



# Growth of silver nanowires on anatase structured TiO<sub>2</sub> thin films by thermal reduction method

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## Abstract:

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This research work aims at understanding the growth mechanism for silver nanowires by thermal reduction of silver nitrate solution on solid substrate surfaces of titania thin films. Various silver nanostructures were formed under different parameters such as the crystallinity and the phase of the substrates and the thermal processing conditions. Under proper experimental condition, silver nanowires with 30-100 nm in diameter and 1-50  $\mu\text{m}$  in length were formed only on anatase film surfaces. Time series growth of various silver nanostructures revealed that the silver nanowires might be formed from the aggregation of silver nanoparticles. The factors influencing the growth kinetics of silver nanowires include thermal reduction temperature, concentration of silver nitrate, thermal reduction time and the amount of silver nitrate solution.

**DOI Number: 10.14704/nq.2022.20.8.NQ44885**

**NeuroQuantology 2022; 20(8): 8637-8645**

## 1. Introduction

Since silver is the material with the best electrical and thermal conductivity, the research on silver nanostructures have been fascinated and have also attracted world-wide interests. With great potential applications in

many fields from fundamental science to engineering technology, one-dimensional (1-D) metal nanostructures such as nanowires, nanorods, and nanotubes have been very popular topics of research [1-5]. They have been used to experimentally probe the effects of quantum confinement on electronic,



magnetic, and other related properties, and they could be used as active components or interconnects in fabricating electronic, photonic, and sensing devices. As the size of electronic devices became smaller, one dimension metal nanostructures like nanowires, nanorods and nanotubes become more and more important. Silver nanowires are particularly interesting to explore because bulk silver exhibits the highest electrical and thermal conductivities among all metals. Other modern applications of silver nanowires have also been discovered in many fields including catalysis, electronics, photonics, and photography [6-9].

There are lots of physical and chemical methods to fabricate silver nanowires. In order to obtain a large amount of one-dimensional silver nanostructures, the most popular ones were template and chemical methods [6-10]. Although the use of templates can have good control over the aspect ratios of nanowires, complicated procedures and limited scale are the major disadvantages. However, non-template solution-phase chemical processes have been demonstrated for fabricating silver into 1-D nanowires with the help of seeds [11-12] or without seeds (seedless or self-seeding) [13-14]. Most of the soft, solution-phase chemical approaches involve polymer surfactants that serve as capping agents. Thus, harsh conditions or multiple purifications may be required to remove unwanted materials. Caswell et al. recently reported a seedless and surfactant less wet-chemical approach in which the trisodium citrate acted not only as the reducing reagent but also as a capping agent [15].

Using photo-reduction method to reduce silver ions from silver nitrite solution is a common method to test the photocatalytic properties of titania thin films under photo radiation. In most cases, the reduced silver metal is in the forms of particles, but if heat is used as energy source, the silver would result in nanowire form with length in 30-100  $\mu\text{m}$  and 1-50 nm in diameter [15]. In this paper, we report the progress on the understanding of formation of silver nanowires via the simple

route of heating aqueous silver nitrate on a titanium dioxide surface. Several parameters, including crystallinity and phase of titania, concentration of silver nitrate solution, and heat-treating time, were examined to see how they affect the formation of silver nanowires.

## 2. Experimental

The substrates used to prepare silver nanostructures were pure titania thin films deposited on Si or quartz coupons by electron-beam evaporation system under the following processing parameters: substrate temperature at 250 °C, oxygen gas flow of 4 sccm, working pressure of 0.7 Pa, and the film thickness was fixed at 400 nm. The as-synthesized TiO<sub>2</sub> films were then annealed at different temperatures of 350, 500, 800 and 1000 °C for 8 hours to vary their crystallinity and phase.

In the preparation of silver nanostructures by thermal reduction method, the titania thin film substrates were placed in the silver nitrite, AgNO<sub>3</sub> (Sigma), solution and then pulled out. Thus, a layer of silver nitrite solution was absorbed on substrate surface. These substrates with silver nitrate on them were placed in an aluminum oxide crucible and heat-treated in a furnace in air. The heat-treatment temperature was raised at a rate of 5°C per minute to 200°C, maintained for 20 minutes, and then raised again at the same rate to 300°C. They were finally furnace-cooled after being held at 300°C for 3 hours. The variant parameters are titania thin film crystallinity, concentration of silver nitrite and thermal reduction time to study their effects on the formation of silver nanostructures.

