Silver nanostructures synthesis via optically induced electrochemical deposition

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We present a new digitally controlled, optically induced electrochemical deposition (OED) method for fabricating silver nanostructures. Projected light patterns were used to induce an electrochemical reaction in a specialized sandwich-like microfluidic device composed of one indium tin oxide (ITO) glass electrode and an optically sensitive-layer-covered ITO electrode. Silver polyhedral nanoparticles, triangular and hexagonal nanoplates, and nanobelts were controllably synthesized in specific positions at which projected light was illuminated. The silver nanobelts had rectangular cross-sections with an average width of 300 nm and an average thickness of 100 nm. By controlling the applied voltage, frequency, and time, different silver nanostructure morphologies were obtained. Based on the classic electric double-layer theory, a dynamic process of reduction and crystallization can be described in terms of three phases. Because it is template- and surfactant-free, the digitally controlled OED method facilitates the easy, low cost, efficient, and flexible synthesis of functional silver nanostructures, especially quasi-one-dimensional nanobelts.

Compared with their bulk counterparts, nanostructured materials (NSMs) are fascinating topics of research because of their size-dependent novel physical, chemical, optical, and magnetic properties. The dimensionality of NSMs and its influence on their applications have been fully studied, especially one-dimensional (1D) nanostructures. Besides dimensionality, morphology is another important factor that influences the unique properties of NSMs. Metallic nanostructures with fine size- and shape-controllability show great potential applications in electronic nanodevices, biological diagnostics, and surface-enhanced Raman scattering (SERS) detection. For example, the controllability of the dimensions and aspect ratios of one-dimensional silver nanostructures such as nanowires and nanorods has been extensively studied for applications in flexible conductors and sensors. Nanobelts, or nanoribbons, as quasi-one-dimensional nanostructures, were first proposed for semiconducting oxides, and have attracted extensive attention for those substrates as well as various metal materials because of their well-defined geometrical morphologies with rectangular cross-sections, potential applications in bio-nanodevices, and better inherent high-temperature stability.

To date, a wealth of methods is available for generating silver nanobelts, including template-directed methods, seed-mediated methods, galvanic-cell reaction approaches, and electrochemical reduction methods. Liu et al. presented an electrochemical silver mirror reaction in anodic aluminum oxide (AAO) nanochannel templates to grow silver nanobelts with dimensions that depended on the AAO template. It has been demonstrated that large-scale ultralong silver nanobelts can be synthesized at the interface between dibutyl sebacate (DBS) and silver nitrate solutions, which serves as a soft template, via a chemical electro-deposition technique. By using biomass-derived monolithic activated carbon (MAC) as a template, Zhao et al. reported a galvanic-cell reaction method to obtain silver nanobelts with widths of 1.09 μm and a thickness of 0.29 μm, in high yield. Recently, they improved the method by forming metallic particles on the MAC surface as growth initiators prior to nanobelt growth, and harvested silver nanobelts with widths as low as tens of nanometers and thicknesses of ca. 13 nm. Zhu et al. reported an electrochemically modulated reduction method using a sacrificial cathode...
electrode with a nanochannel template to fabricate silver nanobelt-bundle arrays that were 25 nm thick, 300 nm wide, and 50 μm long. These methods always require templates, or complex surfactants as capping agents, to guide the anisotropic quasi-1D nanobelt growth, which makes the fabrication process complex and inflexible. Additionally, external templates and agents have the potential to introduce impurities and contaminants into the final product. In this paper, we present a template- and surfactant-free method for producing different silver nanostructure morphologies, especially silver nanobelts with rectangular cross-sections, via optically induced electrochemical deposition (OED) in a microfluidic device. By virtue of an optically induced electrokinetics (OEk) platform previously developed by our group, we use programmable light patterns to produce controlled and localized electric fields in a photosensitive microfluidic chip, thus inducing the local electrochemical deposition of silver nanostructures. This new method has several advantages over traditional electrochemical reduction approaches: it offers a significant reduction in fabrication time (in terms of several seconds), is reagent-free (without the need for extra reductant or surfactant), and is template-free (with no lithographic process or complicated pre-elaboration). We have studied the parameters to controllably tune the final morphology of the silver nanostructures. We believe that this simple approach provides new opportunities to flexibly produce structured and functional nanomaterials for applications in fields such as photonics, biology, electronics, and other interdisciplinary areas.

