Fast Track Communication

A simple method of growing silver chloride nanocubes on silver nanowires

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Abstract

The growth of AgCl nanocubes directly on the sidewalls of Ag nanowires is demonstrated. The nanocubes can be simply obtained through extended low temperature annealing of polyol-synthesized silver nanowires in a vacuum. The length of time and temperature of the anneal and the diameter of the nanowire affect the size and density of the nanocubes obtained. It is hypothesized that the AgCl material is supplied from reactants leftover from the silver nanowire synthesis. This novel hybrid nanostructure may have applications in areas such as photovoltaics, surface enhanced Raman spectroscopy, and photocatalysis.

Keywords: hybrid nanostructure, silver nanowires, silver chloride nanocubes

(Some figures may appear in colour only in the online journal)

1. Introduction

The crux of nanotechnology is exploiting the unique properties that arise when material feature sizes are on the order of or smaller than $\sim100$ nm. The size, shape, and composition of nanostructures can all significantly affect their characteristics [1–10]. For example, the size of a nanostructure can lead to changes in surface energy, electronic band structure, and thermal conductivity, among many other properties [11–16]. Because of this, a multitude of nanostructures such as spheres, wires, cubes, plates, and polyhedra of varying sizes have been synthesized and studied over the past couple of decades [1–3].

Integrating more than one shape, feature size, and/or material into one hybrid nanostructure can impart increased functionality [17–23]. In this work, nanocubes are grown on the surface of nanowires. Nanowires, unlike nanocubes and nanoparticles, have one long dimension. This long axis can be used to transport electrical current and heat, it makes nanowires easier to contact for use in devices, and it allows for a connected network to be achieved at a far lower particle density, the latter being useful for applications such as transparent electrodes. By adding nanocubes on nanowire sidewalls, the advantages of nanocubes, such as their larger surface-area-to-volume ratio and surface plasmon resonance at different wavelengths, can be combined with nanowires. Furthermore, if the nanocubes and nanowires are different materials, the properties of each material can be exploited and combined in a useful way. Nanowires with nanoparticles on their surface have been used in applications such as sensors, catalysts, and photovoltaics [18–20].

There exist several methods of decorating the surface of nanowires with nanoparticles or nanocubes. The nanowire is first synthesized and nanoparticles are then grown or attached on their sidewalls through methods such as chemical vapour deposition or solution synthesis [24, 25]. For example, for surface enhanced Raman spectroscopy (SERS) applications, silver nanocubes were attached onto silver nanowires by mixing pre-synthesized individual nanocubes and nanowires together in solution [26]. However, the spatial orientation of the nanocubes with respect to the nanowire sidewalls was not controllable. This is not ideal since the maximum surface plasmon resonance happens when the face of a nanocube is flat against the sidewall of the nanowire [26]. In another report, silver phosphate cubes were grown around silver nanowires in...
solution. The average edge length of the cubes however was 500 nm, 10 times larger than the diameter of the nanowire and too big to be used in nanoscale applications [27].

In this work we show for the first time that nanocubes can be synthesized directly on the sidewalls of a metallic nanowire through a simple anneal in a vacuum. This is also the first report of AgCl nanocube/Ag nanowire hybrid structures. The size and density of the nanocubes are controlled through the annealing temperature and time. The cubes lie flat against the nanowire facets and are likely epitaxial. These structures have many potential applications. Firstly, the nanocubes increase the surface area of the nanowire which is beneficial for catalytic, sensing, and antibacterial applications [28, 29]. Secondly, films of silver nanowires have been used as substrates for SERS applications to increase signal intensity [30]. The addition of nanocubes on their surfaces can further enhance the SERS signal [31], which improves sensitivity of detection. Thirdly, films of silver nanowires are a promising transparent electrode for use in photovoltaic devices [32]. Having nanocubes on the nanowire surfaces may increase light absorption in a thin-film solar cell due to increased light scattering, as has been shown to be the case when nanoparticles are added to the transparent electrode of solar cells [33–35]. Fourthly, the nanocubes are silver chloride, which is a visible-light driven photocatalyst useful for water splitting and the decomposition of organic pollutants [36, 37]. Their attachment to a silver nanowire can enhance their photocatalytic performance since the silver can promote charge separation and transport generated electrons [29, 38, 39]. In addition to these potential applications, this communication helps to explain why many groups observe nanoparticles on silver nanowires in transparent electrodes [40, 41].

