

# A technique for controlling the alignment of silver nanowires with an electric field

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## Abstract

Highly aligned silver nanowire arrays are synthesized under direct current electric field (DCEF) treatment by a solid state ionics method without any template at normal temperature and pressure. The degree of alignment of the synthesized nanowires increases with increase of the DCEF strength. The mechanism of the effect of the DCEF on the nanowire alignment is discussed briefly. Moreover, the alignment of the individual nanowires in a bundle is further proved by observing the polarization dependence in the experiment of the polarized reflection measurements.

## 1. Introduction

One-dimensional (1D) metallic nanowires present strong anisotropy in electron confinement, electrical conductivity and resulting optical properties and thus are ideal building blocks for functional nanoscale electronic [1] and photonic structures [2–4]. Silver nanowires are of special importance, because silver exhibits the highest electrical conductivity among all metals and silver nanowire surfaces can significantly enhance the Raman scattering signal of molecules adsorbed on the surface [5]. Thus developing a convenient method for preparing well-aligned silver nanowire arrays is very important for the fabrication of functional micro/nanoscale electronic devices and surface enhanced Raman scattering (SERS) substrates for detecting extremely low concentration chemical species.

Many attempts to improve the alignment of nanowires have been made utilizing a variety of nanofabrication techniques, such as porous alumina template use and the copolymer template assisted electrodeposition method [6, 7], the Langmuir–Blodgett technique [5], the microfluidic approach [8] and template-free routes [9, 10]. However, these approaches have some limitations, such as in the preparation

of templates and the inevitable collapses of nanowire arrays in the dissolving of the templates [6, 7], the complicated synthesis procedure including the preparation and assembly of nanowires [5, 8] and the requirement for unusual preparation environments [9, 10]. Therefore, it is a great challenge to directly produce aligned nanowires without the assistance of templates at normal temperature and pressure.

On the basis of our previous work [11, 12], in this paper, we show that well-aligned single-crystalline silver nanowire arrays can be synthesized directly under DCEF treatment by a simple solid state ionics method without any templates at room temperature and normal atmospheric pressure. By increasing the DCEF strength, the alignment degree of the synthesized nanowires can be improved, i.e., from disordered silver nanowires to well-aligned silver nanowire arrays. These nanowire arrays are characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), x-ray energy dispersive spectroscopy (EDS) and selected-area electron diffraction tests.

## 2. Experiment

Solid electrolyte RbAg<sub>4</sub>I<sub>5</sub> film (thickness ~80 nm) was deposited on the NaCl substrate by vacuum thermal

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evaporation [13]. Then we used silver films (thickness  $\sim 136$  nm) deposited on both ends of the  $\text{RbAg}_4\text{I}_5$  film as electrodes to contact the two sides of the  $\text{RbAg}_4\text{I}_5$  film. The distance between the cathode and the anode was about 1 mm. Then a direct current constant-voltage source was applied. The schematic diagram of the experimental set-up is shown in [12].

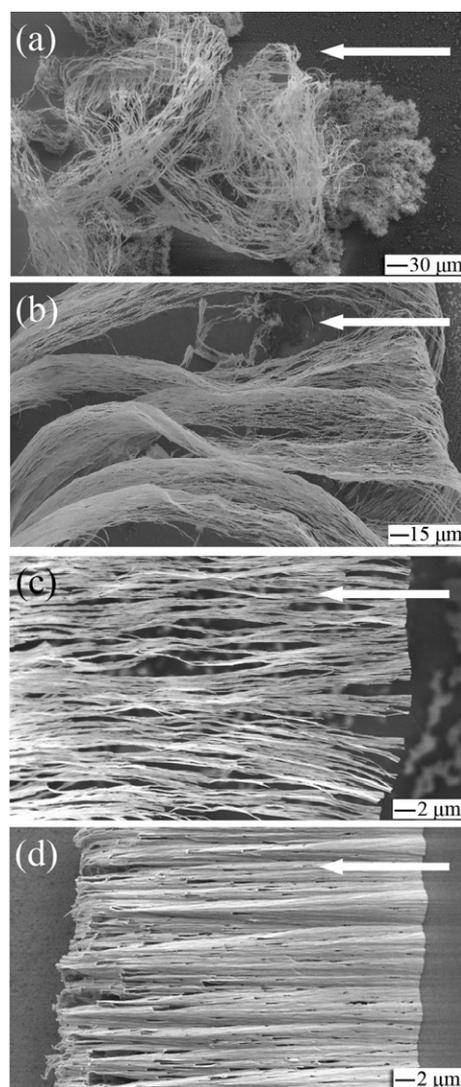
$\text{RbAg}_4\text{I}_5$  is a solid electrolyte at room temperature [14, 15], which means that silver ions are not confined to specific crystalline lattices. They are essentially free to move through the crystalline channels of the  $\text{RbAg}_4\text{I}_5$  film under the applied electric field. Compared with the wet chemical method [16–18], the  $\text{RbAg}_4\text{I}_5$  film functions like the silver salt ‘solution’, such as  $\text{AgNO}_3$ . It provides a solid state channel for silver ions migration and makes the nucleation of silver ions at the cathode possible.

