



Editors Choice

Polyol synthesis of silver nanostructures: Inducing the growth of nanowires by a heat-up process



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ABSTRACT

The polyol synthesis of silver (Ag) nanostructures typically involves the rapid injection of Ag precursor to a preheated, ethylene glycol solution containing polymeric stabilizers and other additives. Here we report that Ag nanowires can be synthesized in high yields by applying a heat-up process in the polyol synthesis. Electron microscopy studies revealed that multiple-twinned Ag seeds were generated preferentially during the heat-up procedure, and then grew into nanowires. We also demonstrate that these Ag nanowires can be applied as electrode materials for the fabrication of flexible and transparent organic field-effect transistors with a reasonably high hole-mobility.

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1. Introduction

One-dimensional nanostructures, such as nanowires, of silver (Ag) have attracted increasing attention owing to high electrical conductivity, ease of processing, and great potential for applications in transparent electrodes and highly stretchable conductors [1–6]. During the last decade, there has been a great effort to develop an effective strategy for synthesizing Ag nanowires. Since the first report by Xia and co-workers [7], the polyol reduction of AgNO₃ in the presence of poly(vinyl pyrrolidone) (PVP) has been a preferred method for synthesizing Ag nanowires [8–12], in which ethylene glycol (EG) is typically used as both a reducing agent and a solvent. This polyol synthesis allows for the rapid and scalable synthesis of Ag nanowires, but often suffers from low wire-to-particle yields as well as the formation of nanowires with low aspect ratios. In the solution-phase synthesis of metal nanostructures, the morphology of the final product is mainly determined by crystallinity of seeds [13,14]. Nanowires are grown from multiple-twinned seeds with a decahedral structure, while seeds with a single-crystal structure tend to evolve into polyhedral nanocrystals with a cubic or octahedral shape. For the high-yield production

of Ag nanowires, therefore, it is necessary to develop an efficient way to promote the formation of multiple-twinned seeds at the nucleation stage of the synthesis.

The polyol synthesis of metal nanostructures is typically conducted by using a hot-injection process, in which an EG solution containing a metal salt precursor is injected to a preheated, EG solution containing polymeric stabilizers such as PVP, and both nucleation and growth processes occur at high temperatures [15]. Nanocrystals of metals or metal oxides can also be prepared by using a heat-up method, which involves slow heating of the reaction mixture containing both precursors and stabilizers from a low temperature to the desired reaction temperature [16–23]. In this case, the nucleation and growth starts to take place at relatively low temperatures. The heat-up method has been utilized to produce uniformly sized Ag nanocrystals. Recently, we have shown that in the aqueous-phase synthesis of Ag nanoplates, a heat-up process can enhance the lateral growth of nanoplates compared to a hot-injection process [23]. However, the effect of the heat-up process on the polyol synthesis of Ag nanostructures remains largely unexplored.

Here we report the polyol synthesis of Ag nanostructures, and demonstrate that it is possible to promote the formation of nanowires by using a heat-up process. We found that multiple-twinned Ag seeds are generated preferentially at the nucleation stage of the heat-up synthesis, and then grow into long nanowires with an average length of about 20 μm. Unlike the heat-up synthesis, most of Ag seeds formed at the nucleation stage of the hot-injection synthesis had a single-crystal structure, which evolved into

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nanocubes. We applied Ag nanowires prepared from the heat-up synthesis as electrode materials for flexible and transparent organic field-effect transistors (FETs). The resulting FETs based on Ag nanowire source-drain electrodes exhibited a hole mobility ($0.14 \text{ cm}^2/\text{Vs}$) comparable to that of FETs with Au electrodes.

2. Experimental

2.1. Synthesis of Ag nanowires

In the heat-up synthesis of Ag nanowires, 24.5 mg of PVP (MW = 55000, Aldrich) and 23.9 mg of AgNO_3 (Aldrich) were dissolved in 1.5 mL of EG (Aldrich), separately. The above two solutions and 30 μL of EG solution of FeCl_3 (4 mM) were added to 5 mL of EG hosted in a 20-mL vial at room temperature. After capping the vial, the reaction mixture was heated from room temperature to 151.5°C at a heating rate of $1.4^\circ\text{C}/\text{min}$ under magnetic stirring, maintained at this temperature for 1.5 h, and then quenched to room temperature. In the hot-injection synthesis, 5 mL of EG was hosted in a 20-mL vial at room temperature and heated to 151.5°C under magnetic stirring. Then, 30 μL of EG solution of FeCl_3 (4 mM) was added to the reaction solution. After 15 min, 1.5 mL of EG solution containing 24.5 mg of PVP was added to the reaction solution. After 5 min, 1.5 mL of EG solution containing 23.9 mg of AgNO_3 was injected to the reaction solution. The reaction mixture was maintained at the reaction temperature under magnetic stirring for 1.5 h, and then quenched to room temperature.

2.2. Characterization

Scanning electron microscopy (SEM) images were obtained using a Jeol JSM-6701F microscope operated at 15 kV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were captured using a Jeol JEM-2100F microscope operated at 200 kV. UV-vis spectra were recorded with a Hewlett-Packard 8453 UV/vis spectrometer. The sheet resistance of Ag nanowire films was measured with a four-point-probe technique with Keithley 2182A and 6221.

