Synthesis of Ultra-long Silver Nanowires by SNS-directed Method and their Characterization

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Abstract: Ultra-long silver nanowires (AgNWs) were synthezised via a short AgNMs seeds-directed (SNS-directed) route, and the influence of preparative conditions on the seeds and AgNWs were investigated by using different analytical methods including SEM, TEM, SAED and XRD and UV-Vis. The results indicated that $AgNO_3$ concentration had effect on SNS and ultra-long AgNWs. Under the optimized SNS-directed conditions, the uniform ultra-long AgNWs with a length of 70~100 μm and a diameter of 90~200 nm developed in 5 minutes.

Key words: metal material; silver nanowires (AgNWs); SNS-directed method; ultra-long
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银纳米线晶种诱导法合成超长银纳米线及其分析表征

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摘 要：采用晶种诱导的方法合成了超长银纳米线，用扫描电镜(SEM)、透射电镜(TEM)、选区电子衍射(SAED)、X 射线衍射(XRD)和紫外可见光谱(UV-Vis)等表征手段考察了制备条件对晶种和银纳米线的影响。结果表明，$AgNO_3$ 浓度对晶种和银纳米线的形貌有影响。在优化条件下，5 min 内即可诱导合成长度为 70~100 μm，直径为 90~200 nm 的具有良好均一性的超长银纳米线。

关键词：金属材料；银纳米线；晶种诱导方法；超长

Silver nanomaterials are of increasing interest due to their use in a large number of application fields, such as optoelectronic devices[1-3], bio-sensing[4], and catalysis[5]. Specially, silver nanowires (AgNWs) is a well-known material having vast applications in the field of surface-enhanced Raman spectroscopy[4-7], electronic devices[1-2, 8], etc. Additionally, future electronic devices will be bent, stretched, twisted, compressed and deformed into complex. Meanwhile, they must still maintain good performance, reliability and integration. In many of these electronics, transparent electrodes are core components of touch screens, organic light emitting diodes, liquid crystal displays and solar cells that have been exhibiting a tremendous rapid growth over the years. Transparent electrodes made of AgNWs exhibit higher flexibility when compared to those made of tin doped indium oxide (ITO) and expected to be applied in plastic electronic. However, many transparent electrodes composed of AgNWs show high haze because the wires cause strong light scattering in the visible range. Fortunately, the haze can be easily reduced by increasing the length of AgNWs with a small diameter[9]. Therefore, AgNWs have gained attention

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as alternative transparent conductors because they have the best conductivity, simple and large-scale preparation.

The performance of the AgNWs electrodes mainly depends on a myriad of characteristics including the nanowires structure (length, diameter, size dispersity and composition) as well as the overall network morphology[10]. Some conclusions have suggested that the length and diameter of the wires are critical factors for enabling the high transparency with a low haze, high electrical conductivity. This is because long wires with small diameters can form a more effective network with smaller wire number density by providing longer percolation paths and reducing the inter-nanowire junctions where the major contact resistant drop occurs[8]. Therefore, extending the length of wires and keeping the diameter as low as possible are simple solution processes that have been a great challenge in the field of AgNWs. However, various methods have been exploited to synthesize AgNMs and significant improvements have been achieved using polyol reduction to prepare Ag nanowires. Over the past few years, polyol process of heated ethylene glycol (EG) serves as both the solvent and a precursor to the reducing agent, with solutions of $AgNO_3$ and poly(vinyl pyrrolidone) (PVP) being simultaneously added using a two-channel syringe pump is the most common method[11-14]. In the polyol process, many factors such as concentration of $AgNO_3$, additive agents, temperature, stirring speed, ratio of chemicals, reaction times and injection speed of chemicals have always affected the yield and morphology of AgNWs[8, 12, 15-19]. Therefore, very few methods attempted to synthesize long AgNWs with better repeatability and reproducibility resulting from so many influencing parameters. Recently, Araki et al[9] have prepared ultra-long AgNWs at a low temperature of 383 K with low stirring speeds. The length is in the range of 20~100 μm with a wide distribution and large diameter. At the same time, Jiu et al[8] prepared very-long AgNMs for transparent electrodes. The length of the very-long AgNMs is over three times longer than that of normal AgNWs and these wires have uniform around 60 nm diameter, independent of the stirring speed. However, this method need preheated at 105℃ to grow AgNWs for 5 h until the reaction was completed. Therefore, the method for rapid, convenient, and efficient synthesis of AgNWs with high aspect ratio and uniformity is always a great challenge in the synthesis of AgNWs.