### 3. Results and discussion

At room temperature and atmospheric pressure, different strengths of DCEF were applied to the samples. When the DCEF strength was small (about  $100 \text{ V m}^{-1}$ ), free-standing silver nanowires grew spirally toward the anode. The nanowires were ordered on the small scale but disordered on the large scale at the cathode (figure 1(a)). On increasing the DCEF strength to about  $200 \text{ V m}^{-1}$ , silver nanowires self-assembled into separate bundles (figure 1(b)). Each bundle typically consisted of hundreds of single nanowires. The direction of the nanowire growth in each bundle is opposite to the direction of the DCEF on the whole. When the DCEF strength was increased up to  $300 \text{ V m}^{-1}$ , the nanowires aligned along the direction opposite to the DCEF though some of them appreciably deflected in orientation. The structure of the aligned nanowires is just like a well-aligned raft (figure 1(c)). If the applied DCEF was increased to  $400 \text{ V m}^{-1}$ , we found that all the silver nanowires grew highly parallel to the direction opposite to the DCEF and clustered together to form a sheet-like structure (figure 1(d)). This indicates that the alignment of the silver nanowires is improved greatly on increasing the applied DCEF strength.

Figure 1 shows that the alignment and density of the nanowires are both improved on increasing the strength of the DCEF. At the beginning, silver ions diffuse toward the cathode to form a planar interface. The stability of the interface is in strong relation to the distribution of ‘solute’ and the strength of the DCEF. The perturbation of an interface grows due to the build-up of the ‘solute’. The growth direction of the nanowires depends on the direction of the applied DCEF. When the strength of the DCEF is increased, the silver ions tend to migrate along the direction of the DCEF. So, the growth direction of the nanowires becomes much closer to the direction opposite to the DCEF. On the other hand, on increasing the strength of the DCEF, lots of silver ions will accumulate at the interface to form a clustered array of nanowires because of the enhanced diffusion of silver ions in the solid electrolyte, and then the nanowires will become denser.

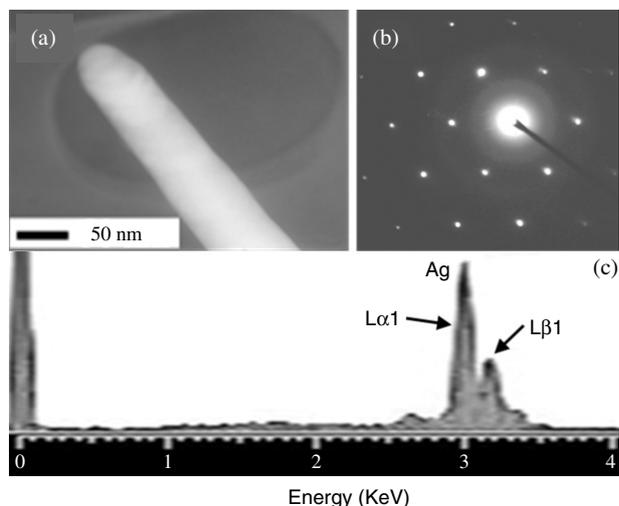
Due to the room temperature and atmospheric pressure synthesis surroundings, without any template, and the solid phase synthesis procedure, we see promise for prospective applications of this technique. It provides a possible route



**Figure 1.** SEM images of (a) disordered silver nanowires achieved under  $100 \text{ V m}^{-1}$  DCEF strength applied for about 60 min, (b) wavy silver nanowire bundles achieved under  $200 \text{ V m}^{-1}$  DCEF strength applied for about 30 min, (c) well-aligned silver nanowire raft achieved under  $300 \text{ V m}^{-1}$  DCEF strength applied for about 10 min and (d) highly aligned silver nanowire sheet achieved under  $400 \text{ V m}^{-1}$  DCEF strength applied for about 5 min. The direction of the DCEF is indicated by a white arrow.

for artificially ‘sculpting’ nanowire structures on  $\text{RbAg}_4\text{I}_5$  thin film surface using an induced electric field. For example, with the aid of a scanning tunnelling microscope (STM), it is possible to ‘draw’ lines and shapes on the prepared  $\text{RbAg}_4\text{I}_5$  thin film surface, while for the soft liquid phase processing [17] or the so-called wet chemical method [18], it is difficult to control the synthesis procedure and nucleation dimensionality since the wet surroundings are suitable for three-dimensional (3D) nucleation.