2.3. Fabrication of FETs

Poly(ethylene naphthalate) (PEN) coated with indium tin oxide (ITO) was used as a plastic substrate for the fabrication of the top-contact, bottom-gate pentacene FETs. The dimethylformamide solution comprising 10 wt.% poly-4-vinylphenol ($M_w = 20000 \text{ g/mol}$) and 5 wt.% poly(melamine-co-formaldehyde) (PMF, $M_w = 511 \text{ g/mol}$) was spin-coated onto the ITO/PEN substrate, followed by thermal annealing at 120°C in a vacuum oven for 12 h. The specific capacitance of the cross-linked poly-4-vinylphenol gate dielectric (thickness = 503 nm) was 7.1 nF cm^{-2} . Then, 50-nm-thick pentacene films were deposited from a quartz crucible onto the cross-linked poly-4-vinylphenol substrates at a rate of 0.2 \AA s^{-1} using an organic molecular beam deposition (OMBD) system. Finally, the Ag nanowire source-drain electrodes were patterned onto the pentacene layer through the shadow mask using the spray-coating method. The channel length and width were 100 and 1000 μm , respectively. For comparison, pentacene FETs with Au source-drain contacts were also fabricated.

3. Results and discussion

A typical procedure of the heat-up synthesis of Ag nanowires involved a continuous heating of an EG solution containing AgNO_3 , PVP, and a trace amount of FeCl_3 from room temperature to the

reaction temperature of 150°C at a rate of $1.4^\circ\text{C}/\text{min}$, followed by maintaining the reaction mixture at that temperature for 1.5 h. Figure 1a and b, shows typical scanning electron microscopy (SEM) images of the product from the heat-up synthesis. It can be seen that Ag nanowires were obtained as the major product in a high yield. The nanowires had an average length and diameter of 21 μm and 84 nm, respectively (Figures 1c and S1). The as-synthesized product contained very few particles with sizes of 50–100 nm. For comparison, we also conducted the synthesis using a hot-injection method, in which AgNO_3 precursor dissolved in EG was rapidly injected to an EG solution of PVP and FeCl_3 that had been preheated to the reaction temperature of 150°C . In this hot-injection synthesis, the molar concentrations of all the reagents in the reaction mixture were kept the same as in the heat-up synthesis. The SEM analysis revealed that the product from the hot-injection synthesis mainly contained polyhedral nanocrystals in addition to a small portion of nanowires (Figures 1d and S2). Most of the polyhedral nanocrystals had a cubic shape and sizes of 100–150 nm. These results clearly indicate that the heat-up process promotes the formation of Ag nanowires.

Silver nanostructures dispersed in a liquid medium display a color due to surface plasmon resonance (SPR), which depends on their size and morphology [13,24]. To investigate the morphological evolution of Ag nanostructures during the synthesis, we performed UV-vis spectroscopy analysis. Figure 2a shows UV-vis spectra recorded at different growth stages of Ag nanowires in the heat-up synthesis. At $t = 90 \text{ min}$, an absorption peak centered at 420 nm appeared, indicating the formation of Ag nanoparticles. The transmission electron microscopy (TEM) analysis revealed that the sample taken at this stage mainly contained Ag nanoparticles with sizes of 10–20 nm, and that they had multiple-twinned structures, as indicated by an inhomogeneous contrast inside each nanoparticle (Figure 2b). A high-resolution TEM (HRTEM) image of a single nanoparticle confirmed its multiple-twinned structure consisting of multiple domains with a twin boundary between two neighboring domains (Figure 2c). This observation indicates that the formation of multiple-twinned seeds is favored at the nucleation stage of the heat-up synthesis. As the reaction proceeded, the optical signature of Ag nanowires began to appear, as indicated by two peaks at 350 and 380 nm in the UV-vis spectrum recorded at 135 min [8]. The peak at 380 nm is associated with the transverse plasmon resonance of Ag nanowires. These two peaks were further increased in intensity with prolonged reaction times. The TEM image of the sample taken at 150 min showed that a large portion of multiple-twinned seeds had grown into nanowires and nanorods (Figure 2d).

Figure 3a shows UV-vis spectra recorded at different stages of the hot-injection synthesis. At the very early stages of the synthesis, a narrow absorption peak developed at 407 nm, which can be attributed to in-plane dipole SPR of spherical Ag nanoparticles [13]. A TEM image of the sample taken at 30 min revealed the formation of Ag nanoparticles with a nearly spherical profile and sizes of 10–30 nm (Figure 3b). Most of the nanoparticles were homogeneous, indicating that they had a single-crystal structure without twinning. The crystallinity of the nanoparticles was further confirmed by the HRTEM analysis. The HRTEM image in Figure 3c clearly shows a highly ordered, continuous fringe pattern for a single-crystalline nanoparticle. At $t = 60 \text{ min}$, a broad band was observed at 480 nm, which can be assigned to SPR of Ag nanocrystals with a cubic shape [13]. A TEM image of the sample taken at this stage confirmed the formation of Ag nanocubes (Figure 3d).

It was found that chloride ions are necessary for the high-yield formation of Ag nanowires. As a control experiment, we have conducted the heat-up synthesis in the absence of chloride ions. In this case, Ag nanocrystals with large sizes and irregular shapes

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