Herein, we report a novel highly efficient recipe for the rapid and uniform synthesis of AgNMs by using the pre-synthesized nanowires via short silver nanowires seeds(SNS)-directed method.

1 Experiment

1.1 Synthesis of silver nanowires seeds (SNS) and ultra-long AgNMs

$AgNO_3$ and ethylene glycol were purchased from Shanghai Chemical Co.. Poly(vinylpyrrolidone) (PVP, M_w≈55000) came from China National Medicines Co. Ltd.. All chemicals materials were analytical grade and used without further purification.

SNS was prepared according to the method of SUN et al[20]. With different concentration of $AgNO_3$, for a typical synthesis of ultra-long AgNWs, a one-pot reaction was employed to mix all compounds and solvents. Briefly, 0.4 g PVP was first added to 50 mL ethylene glycol (EG) and completely dissolved using magnetic stirring at 170℃. Afterwards, 1 mL SNS solution of EG prepared in the first step was added to the PVP solution. Complete dissolution was required to obtain a uniform solution. Finally, 40 mL of $AgNO_3$ solution (0.5 mol/L) was dumped into the mixture and stirred for 5 min at 170℃ and then cooled down to room temperature. The products were adequately washed with de-ionized water and acetone. Finally, the AgNWs were re-dispersed in ethanol for future use.

1.2 Samples characterization

PERSEE Genera TU-1901 UV-Visible spectro-photometer was used to monitor the UV-Vis spectra of SNS and ultra-long AgNWs. The crystal structure of the as-prepared product was examined using powder X-ray diffraction (XRD) and selected area electron diffraction (SAED). The morphologies of the samples were observed using a TESCAN S3400N scanning electron microscope.

2　Results and discussions

2.1　UV-Vis spectra in preparation process

Fig.1 shows the UV-Vis absorption spectra of SNS and ultra-long AgNWs.

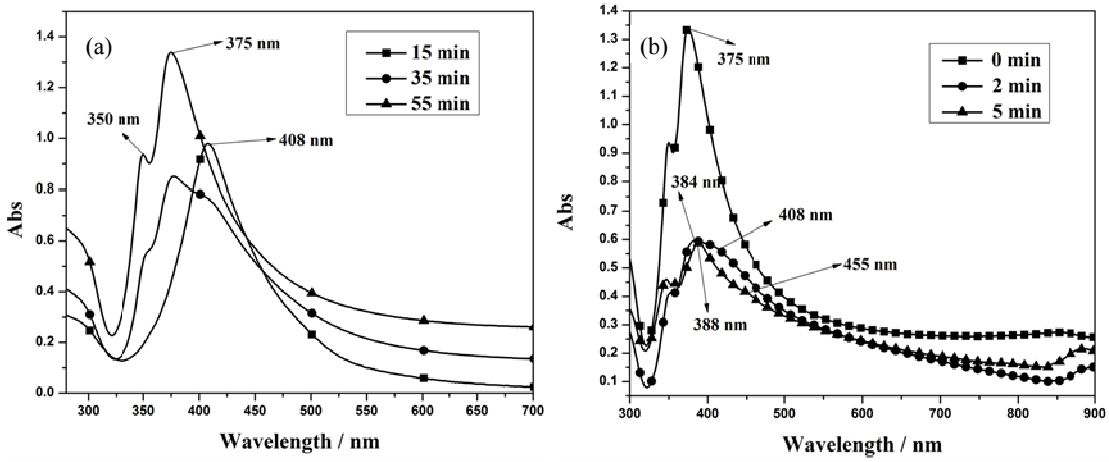


Fig.1 UV-Visible absorption spectra at different time in preparation of SNS (a) and ultra-long AgNMs (b)