**Methods**

**Materials and OED system.** Silver nitrate (AgNO₃, >99.8%; AR), purchased from Sigma Aldrich, was dissolved in Millipore water (resistivity, 18.2 MΩ, Millipore Systems) to prepare sample precursor solutions at concentrations of 10, 50, 100, and 200 mmol/L. The solutions were degassed in an ultrasonic cleaner at 40 kHz for 20 min (KUDOS, SK5210LHC) and further filtered through a 0.22 μm Millipore filter to remove undissolved solute. Figure 1 shows a schematic diagram of the experimental OED system, which includes three modules, as described in our earlier papers. In brief, we use a computer equipped with graphics software to generate programmable light patterns on demand, which are projected on the sandwiched OEk microfluidic chip by an LCD projector (VPL-F400X, Sony, Japan) and an objective (CF Plan 50X/0.55 EPI ELWD, Nikon, Japan). As shown in the enlarged circular area (Fig. 1), the sandwich-like OEk microfluidic chip, assembled from a top layer of indium tin oxide (ITO) glass and a bottom layer of ITO glass coated with a 1 μm film of hydrogenated amorphous silicon (α-Si:H) by the plasma-enhanced chemical vapor deposition (PECVD) method, is separated by a 60 μm spacer to form a reaction chamber. The α-Si:H film is a photoconductive layer which has a low dark conductivity of 10⁻¹¹ S/m and an augmented illuminated conductivity of 10⁻⁵ S/m due to its photo-activated electron-hole pairs. The entire microfluidic module is mounted on a three-dimensional adjustable platform for automatic motion control, monitored by a charge-coupled device camera (CCD, DaHeng Image DH-SV1411FC, China), and the alternating current (AC) voltage is applied by a signal generator (Agilent 33522A, USA).

**Preparation and characterization of silver nanostructures.** The formulated silver precursors with different concentrations were injected into the OEk chip and powered by a sinusoidal AC voltage with a frequency and magnitude in the range of 1 to 100 kHz and 2 to 15 Vpp respectively. After the fabrication process, the prepared silver nanostructures were placed on the substrate, gently rinsed with anhydrous ethanol, and air dried at room temperature. Morphology observation was performed on a scanning electron microscope (SEM, Zeiss EVO MA, Germany). Dimensional data were characterized and collected via atomic force microscopy (AFM, Bruker Dimensional Icon, USA).
Results and Discussion

Virtual electrode-solution interface process. In an electrochemical reduction system, the kinetics at the interface between the electrode and bulk solution plays a pivotal role in the formation of the final products. In our OED system, at the interface between the illuminated solid α-Si:H substrate (namely, the virtual electrode) and bulk solution, a thin electric double layer (EDL, typically several nanometers) provides the voltage potential, reactive species, and environment for the overall reaction. Figure 2(a) shows a simplified equivalent circuit model of the OEK chip, where $C_{\alpha}$ and $R_{\alpha}$ denote the capacitance and resistance of the α-Si:H layer, $C_L$ and $R_L$ denote the capacitance and resistance of the bulk solution, and $C_{EDL}$ and $R_{EDL}$ indicate the equivalent capacitance and resistance of the EDL between the solid electrode and bulk solution, respectively, which vary depending on the applied voltage. The OED process described in Fig. 2(b) can be divided into three phases. Phase I represents the reduction of silver ions (Ag(I)) to elemental silver atoms (Ag(0)). This stage includes the mass transfer of Ag(I) from the bulk solution to the electrode-solution interface, and the electrochemical reduction of Ag(I) into Ag(0) at the EDL layer close to the virtual electrode under the effects of dynamic electron transfer. Phase II describes the nucleation and primary crystallization processes for the reduced ad-atoms (M$_{ad}$) from seeds to nanoparticles (NPs). Phase III describes the crystal growth of the primary crystal nanostructures. The enlarged circular area shows the detailed structure of the bottom α-Si:H substrate. This figure has been enlarged in one direction for clarity.

