DOI: 10.1002/chem.201000563

Synthesis of Ag_2O Nanocrystals with Systematic Shape Evolution from Cubic to Hexapod Structures and Their Surface Properties

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Abstract: We report the development of a facile method for the synthesis of Ag_2O crystals with systematic shape evolution from cubic to edge- and corner-truncated cubic, rhombicuboctahedral, edge- and corner-truncated octahedral, octahedral, and hexapod structures by mixing $AgNO_3$, NH_4NO_3, and NaOH at molar ratios of 1:2:11.8. A sufficient volume of NaOH solution was first added to a mixture of $AgNO_3$ and NH_4NO_3 solution to promote the formation of $Ag(NH_3)_2^+$ complex ions and the growth of Ag_2O nanocrystals with good morphological control. The crystals are mostly submicrometer-sized. X-ray diffraction, scanning electron microscopy, and transmission electron microscopy characterization has been performed to determine the crystalline surface facets. A band gap value of approximately 1.45 eV has been found for the octahedral Ag_2O crystals. By changing the molar ratios of $AgNO_3/NH_4NO_3/NaOH$ to 1:2:41.8, corner-depressed rhombicuboctahedra and elongated hexapods were obtained as a result of enhanced crystal growth along the [100] directions. Smaller nanocubes with average sizes of approximately 200 and 300 nm and octapods can also be prepared by adjusting the reagent molar ratios and their added volumes. Both the octahedra and hexapods with largely silver atom-terminated {111} surface facets responded repulsively and moved to the surface of the solution when dispersing in a solution of positively charged methylene blue, but can be suspended in a negatively charged methyl orange solution. The cubes and octapods, bounded by the {100} faces, were insensitive to the molecular charges in solution. The dramatic facet-dependent surface properties of Ag_2O crystals have been demonstrated.

Keywords: copper oxide · crystal growth · morphology control · nanostructures · silver oxide

Introduction

Silver(I) oxide (Ag_2O) is a p-type semiconductor with a reported band gap of 1.46 eV.[1] With this low band-gap energy, Ag_2O may be considered as an attractive light absorption material for use in photovoltaic cells.[1] Ag_2O powder can be easily prepared by mixing solutions of silver nitrate and an alkali hydroxide. Ag_2O has the same cubic cuprite crystal structure as that of Cu_2O (a body-centered cubic packing of oxygen atoms with copper atoms occupying one-half of the tetrahedral sites). A wide variety of Cu_2O nano- and microstructures such as cubes, cuboctahedra, truncated octahedra, octahedra, rhombic dodecahedra, hexapods, and octapods have been prepared by wet chemical, electrochemical deposition, and solvothermal synthesis methods.[2–11] The synthesis of Cu_2O nanocrystals with systematic shape evolution from cubic to octahedral and hexapod structures has also been demonstrated.[3,4] In addition, plane-selective surface properties of Cu_2O crystals have been studied by using Cu_2O crystals with sharp faces.[4,12] Au–Cu_2O core–shell heterostructures with precise morphological control of the shells have recently been fabricated to add to the structural variety of Cu_2O crystals.[13] Considering the opportunities to extend the property examinations of Cu_2O nanocrystals to Ag_2O nanostructures and the seemingly simple preparation of Ag_2O crystals, it is surprising that very few reports are available describing the synthesis of Ag_2O nano- and microcrystals with well-defined morphologies. Penner et al. have shown that Ag_2O micro- and nanoparticles can be electrochemically synthesized by anodizing a sacrificial silver wire in a basic aqueous sulfate solution.[14] Cubic particles with a depression in each face and eightfold symmetric octapods were produced. More recently, Ag_2O cubic, truncated octahedral, and octahedral nano- and microcrystals were synthesized by varying the concentrations

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000563.

of $AgNO_3$ and $NH_3{\cdot}H_2O$ used, while keeping the amount of NaOH added constant.[15] The product morphologies obtained are somewhat limited despite a broad range of reagent concentrations used. It is therefore highly desirable to develop synthetic procedures that can more systematically tune the morphologies of Ag_2O nanocrystals formed, and allow the investigation of their comparative surface properties.

