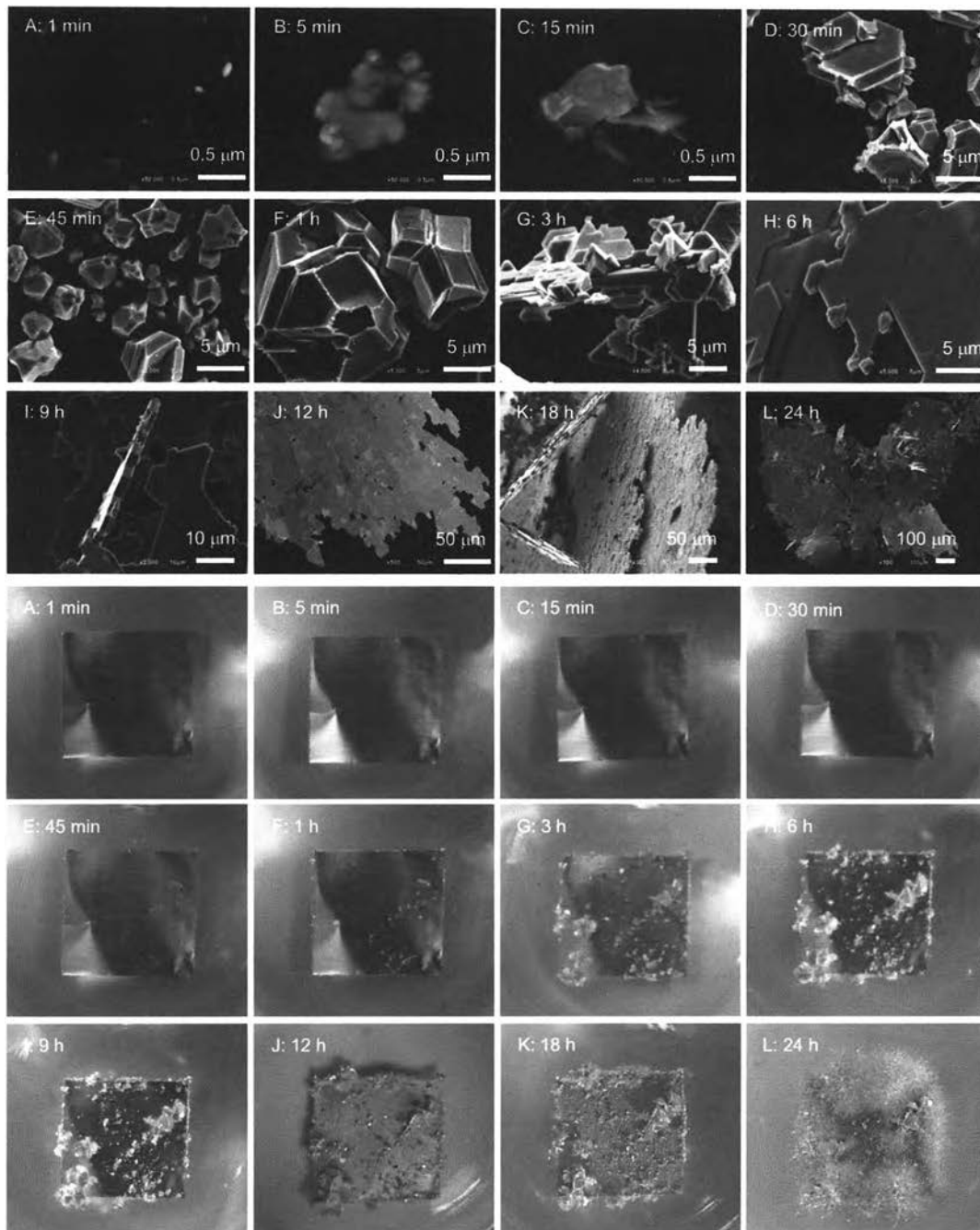


Figure 4.10 Digital images/ SEM micrographs of silver microstructures synthesized by a galvanic replacement reaction between an aluminum foil ($1.5 \text{ cm} \times 1.5 \text{ cm} \times 30 \text{ }\mu\text{m}$) and 100 mL 0.05 M silver nitrate solutions. The solution was under a constant agitation. The obtained silver microstructures are pentagonal rods/dendrites.