Various analyses were done on the samples. Low-angle X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2500V diffractometer. Raman spectra were obtained using a RENISHAW 1000B spectrometer to verify the structure of TiO<sub>2</sub> substrates. The morphology and size distribution were characterized by a field-emission scanning electron microscopy (FESEM; JEOL JEM6500-F). The structure and preferred growth direction of silver nanowires were confirmed by transmission electron



microscopy (TEM; JEOL JEM3010). Besides, UV-visible spectra were used to character the surface plasmon effect of silver nanostructures.

### 3. Result and discussion

The as-deposited titania films grown at a substrate temperature of 250 °C are amorphous or of anatase phase of low crystallinity. Annealing the films at various temperatures of 350, 500, 800 and 1000 °C for 3 hours each changed their crystallinity and phases as shown in Fig. 1(a). After the annealing at 350 °C, the film crystallized in anatase phase and at 500 °C, the film structure remained as anatase but with better crystallinity based on the intensity and the full width at half maximum (FWHM) of the peaks in the XRD and Raman spectra (not shown). When the temperature was at 800 °C, some rutile phase appeared and the film structure became mixed phases of anatase and rutile. When the temperature was further raised to 1000 °C, the film transformed almost completely to rutile phase.

To prepare silver nanostructures, the same thermal reduction procedure at 300 °C for 3 hours was applied on the five titania thin films with different crystallinity and phase. The structure and morphology of the resultant silver nanostructures were shown in the XRD patterns in Fig. 1(b) and in the SEM micrographs in Fig. 2, respectively. The XRD results showed that most of the silver nanostructures on titania films were of face-centered cubic (FCC) crystal structure regardless their geometrical shapes, but additional XRD peaks matching those for silver nitrite were observed for samples a-800 and a-1000.

The SEM images in Fig. 2a and 2b showed that with the crystallinity of titania increase, the silver nanowires were longer and yielded better. On the titania annealed at 350 °C, the length of silver nanowires was 10-20 μm, while on the titania annealed at 500 °C, the length of silver nanowires reached 50 μm and the quantity of NWs output increased about 3 times per unit area. On the titania annealed at 800 °C, only chunks of silver microparticles and some small rod-like silver nanostructure

formed. Finally, on the titania annealed at 1000 °C, there was no one-dimension silver nanostructures formed, which is very similar to those on as-deposited titania film [15]. The titania film annealed at 500 °C yield the highest Ag NWs, and the films were used as substrate in the subsequent studies. It is clear that the formation of Ag NWs is associated with anatase crystallinity.

In order to explored the effect of different concentration of silver nitrite solution, a series of samples were prepared at 0.0125 M, 0.025 M, 0.05 M, 0.07 M, 0.09 M, 0.1 M, 0.2 M, 0.5 M and 1 M. After thermal reduction at 300 °C for 3 hours, the resultant FESEM images are shown in Fig 3. The statistical data of silver nanowires and particles size was obtained from the FESEM images, and then plotted against silver nitrite concentration as shown in Fig 4. The average particle size increased with concentration and the length of silver nanowires increase to thirty times long, but there was no significant increasing in diameter. The diameter of nanowires was tended to be 100 nm. It meant that silver atoms precipitated from solution preferred to enter the longitudinal side of silver nanostructures and resulted in one dimension growth. Otherwise, the amount of silver nanostructures with aspect ratio larger than twenty increased from 10 % to 100 %. With concentration increase, the yield of nanowires increased and nanorods decreased.

Furthermore, in order to understanding the growth stage in the thermal reduction method, changed the thermal reduction time from 10 to 120 minutes and observed the products each ten minutes. The thermal reduction was controlled at 300 °C and the concentration was 0.1 M. As time went on, the size of silver particles became larger and the number of silver particles in unit area became less. When it was 30 minutes, there were some one-dimension structure formed as Fig 5. The yield and length of nanowires both increased with time increase. Fig 6 was the XRD pattern for the products of different growth stages. Compared with database, there was silver nitrite after 30 minutes heat treatment. After



50 minutes, there was only silver FCC structure. Plotted the average size of silver nanowires and particles as Fig 7. The size of them increases about three times with time increase to 120 minutes.

Quartz (1\*0.5 inch) also be used to be the substrate for titania deposition, and through the same thermal reduction condition (300 °C,3 hr). The final silver nanostructures were like Fig 8 and the surface resonance absorption spectra as Fig 9. The evident absorption peaks as 350 nm and 380 nm( $\Psi$ ) were the transverse plasmon resonance absorption peaks for silver nanowires, 480 nm and 570 nm (+) were the longitudinal plasmon resonance absorption peaks for silver nanowires, 410 nm(# ) was the absorption peaks for silver nanoparticles.