In this study, we have successfully developed a procedure for the synthesis of Ag_2O nanocrystals with systematic shape evolution from cubic to octahedral and hexapod structures by adjusting the amounts of NH_4NO_3, $AgNO_3$, and NaOH solutions added to make the reaction mixture, while keeping their molar ratios constant. The degree of branch formation to generate the hexapod structure can also be controlled by raising the amount of NaOH used. Furthermore, we found that the sizes of Ag_2O nanocubes can be tuned within a range by simply varying the concentration of $AgNO_3$ added. Octapods can also be prepared. Their structure characterization has been carefully performed. Using these nanocrystals with mainly {111} or {100} exposed faces (i.e., octahedra, hexapods, cubes, and octapods), we have examined their comparative surface properties by dissolving the crystals in positively charged methylene blue solution or negatively charged methyl orange solution. Octahedra and hexapods with {111} surface facets were found to respond to the molecular charges in the solution.

Results and Discussion

The procedure used to synthesize Ag_2O nanocrystals is illustrated in Scheme 1. Systematic shape evolution of the nanocrystals is achieved by progressively increasing the volume of 0.1 M $AgNO_3$ solution added. The direct reaction of $AgNO_3$ and NaOH can proceed so rapidly that the structures of Ag_2O particles produced cannot be easily controlled. The formation of the $Ag(NH_3)_2^+$ species, followed by its conversion to AgOH and then Ag_2O, enables the growth of Ag_2O nanocrystals with a high degree of morphology control. Systematic shape evolution is thus possible by varying the amounts of $AgNO_3$, NH_4NO_3, and NaOH used but maintaining their molar ratios. NH_4NO_3 was used as the source of ammonia instead of NH_3 solution to ensure the metal complex formation; rapid introduction of NH_3 makes the solution basic such that Ag_2O crystals can form quickly without satisfactory control of their morphologies. The pre-added NaOH of a sufficient amount serves the purpose of forming NH_3 species. The molar ratio of NH_4NO_3 to pre-added NaOH is set at 1:0.9. Final addition of NaOH drives the formation of Ag_2O nanocrystals. To effectively form Ag_2O, a final molar ratio of $AgNO_3$/NaOH at 1:11.8 was found to yield products with excellent morphological control. If the total amount of NaOH added was reduced substantially, initially formed Ag_2O crystals may dissolve and the $Ag(NH_3)_2^+$ complex can form again. The reactions given in Equations (1)–(4) take place to form Ag_2O:

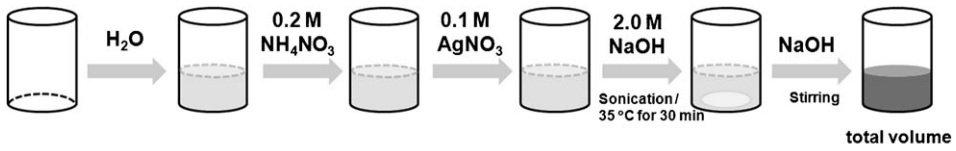
$$NH_4NO_3 + NaOH \rightarrow NH_3 + H_2O + Na^+ + NO_3^- \quad (1)$$

$$AgNO_3 + 2\,NH_3 \leftrightarrow Ag(NH_3)_2^+ + NO_3^- \quad (2)$$

$$Ag(NH_3)_2^+ + NaOH \leftrightarrow AgOH + 2\,NH_3 + Na^+ \quad (3)$$

$$2\,AgOH \leftrightarrow Ag_2O + H_2O \quad (4)$$

Scanning electron microscopy (SEM) images of the Ag_2O crystals synthesized following the procedure depicted in Scheme 1 are shown in Figure 1. By gradually increasing the volume of $AgNO_3$ solution added, and keeping the molar ratios of $AgNO_3$ to NH_4NO_3 and NaOH constant at 1:2:11.8, Ag_2O crystals with systematic shape evolution were synthesized. Particle morphologies change from cubic to edge- and corner-truncated cubic, rhombicuboctahedral, edge- and corner-truncated octahedral, octahedral, and hexapod structures. For this series of geometric transformation, the {100} faces of a cube gradually decrease, while the {111} facets steadily increase to form an octahedron and a hexapod. The proportion of the {110} faces reaches a maximum in a rhombicuboctahedron. Cu_2O microcrystals with a rhombicuboctahedral shape have been reported recently.[16] The Ag_2O octahedra still show a slight edge truncation. The particle sizes are around 370 nm for the cubes, 480 nm for the truncated cubes, 570 nm for the rhombicuboctahedra, 760 nm for the octahedra and truncated octahedra, and 1400 nm for the hexapods (see the Supporting Information Table S1 for average particle sizes and their standard deviations and Figure S1 for particle size histograms). Due to rapid growth of crystals, these particles are generally in the submicrometer-sized range. Figure 2 shows additional SEM images of these Ag_2O crystals viewed