A separate experiment was conducted in order to verify the significance of the pre-developed pentagonal rods. In a system with constant agitation, decahedrons, pentagonal rods, and microfiber structures did not evolve. Although a gentle agitation was applied, only some of the galvanically generated silver particles were detached from the foil. The remaining particles eventually transformed to complex microcrystals and microsheets (Figure 4.10). Another set of experiments was performed in order to verify the significance of the transition in the growth mechanism induced by the concentration gradient. Decahedra and pentagonal rods were pre-generated by a 9 h galvanization without any agitation. A gentle agitation was later imposed. However, the fibrous structures did not evolve from the existing pentagonal rod. A prolonged 24 h galvanization, however, create microcrystals (Figure 4.10 and 4.11C).

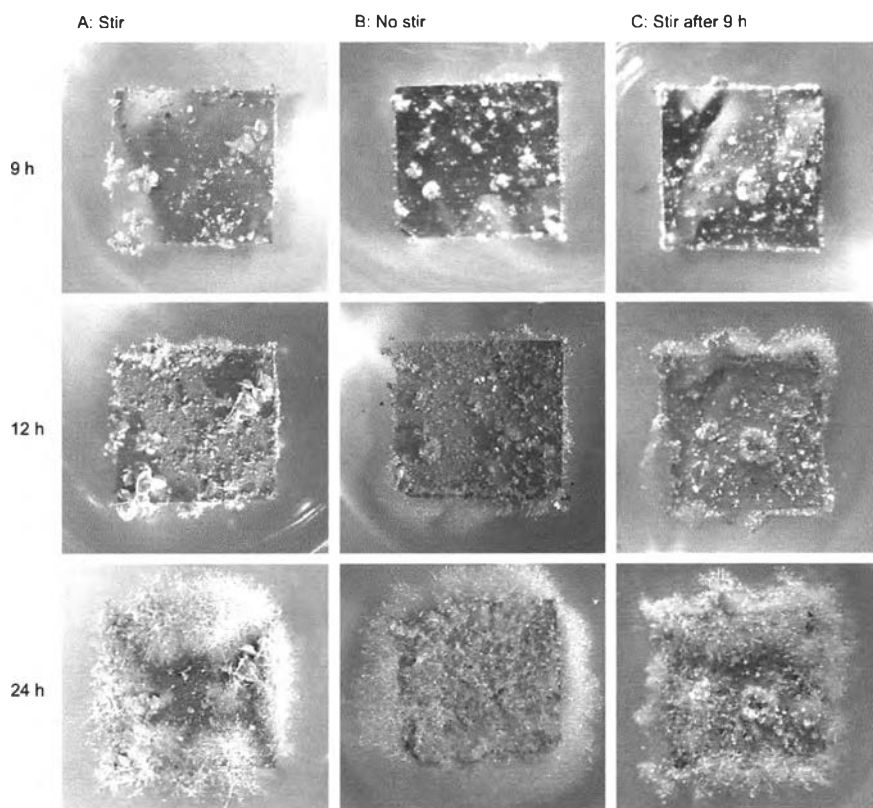


Figure 4.11 Digital images of silver microstructures synthesized by a galvanic replacement reaction between an aluminum foil ($1.5 \text{ cm} \times 1.5 \text{ cm} \times 30 \text{ }\mu\text{m}$) and 100 mL 0.05 M silver nitrate solution. The solution was under a constant agitation, without an agitation, and without an agitation for 9 h before starting a gentle agitation.