#### 4.Conclusion

If substrate provided sufficient electrons, silver nanowires can be formed and anatase phase TiO<sub>2</sub> had the best efficiency. The reduced silver atoms preferred to entered silver nanostructure in longitudinal axis. The growth kinetics of the silver nanowires was greatly depended on the TiO<sub>2</sub> crystallinity, the concentration and amount of silver nitrate solution, the heat reducing temperature etc. The growth mechanism was suggested as the movement and aligned of silver nanoparticles toward 1-D structure.

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#### Figures:



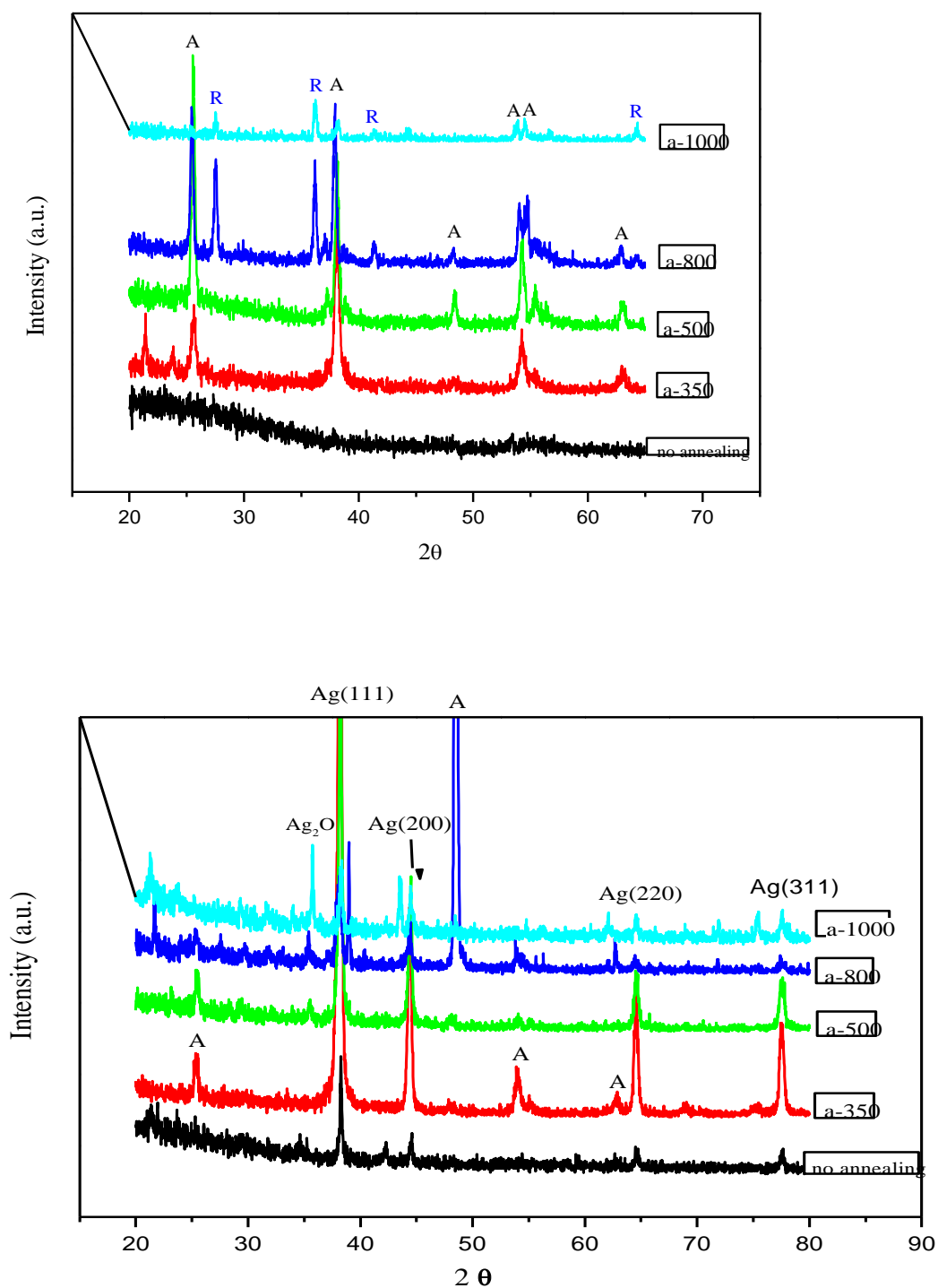


Fig. 1: XRD patterns of (a) Titania films annealed at various temperatures and (b) Silver nanostructures grown on these films by thermal reduction at 300°C for 3 hrs