图 1　银纳米线晶种(a)和超长银纳米线(b)合成过程中不同时间的紫外-可见光谱

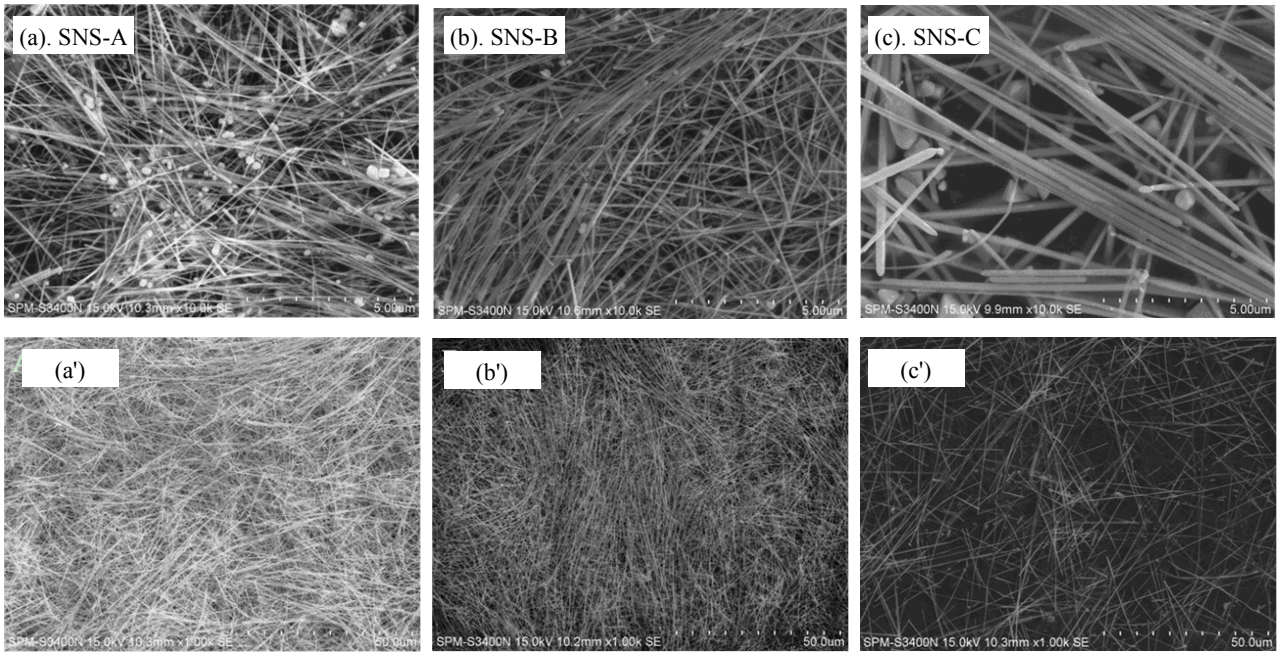
From Fig.1(a) for SNS it can be seen that, at t=15 min, the appearance of a strong plasmon peak at 408 nm indicated the formation of silver nanoparticles with diameters of 20~30 nm[21]. The intensity of this plasmon peak obviously changed until 35 min when a new peak developed at 375 nm. This new peak could be attributed to the typical longitudinal resonance of AgNMs, suggesting the final formation of AgNMs. As the length of these nanowires grew with time, the transverse plasmon mode (at 375 nm) was greatly increased in intensity, while the plasmon peak for nanoparticles decreased. At the same time, optical signatures similar to those of bulk silver started to appear, as indicated by the shoulder around 350 nm which could be attributed to the plasmon resonance of bulk silver film. As the reaction proceeded (at 55 min), the two plasmon peaks at 375 and 350 nm were further increased in intensity and the plasmon peak positioned at 408 nm disappeared. This observation indicates that the final product synthesized was the pure AgNMs.

Fig.1(b) shows the UV-Vis absorption spectra of ultra-long AgNMs taken from the sample obtained at 170℃ for only 5 min suspended in water. At t = 2 min, the appearance of a strong plasmon peak at 408 nm indicated the formation of silver nanoparticles with the addition of $AgNO_3$. Interestingly, the plasmon peak at 408 nm for nanoparticles disappeared as the reaction processed. The position of the first peak at 375 nm for AgNMs has red shift (2 min for 384 nm and 5 min for 388 nm), which indicated the diameter of the ultra-long AgNMs increased as the addition of the excess $AgNO_3$. Obviously, the peak position shifted from 375 to 388 nm and the peak appeared at 455 nm because of the increased size of anisotropic products.

2.2　Effect of SNS size on preparation of ultra-long AgNWs

SNS with different size were synthesized and the corresponding ultra-long AgNMs were prepared via the SNS-directed route in Ag ion rich conditions. The SEM imagines are shown in Fig.2.