Optimal parameters for synthesis of silver nanostructures. We examined the influence of the external parameters on silver deposition in the OED system. The concentration of the silver nitrate precursor solution was important for the formation of silver nanostructures. For the concentration series 10, 50, 100, and...
200 mmol/L, larger precursor concentrations were found to increase the deposition speed, which is favorable for silver electrode deposition, as described in our previous paper. On the other hand, the synthesis of silver nanobelts requires anisotropic control over the deposition process, which needs a relatively slow deposition speed, so the medium concentration of 50 mmol/L was selected for further experiments.

As the voltage was increased from 2 to 15 Vpp, the silver reduction speed was increased. When the voltage was below 2 Vpp, the current density in the EDL near the virtual electrode was insufficient for reduction of the Ag(I) into Ag(0). In contrast, when the voltage exceeded 15 Vpp, the stronger voltage potential usually damaged the α-Si:H layer, which should preferably be avoided. The voltage range of 5 to 10 Vpp was selected as favorable.

The frequency of the applied voltage is a key factor in the control of the final product's nano-structural morphology, because it greatly influences the properties of the EDL. As shown in Fig. 3, we investigated the influence of the frequency on the deposition sites of the silver nanostructures. When the voltage frequency is below 10 kHz, the reduced silver nanostructures seem to be repelled from the grid-shaped illuminated virtual electrode area, and settle instead at the boundaries of the illuminated pattern. When the voltage frequency exceeds 10 kHz, deposition occurs mainly in the illuminated areas, in accordance with the defined virtual electrode. From our experimental results, a frequency between 20 and 50 kHz should be optimal for silver electrode deposition and will reproduce the designed light pattern with high fidelity. When the frequency is increased above 50 kHz but below 100 kHz, the silver deposition is somewhat sparse due to the reduced deposition cycle. In this range of frequency, the depositions tend to form anisotropic nanostructures such as thin silver nanosheets, triangular nanosheets and nanobelts.

The deposition time was another important factor. The deposition thickness of the silver structures is positively correlated to the deposition time, at the proper frequency and amplitude of the applied voltage. Here, we focused on the fabrication of silver nanobelts at a frequency of 50 kHz and amplitude of 5 Vpp. Figure 4 shows a sequence of silver deposition images recorded at times from 1 to 13 s by SEM. Over time, the continuously reduced Ag(0) is adsorbed on the active sites of already formed primary seeds, crystallizes, and grows into tiny silver fragments, and then, thin silver sheets. These freshly formed silver thin sheets are potential sites for the subsequent growth of silver nanobelts, which can be found in Fig. 4(e–m).

**Morphologically controlled synthesis of silver nanostructures.** Compared to traditional electro-chemical systems, our OED system is sufficiently flexible and programmable for producing optically defined diverse virtual electrodes to control the growth of silver nanostructures. Figure 5 shows silver nanostructures deposited in different electrode configurations, which were defined by optical patterns. The large illuminated area of a solid circle in Fig. 5(a) resulted in massive polyhedral nanoparticles, whereas the relatively focused and reduced areas in Fig. 5(c) obtained larger polyhedral nanoparticles including octahedra and stacked hexagonal nanoparticles under a voltage amplitude of 5 Vpp. Figure 5(b,d) reveal denser and larger structures assembled from plate-like silver polyhedra under augmented voltage amplitudes of 10 Vpp. Larger light pattern areas provide...
correspondingly larger virtual electrode areas which simultaneously increase the quantity of reduced silver atoms at the same solution concentration, and thus favor homogenous nucleation and the synthesis of small nanoparticles. With decreased virtual electrode areas triggered by focused light patterns, the deposited silver nanostructures tend to ripen and form larger nanostructures, such as silver octahedral nanoparticles and hexagonal nanoplates.