2. Experiment

Poly(vinylpyrrolidone) (PVP) directed polyol synthesis is a solution-based method that can be used to synthesize crystalline silver nanostructures of various well-controlled shapes. In this method, a mixture of AgNO₃ and ethylene glycol (EG) is gradually added to a solution containing EG, PVP and NaCl, and is heated to 170 °C. Depending on the concentration of AgNO₃ and the molar ratio of AgNO₃ and PVP, various shapes such as nanocubes, nanowires, spheres, and triangular plates can be obtained. For silver nanowire synthesis, the resulting nanowires have a pentagonal cross-section, with 5 \{100\} sidewalls [42, 43].

In this study, two different sizes of polyol-synthesized silver nanowire dispersed in ethanol were commercially

![Figure 1. 90 nm diameter silver nanowires before (a) and after annealing at 100 °C for 3 days (b) and 7 days (c). (d) 200 nm diameter nanowires after annealing at 100 °C for 7 days.](image-url)
Table 1. Density and average size of the nanocubes on nanowires after annealing at 100 °C.

<table>
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<th>3 days</th>
<th>1 week</th>
<th>2 weeks</th>
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<td>90 nm</td>
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<tr>
<td>Density of NCs</td>
<td>1 NC/μm</td>
<td>0.7 NC/μm</td>
<td>0.3 NC/μm</td>
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<td>Average size of NCs</td>
<td>60 nm</td>
<td>80 nm</td>
<td>100 nm</td>
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<td>200 nm</td>
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<tr>
<td>Density of NCs</td>
<td>1 NC/μm</td>
<td>0.3 NC/μm</td>
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<td>Average size of NCs</td>
<td>80 nm</td>
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obtained; ones with an average diameter and length of 90 nm and 15 μm, respectively (Blue Nano Inc., Charlotte, NC), and 200 nm and 25 μm, respectively (ACS Materials Inc., Medford, MA). Silicon wafer chips were cleaned in a sonication bath with ethanol, acetone and distilled water, each for one minute. The as-received nanowires were diluted with ethanol and drop cast onto the Si. They were then annealed in low vacuum for various lengths of time, ranging for 3 to 14 days, and at temperatures ranging between 100 °C to 150 °C. Scanning electron microscopy (SEM) images were taken of the samples before and after annealing. The average density and size of the nanocubes were calculated from these SEM images by measuring a minimum of 100 nanocubes for each experimental condition. Transmission electron microscopy (TEM) samples were prepared by mechanically rubbing the silver nanowires from the silicon wafer onto TEM grids. Energy dispersive x-ray spectroscopy (EDS) spectra were collected to determine the chemical composition of the nanocubes and nanowires.

3. Results and discussion

An SEM image of the 90 nm silver nanowires before annealing is shown in figure 1(a). The sidewalls of the nanowires are smooth. After annealing for 3 days at 100 °C (figure 1(b)), nanocubes of various sizes are observed on the surface of the nanowires. All cubes appear to have smooth facets and sharp corners. Almost all are oriented such that a cube face lays flat against the nanowire sidewall, and with cube edges aligned parallel to the nanowire axis. Their edge lengths range from 20–120 nm. After annealing for 7 days (figure 1(c)), the nanocubes are larger, with edge lengths ranging from 40–200 nm, but are less dense than with the 3 day anneal. In general, as shown in table 1, as the nanowires are annealed for longer times the obtained nanocubes are larger and less dense, likely because of the increased time for Oswald ripening to occur.

The nanowire diameter also affects the size and density of the nanocubes. An image of 200 nm diameter nanowires annealed for 7 days at 100 °C is shown in figure 1(d). In general (table 1), nanocubes obtained on the larger diameter nanowires are larger and less dense compared to those on thinner nanowires.

The nanowires were also annealed at temperatures of 125 °C and 150 °C. Similar to increasing annealing time or nanowire diameter, higher temperatures also led to larger and less dense nanocubes. However, even at 125 °C the nanocubes had average edge lengths of more than 500 nm. This large size is not as attractive for nanoscale applications and thus 100 °C is a more preferable annealing temperature.