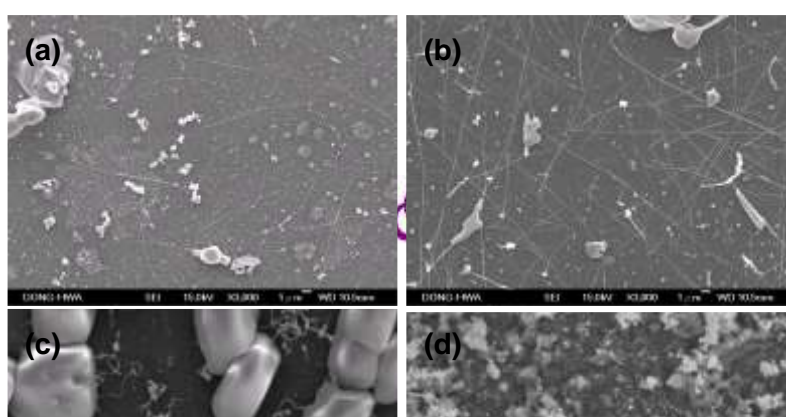
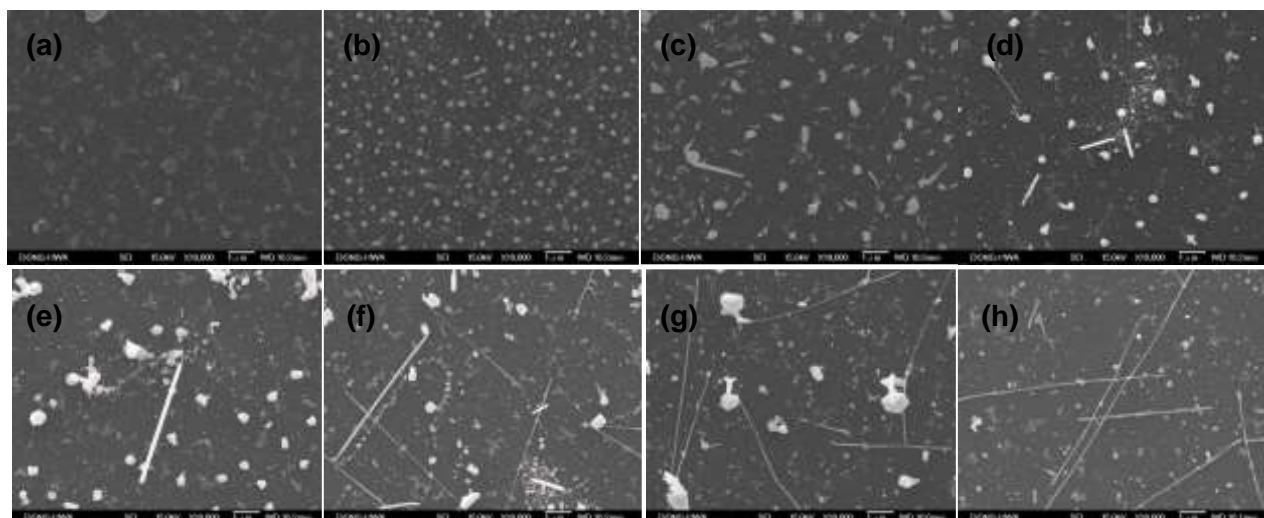


Fig. 2: SEM results for the silver nanostructures s after thermal reduction at 300 °C for 3 hrs on the annealed titania substrates (A) 350 (B) 500 (C) 800 (D) 1000 °C

