Morphological Evolution of Ag$_2$O Microstructures from Cubes to Octapods and Their Antibacterial Activities

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The selective synthesis of inorganic oxides with unique morphology has attracted considerable interest because of their morphology-dependent properties and applications.\textsuperscript{1-3} Efforts on most synthetic inorganic oxides have been focused on preparing a stable morphology rather than providing a strategy for producing various morphologies. Therefore, well-controlled methods for synthesizing inorganic oxides with a systematic evolution of morphology should be developed by adjusting the experimental conditions. Among the morphology-controlled syntheses of inorganic oxides, cuprous oxide (Cu$_2$O) has been widely investigated due to its ease of preparation.\textsuperscript{4-8} The morphology-dependent photocatalytic and antibacterial properties of Cu$_2$O were also studied recently.\textsuperscript{9-11} Although Cu$_2$O and silver oxide (Ag$_2$O) have similar cubic crystal structures, relatively little is known about the morphology-controlled synthesis and physical properties of Ag$_2$O.\textsuperscript{12,13} To date, a study of the morphology-dependent antibacterial effect of Ag$_2$O has reported only for different polyhedral shapes including octahedrons, truncated octahedrons, and cubes.\textsuperscript{14} This study provided a simple precipitation method for the morphological evolution of Ag$_2$O from cubes to octapods. Furthermore, the morphology-dependent antibacterial activity of Ag$_2$O against E. coli was also examined.

Ag$_2$O products with various morphologies were prepared from a silver-pyridine (Py) complex solution. Pyridine was used as the ligand for the Ag$^+$ ions. Pyridine combined with the Ag$^+$ ions to form a [Ag(Py)$_2$]$^+$ complex. This complex reacted with OH$^-$ by adding NaOH, which was then dehydrated to produce Ag$_2$O. The chemical reactions producing Ag$_2$O are as follows:

\[ 2 \text{Ag}^+(\text{aq}) + 4 \text{Py} \rightarrow 2 \text{[Ag(Py)$_2$]$^+$} \ (\text{aq}) \]  
\[ 2 \text{[Ag(Py)$_2$]$^+$} \ (\text{aq}) + 2\text{OH}^- \ (\text{aq}) \rightarrow \text{Ag}_2\text{O} \ (\text{s}) + 4 \text{Py} + \text{H}_2\text{O} \]

Figure 1 shows the X-ray diffraction (XRD) patterns of Ag$_2$O prepared with different amounts of AgNO$_3$; (a) 2.5 mL, (b) 5.0 mL, (c) 7.5 mL, and (d) 20 mL.

Figure 2 shows the SEM images of Ag$_2$O prepared with different amounts of AgNO$_3$; (a) 2.5 mL, (b) 5.0 mL, (c) 7.5 mL, and (d) 20 mL.

Figure 1.

Figure 2.
Increasing the amount of AgNO$_3$

**Figure 3.** Schematic morphology of Ag$_2$O microcrystal evolution from cubes to octapods with increasing amounts of AgNO$_3$.

Generally, morphology of a crystal is affected by both kinetic and thermodynamic growth processes.$^{15,16}$ Crystals with simple shapes, such as spheres, cubes and octahedrons, are formed to minimize the total surface free energy in thermodynamic equilibrium. However, crystals with branched shapes, such as hexapods and octapods, are formed by kinetic growth processes. The reaction rate for forming Ag$_2$O is very slow at 2.5 mL of AgNO$_3$. Therefore, a thermodynamically controlled reaction occurred, and cubic Ag$_2$O was formed with the smallest amounts of AgNO$_3$. As the amount of AgNO$_3$ increased, the reaction rate of Ag$_2$O formation increased. Larger void spaces were formed at the cubic crystal planes by increasing the reaction rate. Finally, a large increase in reaction rate with a large amount of AgNO$_3$ improved the degree of branching, and the Ag$_2$O morphology finally evolved into an octapod. Therefore, the various morphologies of Ag$_2$O microcrystals in this work were formed by a kinetically-controlled process with increasing amounts of AgNO$_3$.

Figure 3 shows a schematic diagram of the morphological evolution of Ag$_2$O microcrystals with an increasing amount of AgNO$_3$.