A	4.478 mL	0.25 mL	0.25 mL	22.5 µL	1 mL 0.25 M	6 mL
B	3.955 mL	0.5 mL	0.5 mL	45 µL	1 mL 0.5 M	6 mL
C	3.433 mL	0.75 mL	0.75 mL	67.5 µL	1 mL 0.75 M	6 mL
D	2.910 mL	1 mL	1 mL	90 µL	1 mL 1 M	6 mL
E	1.865 mL	1.5 mL	1.5 mL	135 µL	1 mL 1.5 M	6 mL
F	0.820 mL	2 mL	2 mL	180 µL	1 mL 2 M	6 mL

Scheme 1. Schematic illustration of the procedure used to grow Ag_2O nanocrystals with systematic shape evolution from cubic to hexapod structures. The molar ratio of $AgNO_3/NH_4NO_3$/NaOH is 1:2:11.8.

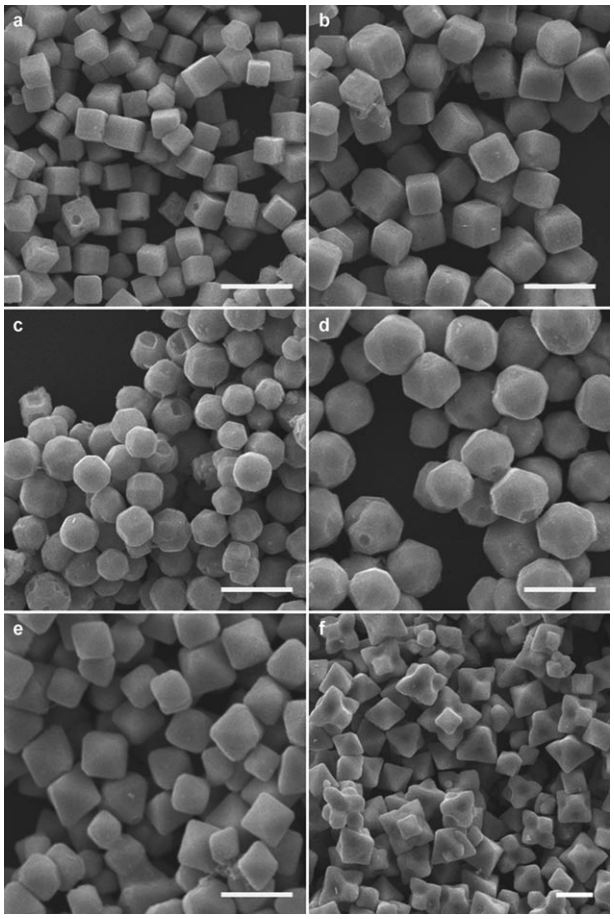


Figure 1. SEM images of the Ag_2O crystals synthesized from samples A–F using the procedure shown in Scheme 1. The particle morphologies are: a) cubes, b) edge- and corner-truncated cubes, c) rhombicuboctahedra, d) edge- and corner-truncated octahedra, e) octahedra, and f) hexapods. The scale bars are all equal to 1 μm.

from two different directions and the corresponding schematic drawings of the particle morphologies. Different crystal facets of a rhombicuboctahedron are also labeled. The mechanism for the formation of these Ag_2O crystals with morphology evolution from cubes to octahedra and hexapods is possibly that as concentrations of the reagents (i.e., $AgNO_3$, NH_4NO_3, and NaOH) in the solution increase, the crystal growth rate along different crystallographic directions is slightly modulated. At lower reagent concentrations, the growth rate along the [111] directions may be faster than that along the [100] directions, resulting in the formation of Ag_2O cubes. At slightly higher reagent concentrations, growth rates along these directions are similar, and rhombicuboctahedra are produced. At even higher reagent concentrations, the growth rates along the [100] directions are enhanced, leading to the formation of octahedra and hexapods. The appropriate reagent concentrations used is also critical to the formation of these crystals with this systematic morphology evolution.