From Fig.2(a~c) it can be seen that, by adjusting the concentration of precursor $AgNO_3$, different sized of SNS were prepared. The diameter of SNS are about 80, 100 and 180 nm when the $AgNO_3$ concentration is 0.1, 0.5 and 0.9 mol/L, respectively. It was reported[22] that at the initial stage of the process, small Ag seeds formed with the addition of new precursor, and heterogeneous nucleation occurred by enclosing a mixture of {111} and {110} facets to lower the total interfacial free energy. Therefore, Ag nanowires can be produced as a result of the faster growth rate of {110} planes than {111} planes. Additionally, the SNS synthesized with too high (0.9 mol/L) or too low (0.1 mol/L) concentration of $AgNO_3$ result in the obtained



(a). $c(AgNO_3)$=0.1 mol/L; (b). $c(AgNO_3)$=0.5 mol/L; (c). $c(AgNO_3)$=0.9 mol/L; (a'). By SNS-A; (b'). By SNS-B; (c'). By SNS-C

Fig.2 SEM images of SNS prepared in different concentration of $AgNO_3$ (a~c) and corresponding ultra-long AgNWs (a'~c')

图 2 不同 $AgNO_3$ 浓度制备的晶种(a~c)对应合成的超长银纳米线(a'~c')的扫描电镜图像

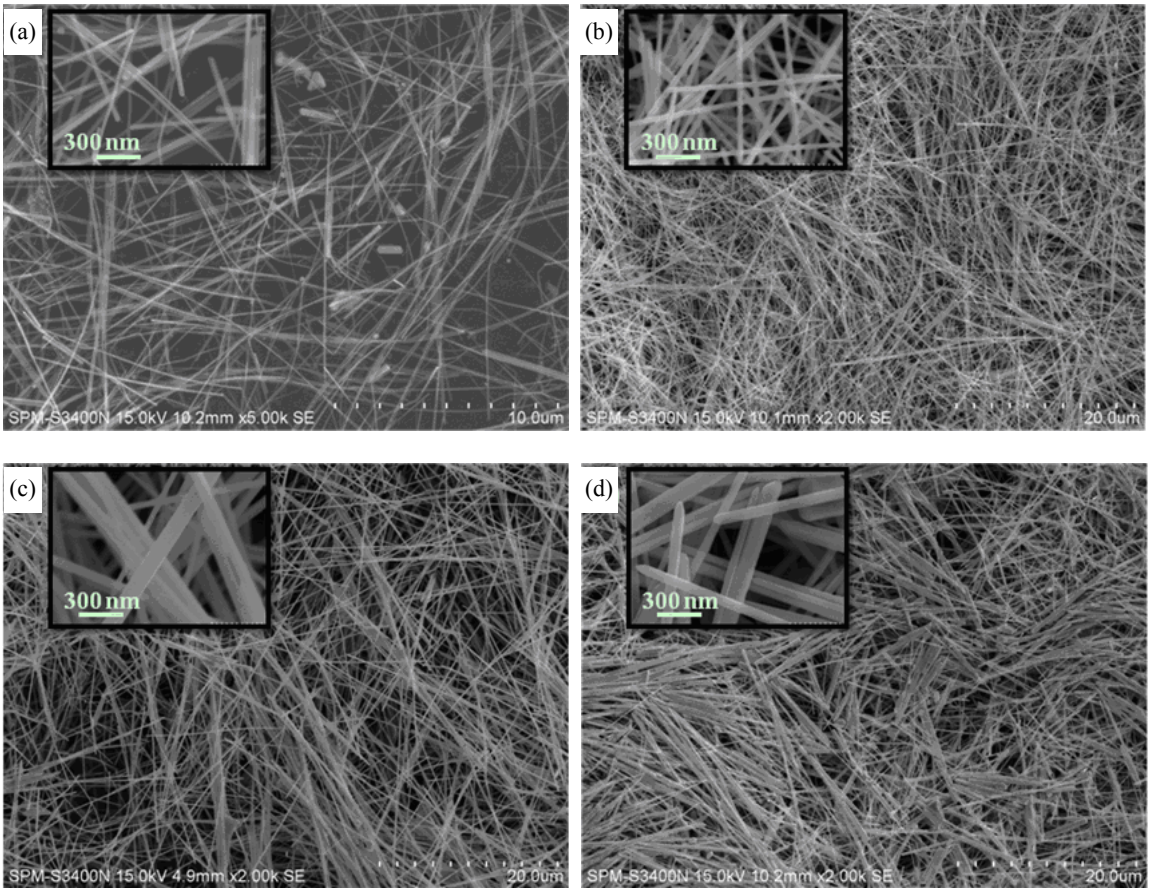
samples with a certain amount of particles (as shown in Fig.2(a) and (c)). Thus, we can conclude that the 0.5 mol/L $AgNO_3$ solution is more favorable for the formation of SNS with better uniformity.