Figure 4 shows *E. coli* growth rates in the absence or presence of various Ag$_2$O morphologies. Figure 4 clearly shows that all Ag$_2$O microcrystals caused an *E. coli* growth delay. The incubation times to grow up to 50% (half-maximal growth times) were 5.0, 9.9, 10.3, 11.0, and 12.0 h in the absence and presence of cubic, cubic with small voids, cubic with large voids, and octapods of Ag$_2$O, respectively. Moreover, bacterial growth was dependent on Ag$_2$O morphology. The antibacterial activities of Ag$_2$O prepared in this work were in the following order: cubes > cubes with small voids > cubes with large voids > octapods. This result suggests that the morphology of Ag$_2$O particles affects antibacterial activity. Cubic Ag$_2$O crystals are enclosed by (100) planes. The surfaces of the (100) planes are polar due to alternating layers of the Ag$^+$ cation and O$^2-$ anions. Ag$^+$ ions are toxic and kill bacteria through a denaturation or oxidation mechanism.$^{14,17}$ Therefore, exposing cubic surface Ag$^+$ cations in Ag$_2$O crystals may enhance their antibacterial activity.

Various Ag$_2$O microcrystal morphologies were prepared selectively using a silver-pyridine complex solution. By increasing the amount of AgNO$_3$, the morphology of the Ag$_2$O microcrystals evolved from simple cubes to octapods. Morphology-dependent antibacterial activity of Ag$_2$O against *E. coli* was observed. Exposure of Ag$^+$ cations from the (100) crystal planes of Ag$_2$O may play an important role in the antibacterial activity against *E. coli*.

**Experimental Section**

AgNO$_3$ (Aldrich, 99.0%), NaOH (Aldrich, 97%), pyridine (Aldrich, 99.8%), and dimethyl sulfoxide (DMSO, Aldrich, 99.9%) were used as received. In a typical synthesis of cubic Ag$_2$O, a mixed solution of water (994.2 mL), 0.1 M AgNO$_3$ aqueous solution (2.5 mL), and pyridine (0.848 mL) was prepared, and then a 1.0 M NaOH aqueous solution (2.5 mL) was quickly added to the mixed solution. The molar ratios of AgNO$_3$, pyridine, and NaOH were 1.0, 40, and 10, respectively. The final mixed solution was incubated for 4 h at room temperature. A mixed solution of water (953.22 mL), 0.1 M AgNO$_3$ aqueous solution (20 mL), and pyridine (6.78 mL) was used to prepare the Ag$_2$O octapods, and then a 1.0 M NaOH aqueous solution (20 mL) was quickly added with the same molar ratios of AgNO$_3$, pyridine, and NaOH as those used to prepare cubic Ag$_2$O. The amounts of AgNO$_3$, pyridine, and NaOH used were eight times those for the preparation of cubic Ag$_2$O to the Ag$_2$O octapods. To investigate the morphological evolution of Ag$_2$O, different amounts of AgNO$_3$ (5.0 mL and 7.5 mL) were also used with the same molar ratios of AgNO$_3$, pyridine, and NaOH as those used to prepare the cubic Ag$_2$O. The products were collected following centrifugation at 4000 rpm for 5 min and were sonicated with water and ethanol several times and then dried for 24 h at room temperature. The structure and morphology of the Ag$_2$O products was characterized by powder XRD (PANalytical, X’pert-pro MPD) and SEM (Hitachi S-4300), respectively.

The antibacterial effects of Ag$_2$O on *E. coli* growth rates were also investigated. First, *E. coli* cells were grown to an absorbance of 0.40 at 600 nm. Subsequently, 50 μL of the *E. coli* culture was aliquotted evenly into 1.5 mL of Luria-Bertani (LB) media containing 2 μg/mL of the various forms of Ag$_2$O. The inoculated *E. coli* cells were grown further in a
37 °C shaking incubator for various incubation times. *E. coli* densities were determined by the optical density at 600 nm. Ag₂O crystals were dissolved in DMSO to prepare the stock cubic and octapod Ag₂O crystal solutions. The optical density was monitored using a UV-vis spectrophotometer (Beckman DU-7500).

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**References**