To obtain silver nanobelts, we set the applied voltage at 50 kHz and 5 V<sub>pp</sub>, which is favorable for the synthesis of silver anisotropic nanostructures rather than compact silver electrodes. By kinetically controlling the deposition process, the reduced silver atoms were deposited on already formed seeds in phase II and crystallized into primary polyhedral nanostructures, rather than forming fresh nucleation sites and resulting in massive silver

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**Figure 4.** Time-dependent growth morphology during silver deposition. (a–m) show the detailed deposition densities based on times of 1–13 s, in sequence. The amplitude and frequency were 5 V<sub>pp</sub> and 50 kHz, respectively. All scale bars represent 1 μm.

**Figure 5.** Primary silver crystallization structures under local electrochemical reaction defined by programmable virtual electrodes. (a) Silver crystal nanoparticles with a solid circular virtual electrode. (b) Stacked silver hexagonal nanoplates with a crossed virtual electrode. (c) Crystallized silver octahedra and hexagonal silver nanoplates with focused dot-shaped virtual electrodes. (d) An array of silver nanoparticles assembled into dense micropillars with focused dot-shaped virtual electrodes. The delamination was caused by the post-rinsing process. The insets show the enlarged detailed morphologies of the silver deposits with different virtual electrodes. The deposits in images (a,c) were formed at voltage conditions of 20kHz/5 V<sub>pp</sub>, whereas (b,d) were formed at 20kHz/10 V<sub>pp</sub>. Inset scale bars in (a–c) represent 1 μm. Inset scale bar in (d) represents 2 μm.
nanoparticles. Figure 6(a) displays a grid-shaped silver deposit decorated with interconnected silver nanobelts, and Fig. 6(b) presents an array of silver nanobelts stemming from a single dot deposited with a dot-shaped virtual electrode. The enlarged area shows the detailed view. The maximum length of the silver nanobelt was ca. 300 μm. (d) A single straight silver nanobelt originating from a silver dot deposit. (d1) and (d2) show the enlarged original point and terminal morphology of the single silver nanobelt in (d). (e) A curled silver nanobelt, which shows the material’s flexibility. (f) SEM image showing a single silver nanobelt with a 120° turn. (g) Possible growth mechanism of silver nanobelts along two neighboring edges of the primary silver hexagonal nanoplates. The nanobelts exhibit 120° turns in the growth direction under the possible fluctuation of conditions. (h) AFM image of two interconnected nanobelts. (j) Rectangular cross-section of a single nanobelt (indicated by the red dashed line in (i)) shows a width of 500 nm and thickness of 50 nm. The inset shows 3D AFM image of the nanobelts in (i).
Conclusion

In summary, we have presented a flexible OED system for the controllable synthesis of silver nanostructures with various morphologies and configurations. By fine-tuning the applied voltage and deposition time, silver polyhedral nanoparticles, hexagonal silver nanoplates, and especially, silver nanobelts, were synthesized. The fabrication process is template-free and agentless. The obtained silver nanobelts were rectangular in cross-section with an average width of 300 nm, average thickness of 100 nm, and length of about 300 μm. A possible theory of silver nanobelt formation process is also discussed in this paper in terms of growth along two neighboring sides of a primary hexagonal silver nanoplate. We believe that the OED system described in this paper has the potential for use in the deposition of other metals as well as nanostructure synthesis with diverse functional configurations.

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Author Contributions

W.J.L. and P.L. proposed the basic idea. W.J.L., H.Y., L.L., G.L. and Y.W. supervised the project. P.L. designed and carried out the experiments and analyzed the data. F.W. assisted in the experimental processes. P.L. and N.L. participated in the discussion and writing of the manuscript.
Additional Information

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