The ultra-long AgNMs can be prepared via the SNS-directed route and continued to grow through successive growth as long as Ag ion rich conditions were maintained. Fig.2(a'~c') show the ultra-long nanowires synthesized using different SNS-directed template. The addition of SNS containing particles (Fig.2(a) and (c)) failed to get AgNWs with good uniformity but generated many by product nanoparticles (Fig.2(a') and (c')). The better SNS the better ultra-long silvernanowires can be obtained, as shown in Fig.2(b').

2.3 Effect of $AgNO_3$ concentration on preparation of ultra-long AgNWs

Concentration of precursor, uniformity and distribution of SNS were all found to play certain roles in the successive growth for ultra-long AgNMs. Fig.3 shows the SEM images of the samples that were synthesized using SNS-B as the seeds and Ag ion rich conditions in the second growth step.

As seen from Fig.3(a~d), when the lower (0.2 mol/L) or higher (0.8 mol/L) precursor concentration were adopted in the second growth step, poor uniformity and shorter AgNMs was obtained, as shown in Fig.3(a) and (d). Additionally, we also found that the reduction rate decreased when the concentration of $AgNO_3$ concentration decreased to 0.1 mol/L, which could be originated from fewer silver nuclei for the growth of AgNMs. Further, the diameter of the ultra-long AgNMs would sharply increase from 90 to 200 nm, when the concentration of precursor is greater than 0.4 mol/L. Thus, the precursor concentration at 0.4 mol/L is the best choice for the second step growth in the synthesis of ultra-long AgNMs.



(a). $c(AgNO_3)$=0.2 mol/L; (b). $c(AgNO_3)$=0.4 mol/L; (c). $c(AgNO_3)$=0.6 mol/L; (d). $c(AgNO_3)$=0.8 mol/L

Fig.3 SEM images of ultra-long Ag nanowires prepared by using SNS-B in different concentrations of $AgNO_3$

图 3　在不同 $AgNO_3$ 浓度下用 SNS-B 做晶种合成的超长银纳米线的扫描电镜图像

2.4 The illustration of SNS-directed synthesis for ultra-long AgNWs

The mechanism of the fabrication of AgNMs seeds in the presence of surfactant, such as PVP, has been proposed firstly by Sun et al[23]. In the synthesis of SNS, the introduction of Pt seeds and the presence of surfactant were indispensable to the formation of AgNMs seeds. The AgNMs growth mechanism was summarized by Li et al[24]. Based upon the results obtained, the synthesis process is divided into two steps: the first step is the synthesis of SNS; the second step is the growth of ultra-long AgNWs via SNS-directed synthetic method. Using the SNS-directed method in this work, it is possible to get AgNWs with high aspect ratio and better uniformity.

2.5 Morphology and structure of SNS and ultra-long AgNWs

From the what has been discussed above, the SNS was prepared via a solution-phase method that generates AgNMs by reducing $AgNO_3$ with EG in the presence of PVP[20]. Fig.4 shows the SEM images for the as-prepared SNS and ultra-long AgNWs, and Fig.5 shows the XRD, TEM and SAED characterizations of ultra-long AgNWs.

It can be found that the SNS with good uniformity and length of 10~20 μm (Fig.4(a)). In contrast, the ultra-long AgNWs prepared using the SNS as template are about 70~100 μm and the diameter of nanowires changed slightly (Fig.4(b)).

Fig.5(a) shows the typical XRD pattern of ultra-long Ag nanowires. The reflection peaks in Fig.5(a) can be assigned to the (111), (200), (220), (311), and (222) planes of pure fcc silver crystals, respectively, which is consistent with the standard value according to JCPDS Card No. 04-0783. However, it is noticeable that the {111} reflection plane is extremely strong compared with the other reflection planes, suggesting the preferential growth of {111} plane of silver crystal.