X-ray diffraction (XRD) patterns of the Ag_2O crystals are presented in Figure 3. All the reflection peaks can be matched to those of Ag_2O. The (200) peak is remarkably strong in intensity for the cubes due to their preferential orientation of deposition on substrates with their square faces parallel to the substrate plane. The intensity of the (111) peak increases relative to that of the (200) peak in the truncated cubes. For the rhombicuboctahedra, the (111) and (200) peaks show comparable intensity. The (220) peak also becomes quite strong because of the substantial presence of the {110} faces. The (111) peak dominates for the edge- and corner-truncated octahedra, yet the (200) and (220) peaks still show significant intensities compared to that of the (111) peak. The XRD patterns show essentially only the (111) peak for the octahedra and hexapods, confirming that the hexapods are bounded by the {111} facets. As a result, the (222) peak is also exceptionally strong for the hexapods.

Transmission electron microscopy (TEM) images of four different morphologies of Ag_2O crystals, their selected-area electron diffraction (SAED) patterns, and representative SEM images are provided in Figure 4. The Ag_2O crystals are viewed along the [100] direction of a cube, the [110] direction of a rhombicuboctahedron and an edge- and corner-truncated octahedron, and the [111] direction of a hexapod. Their corresponding SAED patterns were recorded over the circled regions, and the diffraction spots obtained match those expected for Ag_2O. These crystals were found to be highly sensitive to a focused electron beam. Prolonged irradiation of the particles by an electron beam can result in the appearance of silver diffraction spots and even irregular surface features identified to be silver nanoparticles, as verified by lattice fringe images and SAED patterns (data not shown). Thus, diffraction spots of silver have been observed in all the SAED patterns recorded.

Optical properties of the Ag_2O crystals have been examined and the results are presented in Figure 5. The UV/Vis absorption spectra of samples A–F (see Scheme 1) show only light scattering bands due to the relatively large sizes of these crystals. Two to three light scattering bands can be observed for all the samples. The positions of these bands exhibit a progressive red-shift as particle size increases. The diffuse reflectance spectrum of the dried octahedral Ag_2O crystals has been recorded and converted into a plot of $(\alpha h\nu)^2$ versus $h\nu$ for the determination of their band gap energy. A band gap value of approximately 1.45 eV was determined. This value agrees well with the reported band gap energy of 1.46 eV for Ag_2O.[1]

By increasing the concentration of NaOH introduced to bring the final molar ratios of $AgNO_3/NH_4NO_3/NaOH$ to 1:2:41.8 for samples A–F, crystal growth along the [111] directions is inhibited and that along the [100] direction is enhanced (see Figure 6). The volume and concentration of pre-added NaOH are the same as those given in Scheme 1, but the final NaOH solution added are at concentrations of 1–8 M (see the Supporting Information Scheme S1 for the experimental procedure). Under the effect of an enhanced growth rate along the [100] directions, the nanocubes gradually evolve to form corner-depressed rhombicuboctahedra (Figure 6c). The depression over the {111} faces becomes