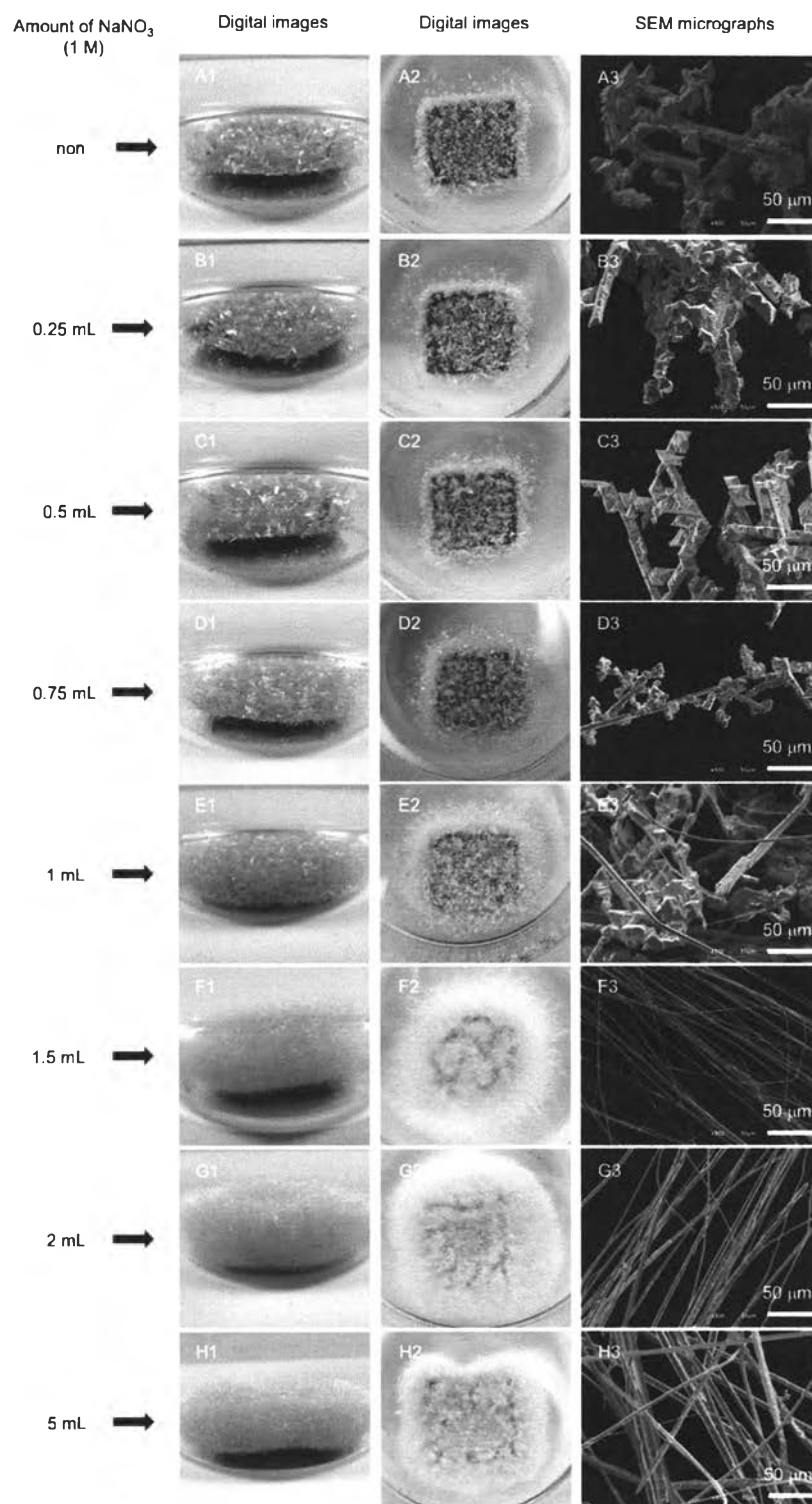


Figure 4.12 Digital images/SEM micrographs of silver microstructures synthesized with different amount of added sodium nitrate (NaNO_3). The reference system consists of an aluminum foil ($1.5 \text{ cm} \times 1.5 \text{ cm} \times 30 \mu\text{m}$) and 100 mL 0.05 M silver nitrate solutions.