EDS spectra of 90 nm nanowires annealed for 7 days at 100 °C in a vacuum are displayed in figure 2. In figure 2(a), the electron probe was focused on a section of a nanowire away from a nanocube. Other than carbon, only silver was detected. When the probe was focused on a nanocube (figure 2(b)), the spectrum contained an additional peak corresponding to chlorine. This suggests that the nanocubes are AgCl, since AgCl is the only compound occurring in the silver-chlorine system. Moreover, it is known that AgCl nanocubes form in the presence of Ag⁺, Cl⁻, and PVP (more discussion on this later). Attempts at TEM imaging and the collection of diffraction patterns to characterize the morphology, lattice structure, and the epitaxial relationship of the nanocubes to the nanowires were made. However, the nanocubes quickly decomposed upon exposure to the electron beam preventing such characterization. This decomposition and the inability to image AgCl nanocubes in the TEM has been reported by others [44, 45].

In the polyol synthesis of silver nanowires, silver ions (Ag⁺) bond with chloride ions (provided by NaCl) and form AgCl nanocrystals to control the growth rate of the silver...
nanostructures [46]. Some AgCl nanocrystals remain in the solution after the synthesis of the nanowires is terminated. When the nanowires are deposited on the Si substrate, the solvent evaporates and the AgCl nanocrystals remain on the surface of the nanowires and the substrate. Elevated temperatures facilitate the diffusion of these nanoparticles. We hypothesize that the nanocubes form because of Oswald ripening of these particles, and the cubic shape is due to the presence of PVP which selectively binds and stabilizes the \{100\} surfaces of AgCl [29]. It has been shown that when AgCl particles are synthesized in solution by mixing AgNO₃, NaCl, and PVP, and heating the solution to 80 °C, AgCl nanocubes with \{100\} sidewalls are obtained [29]. As mentioned above and seen more clearly in figure 3, the nanocubes have sharp edges and their spatial orientation is not random, but rather lies flat on the \{100\} nanowire sidewalls with the cube walls parallel to the nanowire axes. Thus it is likely that the nanocubes are epitaxially related to the nanowire. If the cube faces are \{100\}, as is the case for all AgCl nanocubes in the literature [29, 47, 48], the cube edges are thus along the \(\langle 100 \rangle\) directions. The axes of polyl synthesized Ag nanowires are \(\langle 110 \rangle\) [49]. The \{100\} planes of the AgCl and Ag are thus rotated in-plane 45 degrees with respect to one another and in this orientation, there is only a 4% lattice mismatch.

Further investigation is required to determine the mechanism of nanocube formation. Nanocubes were only observed on the nanowires and not on the Si substrate. This may be because the Ag nanowires promote nanocube growth in some manner, or merely because silver has a higher surface energy than the SiO₂ surface of the silicon substrate and growth and diffusion are easier on higher energy surfaces [50]. The nanowire sidewalls of \{100\} may be particularly favorable because not only are they not the lowest energy plane of an FCC material like Ag, but also because AgCl(100) has a much larger lattice mismatch with Ag(110) and Ag(111) planes making epitaxy on these planes unlikely.

To investigate the effect of leftover components from the nanowire synthesis solution, some nanowire samples were washed with acetone before annealing. Annealing the washed nanowires at 100 °C for 7 days did not result in any nanocube formation which is likely due to the absence of any AgCl nanocrystals. Unwashed silver nanowires were also annealed in air rather than in vacuum. Annealing at 100 °C in air for 3 days resulted in the formation of irregularly shaped nanoparticles on the nanowire sidewalls as well as a few long rectangular prisms with edge lengths of up to 1 μm. The irregular shapes may be due to the absence of PVP for shape control, as PVP decomposes in air below 200 °C in less than one hour, and would be expected to decompose at lower temperatures at longer annealing times [51]. The irregular shapes may also, or instead, be due to the reaction of silver with oxygen and sulfur atoms in the air [52].

4. Conclusions

This study shows that AgCl nanocubes can be synthesized on the sidewalls of silver nanowires with a simple annealing process in a vacuum. The size and density of the nanocubes are dependent on the temperature and length of the anneal, as well as the diameter of the nanowires. The presence of nanocubes on the nanowires could add extra functionality and future work will involve testing them for applications.

Acknowledgments

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References


Figure 3. Nanocubes with sharp edges lie flat on the surface of silver nanowires, with sidewalls parallel to the nanowire axis. These nanocubes were obtained by annealing 200 nm diameter nanowires at 100 °C for 3 days.


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