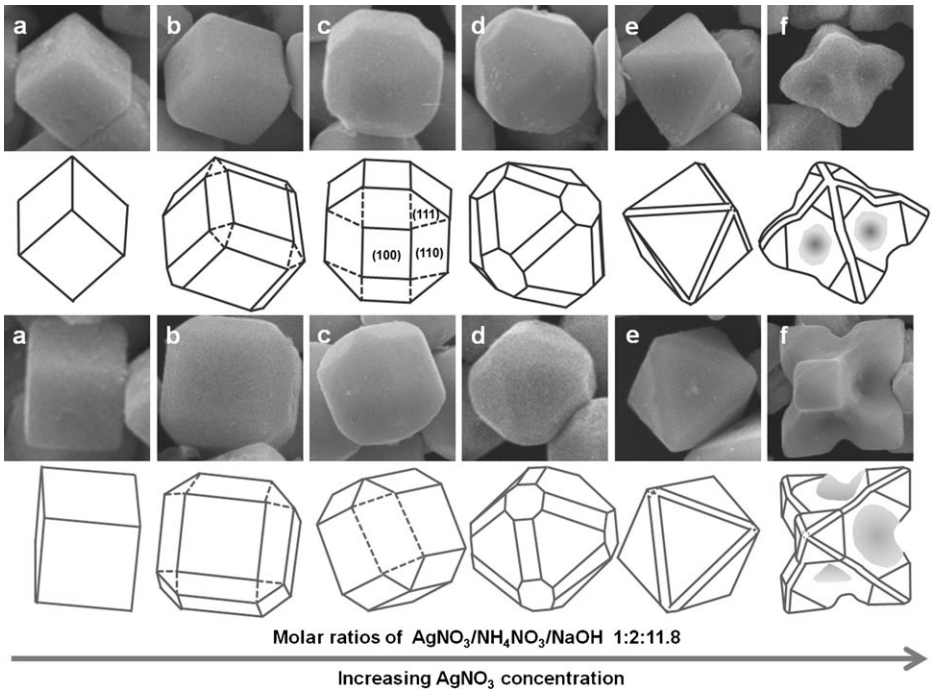


Figure 2. SEM images and the corresponding schematic drawings of the Ag_2O crystals synthesized with morphology evolution from cubic to hexapod structures upon increasing the $AgNO_3$ concentration in the reaction mixture. Two viewing angles are shown for each particle structure.

more pronounced in crystals shown in Figure 6d with the use of 4 M NaOH. Some crystals possess multi-faceted protrusions grown along the six [100] directions. These features are likely to be terminated with mainly {100} end faces and {110} side faces. The arrows marked in Figure 6d help to identify the crystal faces. In some particles, the end faces of these protrusions also exhibit a slight depression. Extended or elongated hexapods are produced with the use of 6 and 8 M of NaOH as a result of the enhanced growth along the [100] directions (Figure 6e and f). The branches in an elongated hexapod have square cross-sections and end with sharp-faced tips resembling that of octahedral corners, implying that each branch is bounded by {111} tip faces. TEM and SAED characterization reveals that the side faces of a branch are bounded by the {110} faces (see the Supporting Information Figure S2). Silver hexapods have also been determined to possess the same crystal faces for their branches.[17] Use of a lower molar ratio of $AgNO_3$/NaOH did not give products with such a pronounced structural change. The formation of these novel structures enrich the variety of Ag_2O nanocrystal morphologies that can be synthesized. A schematic summary of all the experimental conditions used to produce various Ag_2O crystal morphologies is available in Scheme S2 in the Supporting Information.

We found that smaller Ag_2O nanocubes can be synthesized by decreasing the volume of $AgNO_3$ solution used at the same molar ratios of $AgNO_3/NH_4NO_3/NaOH$ as that employed to make Ag_2O crystals with systematic shape evolution from cubic to hexapod structures (that is, 1:2:11.8) (see Figure 7). When 0.125 mL of 0.1 M $AgNO_3$ solution is added, the average nanocube size is approximately 300 nm. Further lowering the volume of the $AgNO_3$ solution added to 0.094 mL, leads to the generation of nanocubes with an average size of approximately 200 nm (see Tables S2 and S3 and Figure S3 in the Supporting Information for the experimental conditions and size distribution histograms). The nanocubes are highly uniform in size. XRD patterns of these smaller nanocubes show essentially the (200) reflection peak (see Figure S4). Similar light scattering bands have been recorded in their UV/Vis absorption spectra with a progressive red shift in the band position as the particle size increases (see Figure S5).

Using the same volume of $AgNO_3$ solution as that added to make the 300 nm Ag_2O nanocubes, but increasing the molar ratios of $AgNO_3/NH_4NO_3/NaOH$ to 1:2:41.8, Ag_2O octapods can be readily synthesized (see Figure 8). The average particle size of these octapods is around 480 nm (see Table S2 and S3 and Figure S3 for particle size distribution histogram). The octapods show perpendicularly crossed depressions over each of their six cubic faces. The center of each face is also highly depressed. This particle morphology suggests enhanced crystal growth along the [111] directions of a cube, and results in the formation of eight branches. XRD patterns of the octapods show essentially the (200) reflection peak (see Figure S4). The SAED pattern of a single octapod also indicates that the branches are bounded by the {100} faces (see Figure 8f).

The ability to synthesize Ag_2O crystals with mainly {100} and {111} exposed faces enables the investigation of their surface properties. A previous crystal model analysis of Cu_2O crystals indicated that the {111} faces contain positively charged copper atoms at the surfaces, whereas the {100} faces are electrically neutral.[4] Cu_2O octahedra and hexapods with essentially {111} exposed faces were found to be catalytically active for the photodegradation of negatively charged methyl orange, whereas perfect cubes with entirely {100} faces were inactive.[4] Cu_2O crystals of different shapes can be suspended in an aqueous methyl orange solution. Surprisingly, octahedra and hexapods cannot be well suspended in a solution containing positively charged methylene blue molecules; a significant amount of the crystals gradually moved to the surface of the solution with increas-