The influence of nitrate ion (NO_3^-) on the formation of fibrous structure was verified and its affect is explained below. Nitrate ion is known to have etching capability by promoting dissolution of newly formed nanoparticles via Ostwald ripening process. In a polyol process, the yield and quality of silver nanowires were improved by eliminating an *in situ* generated nitrate ion.[99] Surprisingly, in our system, we have to add nitrate ion to initiate the development of silver microfibers. Here, we exploited the etching property of nitrate ion for eliminating less stable structures while facilitating the growth of more stable structures. However, high concentration of nitrate ion promotes an extensive dissolution, which results in short microfibers with rough surfaces and large diameters (Figure 4.12). Under the employed condition an addition a 1.5 mL of 1 M NaNO_3 into a 100 mL of 0.05 M AgNO_3 created uniform microfibers with an average diameter of 2 μm .

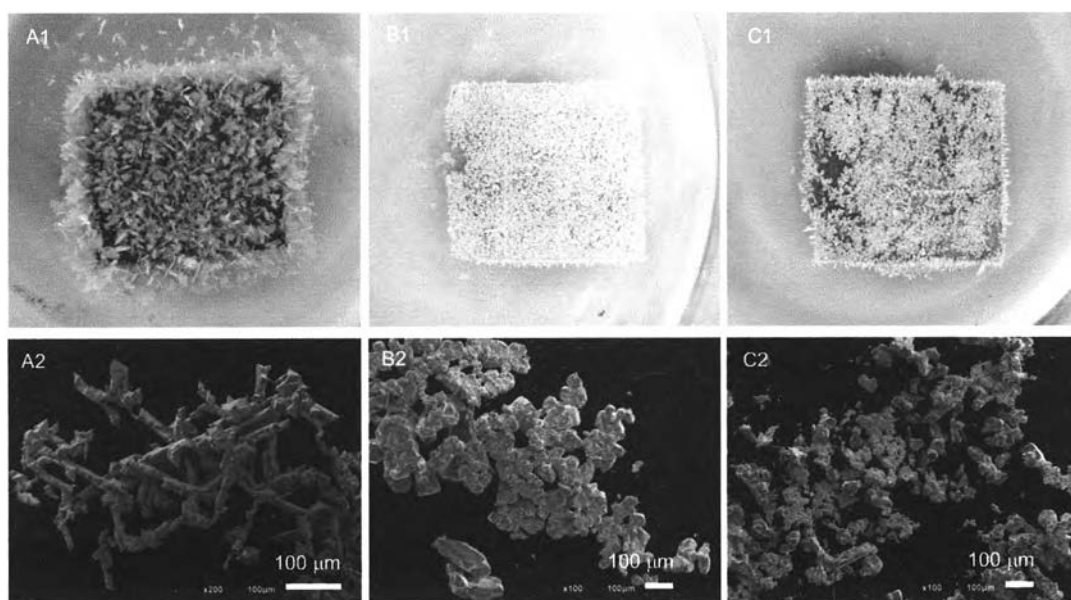


Figure 4.13 Digital images/SEM micrographs of silver microstructures synthesized with different amount of added nitric acid (HNO_3). The reference system consists of an aluminum foil ($1.5 \text{ cm} \times 1.5 \text{ cm} \times 30 \mu\text{m}$) and 100 mL 0.05 M silver nitrate solutions.

An addition of nitric acid was also performed in order to verify the influence of acidity. Since silver nanoparticles dissolve rapidly in acidic media, nitric acid induces an extensive dissolution and thus prevents a formation of pentagonal crystals (decahedron and pentagonal rods). The obtained silver microstructures under an acidic condition were aggregated microparticles. Small particles were obtained at a greater acidity (Figure 4.13).