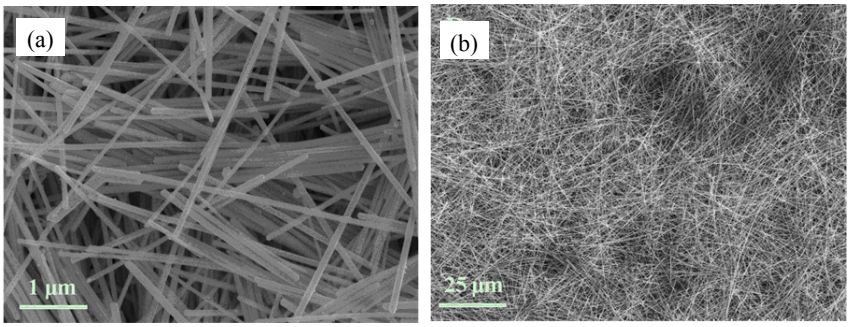


Fig.4 SEM images of Ag nanowires seeds (SNS) (a), and ultra-long Ag nanowires (b)

图 4 银纳米线晶种(a)及超长银纳米线(b)的扫描电镜图像

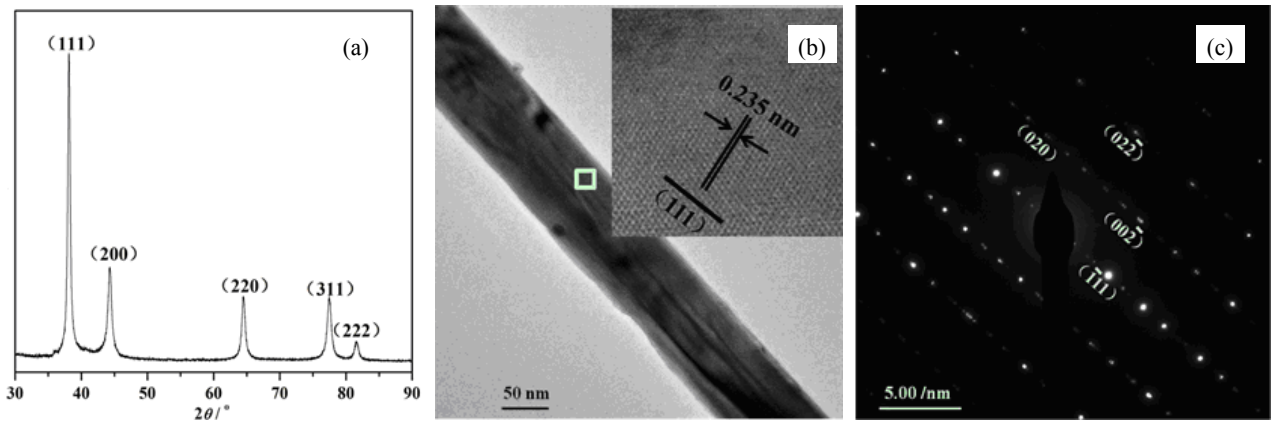


Fig.5 XRD pattern (a), TEM image (b) and SAED pattern (c) of ultra-long AgNWs

图 5 超长银纳米线的 XRD 图谱(a)、透射电镜图像(b)及选区电子衍射图像(c)

In addition, no impurities were detected, indicating the formation of highly pure AgNWs. Fig.5(b) and (c) are the TEM image and SAED pattern taken from the body of AgNMs. The SAED measurement clarifies that the AgNMs are single crystal. Actually, the structure of AgNMs is consistent with the thermodynamic character of the face-centered-cubic silver phase, as demonstrated by the first-principle density functional theory calculation on the formation energy of various silver surfaces[25]. Since the close-packed {111} facets of silver have the lowest surface energy and the silver {110} facets have the highest surface energy, the AgNMs therefore grow along the <110> direction with the {111} facets[26].

3 Conclusions

A novel highly efficient recipe for the rapid and uniform synthesis of ultra-long AgNWs by using the pre-synthesized SNS via SNS-directed method has been demonstrated.

1) The precursor concentration significantly affects the morphologies of SNS. The SNS with good uniformity and length of 10~20 μm can be prepared with 0.5 mol/L $AgNO_3$ solution.

2) The uniform ultra-long AgNWs with length of 70~100 μm and diameter of 90~200 nm were prepared in 5 minutes with 0.4 mol/L $AgNO_3$ precursor.

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