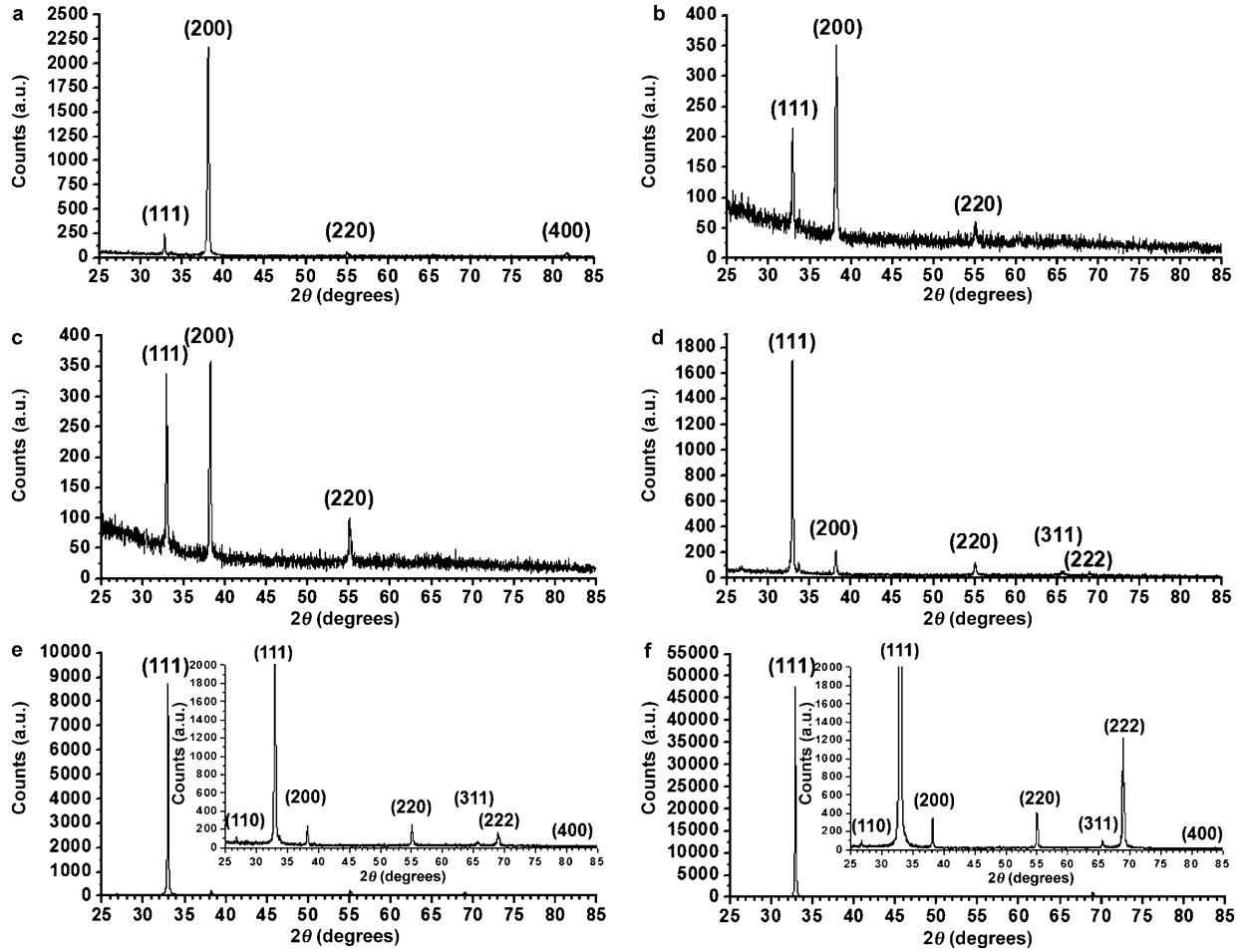


Figure 3. XRD patterns of the Ag_2O crystals synthesized: a) cubes, b) edge- and corner-truncated cubes, c) rhombicuboctahedra, d) edge- and corner-truncated octahedra, e) octahedra, and f) hexapods. Insets in panels e and f show the expanded XRD patterns.

ing stirring time. Electrostatic repulsion is believed to cause this effect for the Cu_2O octahedra and hexapods. The same test can be used to compare the surface properties of Ag_2O crystals because of their identical crystal structure.