4.4.4 Fabrication of platinum pentagonal hollow fibers

The uniquely well-defined, delicate, and long pentagonal microfibers could be employed as a template for functional nano/microstructure fabrication. Figure 4 shows platinum hollow fibers created by a galvanic replacement reaction between the pentagonal silver microfibers and platinum ions. The envelope of the sacrificed silver fibers creates a unique pentagonal hollow feature. The hollow fibers, although brittle, still retain a long fibrous structure even after the removal of silver chloride precipitates. These hollow fibers with nanometer-thick walls have great potential applications as catalyst.[16, 88]

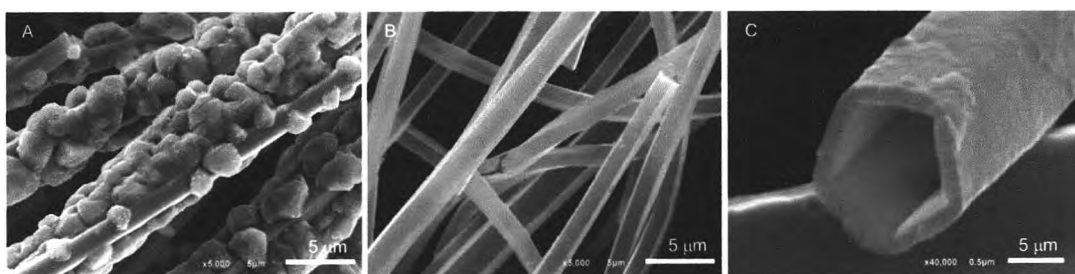


Figure 4.14 SEM micrographs of platinum pentagonal hollow fibers: (A) after a galvanic replacement (before AgCl dissolution) (B) hollow fibers (after AgCl dissolution) and (C) a pentagonal fiber fragment revealing nanometer-thick walls. EDS spectra of the hollow fibers are shown in Figure 4.15.

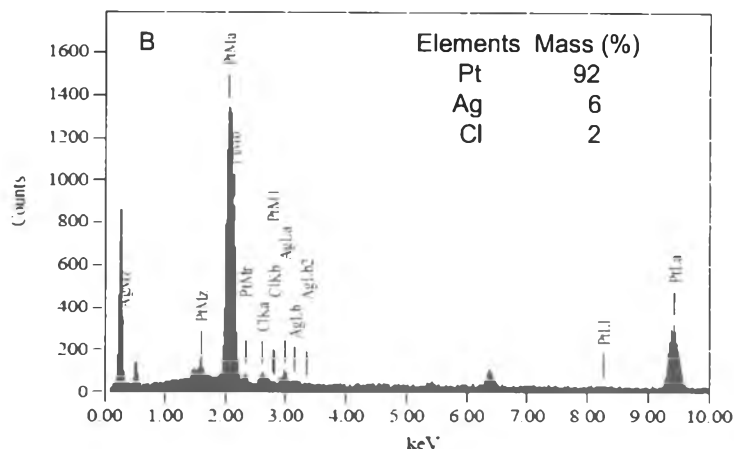


Figure 4.15 EDS pattern of platinum pentagonal hollow fibers.

4.5 Conclusion

In this work, we have demonstrated an efficient, rapid, and straightforward galvanic technique for fabricating pentagonal silver microfiber with an extremely high aspect ratio (upto 7,500) by galvanic replacement technique at room temperature without any aid of capping agent. Nitrate ions play the major role on facilitating the development of the fiber structures. The pentagonal rods are pivotal for the development of the fibrous structure. An onset of fibrous formation is trigger by the change in crystal growth mechanism from a thermodynamic control to kinetic-control. The change was initiated by the concentration gradient at the solid/liquid interface of the growth crystal. The obtained fiber possesses nano-rough surfaces generated by the transverse growth of the fiber. The nano-rough surfaces together with the hotspot created by fiber alignment make the pentagonal microfibers an efficient SERS substrate. The ease handling of the well-defined fiber and its derivative make the fiber a potential in-the-field SERS substrate. We also demonstrate that the long fiber could be employed as a template or complex nanostructure fabrication.