In order to characterize the microstructure of the nanowires, the nanowire bundles obtained under the DCEF strength of  $200 \text{ V m}^{-1}$  were separated from the surface of the  $\text{RbAg}_4\text{I}_5$  film by water rinsing. Then they were ultrasonically dispersed in de-ionized water and drops of the dispersion were placed on a special grid for the TEM. The TEM image of an



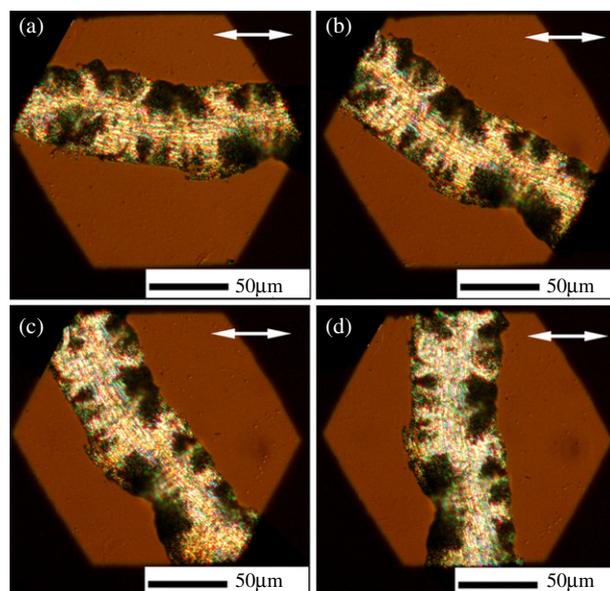
**Figure 2.** (a) TEM image of an individual silver nanowire. (b) Electron diffraction pattern of a randomly selected silver nanowire. (c) EDS spectrum of the silver nanowires.  $L\alpha_1$  and  $L\beta_1$  are the transitions responsible for the x-ray fluorescence lines of silver.

individual silver nanowire shows that the nanowire is about 60 nm in diameter (figure 2(a)). The electron diffraction pattern of the  $(\bar{1}11)$  crystal plane of a randomly selected silver nanowire is displayed in figure 2(b). The diffraction spots suggest that the silver nanowire obtained is single crystalline with a face-centred cubic lattice. Figure 2(c) gives the result of EDS elemental analysis of the silver nanowires, which indicates that the nanowires are composed of pure silver.

To further investigate the degree of alignment of the silver nanowires, the polarization phenomena of the silver nanowire bundles prepared under  $200 \text{ V m}^{-1}$  DCEF strength were studied with a Nikon Metallurgical Microscope, Eclipse ME600L. The polarization direction of the incident light was fixed in the horizontal direction, while a nanowire bundle was rotated around the optical axis of the microscope. As shown in figure 3, the reflected images varied with the angle ( $\theta$ ) between the polarization direction of the incident light and the bundle's axis. When the incident light polarization direction was parallel to the bundle's axis ( $\theta = 0^\circ$ ), the reflectivity was the smallest (figure 3(a)). On increasing the angle ( $\theta$ ), the reflectivity also increased. When the incident light polarization direction was perpendicular to the bundle's axis ( $\theta = 90^\circ$ ), the reflectivity was the largest (figure 3(d)). The result implies that the nanowire bundle possesses strong polarization characteristics. The polarization property is due to the alignment of individual nanowires in the bundle, which makes the bundle similar to a wire-grid polarizer.

#### 4. Conclusion

In summary, we demonstrated that aligned single-crystalline silver nanowire arrays can be synthesized directly under treatment with a DCEF by a simple solid state ionic method. The alignment of nanowires can be effectively controlled by adjusting the applied DCEF strength between the two electrodes, and improved by increasing the DCEF strength. The polarization characteristics of the bundle support the result



**Figure 3.** Images of a silver nanowire bundle obtained with a Nikon Metallurgical Microscope, Eclipse ME600L, equipped with a Nikon Digital Camera, DXM-1200: (a) the polarization direction of the incident light is parallel to the bundle's axis,  $\theta = 0^\circ$ , (b)  $\theta = 30^\circ$ , (c)  $\theta = 60^\circ$ , (d) the polarization of the incident light is perpendicular to the bundle's axis,  $\theta = 90^\circ$ . The white arrows indicate the polarization direction of the incident light. The bundle was illuminated by a 12 V–100 W episcopic halogen lamp and the incident wavelength range was chosen as  $\lambda = 590\text{--}620 \text{ nm}$ . (This figure is in colour only in the electronic version)

of well-aligned nanowire arrays being obtained in the DCEF treatment.

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