Owing to the instability of Ag_2O crystals to light irradiation, the suspension tests of these crystals were performed in methylene blue and methyl orange solutions. Ag_2O octapods, cubes, octahedra, and hexapods were tested. The cubes, octahedra, and hexapods were prepared by using molar ratios of $AgNO_3/NH_4NO_3/NaOH$ at 1:2:11.8. Figure 9 gives the photographs of methylene blue solutions taken after dispersing the Ag_2O octapods, cubes, octahedra, and hexapods for 60 min with stirring. Cubes and octapods with largely {100} exposed faces were found to remain in the solution. Remarkably, a significant number of octahedra and hexapods with mainly {111} facets moved to the surface of the solution. The result is consistent with that observed for Cu_2O crystals. UV/Vis absorption spectra of the Ag_2O cubes and octapods in the methylene blue solution as a function of stirring time show a slow but steady decrease in the extinction as some particles fall to the bottom of the vials (see Figure S6 in the Supporting Information). A drastic decrease in extinction was recorded for the Ag_2O hexapods after stirring for just 10 min, indicating that the hexapods have either moved to the surface of the solution or fallen to the bottom of the vial because of their larger sizes. Ag_2O octahedra showed a substantial drop in extinction initially and after different stirring times, so their repulsive response to the methylene blue molecules is evident but more gradual. When these four different Ag_2O crystal samples were dispersed in vials of methyl orange solutions, no particles were observed to move to the surface of the solution after stirring for 60 min (see Figure S7). Octahedra and hexapods fall to the bottom of the vials because of their larger sizes. The results indicate that the electrically neutral octapods and cubes as well as the positively charged octahedra and hexapods can be suspended in a negatively charged methyl orange solution. All four samples display a similar degree of reduction in extinction after stirring for 10–60 min due to gradual particle settlement (see Figure S8). The results of these tests are consistent with those obtained for Cu_2O crystals, demonstrating that the surface properties of Ag_2O and Cu_2O crystals are similar.

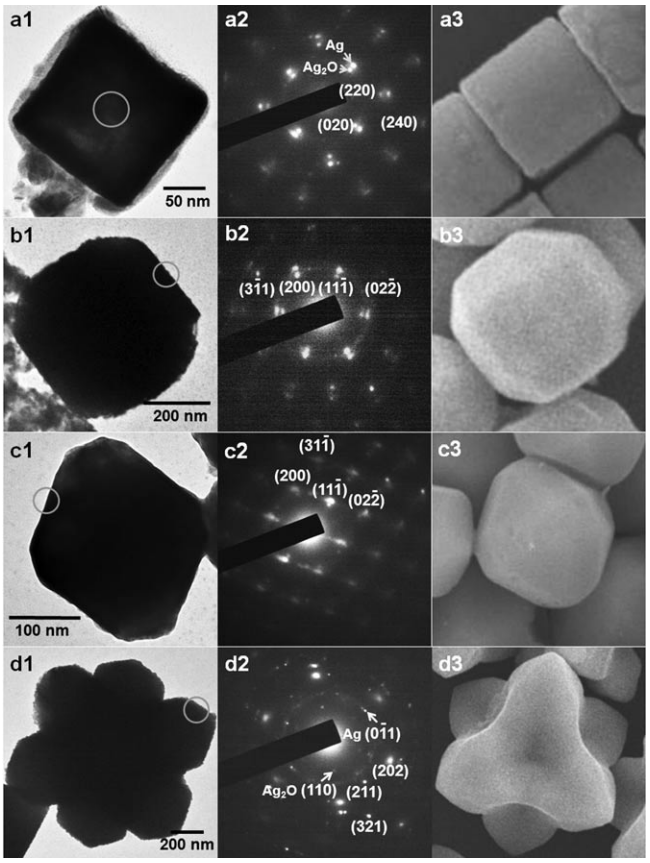


Figure 4. TEM images, their corresponding SAED patterns, and representative SEM images of the various morphologies of Ag_2O crystals synthesized. TEM images show the Ag_2O crystals viewed along a1) the [100] direction of a cube, b1, c1) the [110] direction of a rhombicuboctahedron and an edge- and corner-truncated octahedron, and d1) the [111] direction of a hexapod. Their corresponding SAED patterns were recorded over the circled regions with a2) [004], b2, c2) [022], and d2) [222] zone axes of the cuprite crystal. Diffraction spots corresponding to those of Ag were produced as a result of electron beam irradiation. Smaller particles were chosen for the TEM analysis.