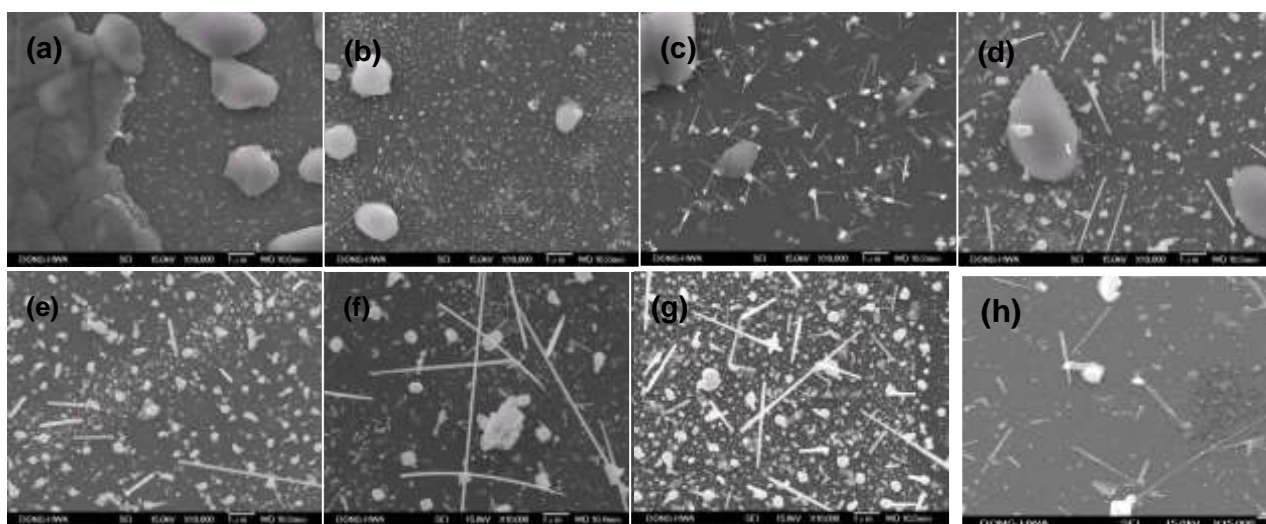


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Fig. 3: Different silver nitrite solution concentration FESEM result (a)0.0125 M (b)0.025 M (c)0.05 M (d)0.07 M (e)0.09 M (f)0.1 M (g)0.2 M (h)0.5 M



Fig. 4: Size distribution of silver nanowires with silver nitrite concentration



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Fig. 5: Different growth stages at 300 °C (a)10 (b)20 (c)30 (d)50 (e)60 (f)90 (g)110(h)120 min



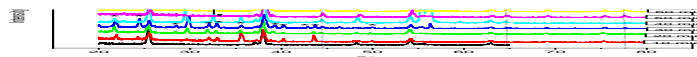


Fig. 6: XRD pattern for different growth stages at 300 °C

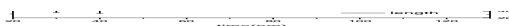


Fig. 7: Size distribution of silver nanowires with different growth stages



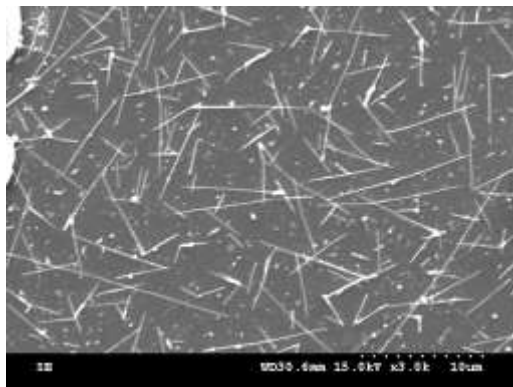
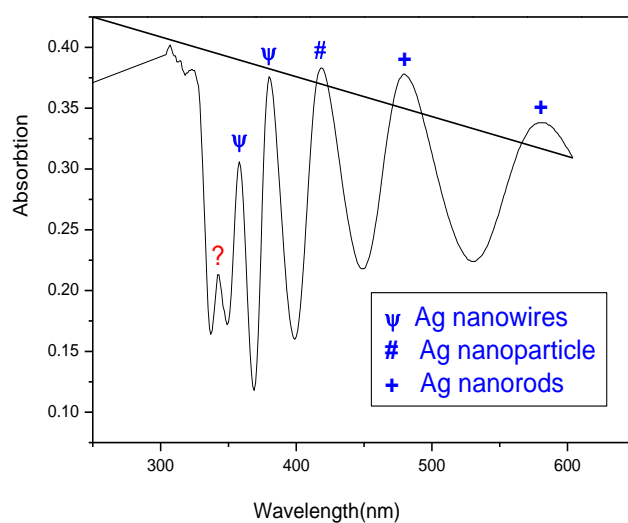


Fig. 8: SEM result for thermal reduction at 300 °C for 3 hours



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Fig. 9: UV-Visible absorption spectrum for silver nanostructures after thermal reduction at 300 °C for 3 hours