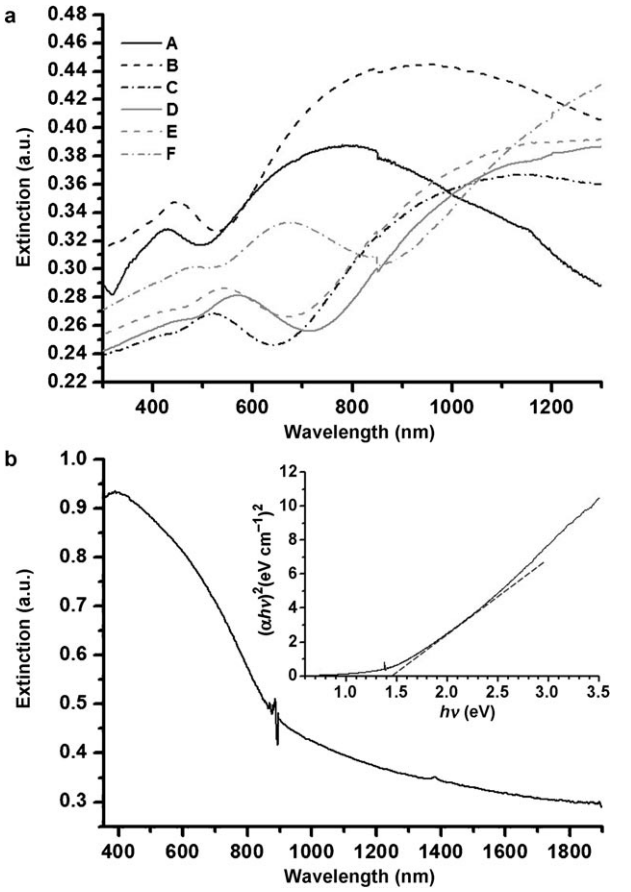


Figure 5. a) UV/Vis absorption spectra of the Ag_2O crystals in samples A–F. b) Diffuse reflectance spectrum of the dried octahedral Ag_2O crystals. Inset shows a plot of $(\alpha h\nu)^2$ versus $h\nu$ for the determination of the band gap energy of octahedral Ag_2O crystals. The values of $(\alpha h\nu)^2$ may not be right due to a lack of information on the sample thickness or path length.

Conclusion

We have developed a procedure for the synthesis of Ag_2O crystals with systematic shape evolution from cubic to edge- and corner-truncated cubic, rhombicuboctahedral, edge- and corner-truncated octahedral, octahedral, and hexapod structures by adding $AgNO_3$, NH_4NO_3, and NaOH at molar ratios of 1:2:11.8. Pre-added NaOH, introduced to a mixture of $AgNO_3$ and NH_4NO_3 solution, promotes the formation of $Ag(NH_3)_2^+$ complex ions for the growth of Ag_2O nanocrystals with good morphological control. Surface facets of these particles were examined by XRD, SEM, and TEM. A band gap value of approximately 1.45 eV was determined for the octahedral Ag_2O crystals. By changing the molar ratios to 1:2:41.8, corner-depressed rhombicuboctahedra and elongated hexapods were formed as a result of enhanced crystal growth along the [100] directions. Smaller nanocubes and octapods can also be prepared by adjusting the reagent molar ratios and their added volumes. The octapods are bounded by the {100} faces. Ag_2O octahedra and hexapods bounded by the positively charged {111} facets respond repulsively when dispersing in a solution of positively charged methylene blue solution, but can be suspended in a solution containing negatively charged methyl orange. Nanocubes and octapods are insensitive to the molecular charges. The dramatic difference in the surface properties of Ag_2O nanocrystals can be further exploited for their applications and synthesis of novel structures.

Experimental Section

Chemicals: Silver nitrate ($AgNO_3$, 99.8%, Showa), ammonium nitrate (NH_4NO_3, 99%, Showa), and sodium hydroxide (NaOH, 99%, Mallinckrodt) were used without further purification. Ultrapure distilled and deionized water was used for all solution preparations.

Synthesis of Ag_2O nanocrystals with systematic shape evolution: For the synthesis of Ag_2O crystals with systematic shape evolution from cubic to hexapod structures, six vials were first labeled A–F. H_2O, 0.2 M NH_4NO_3, 0.1 M $AgNO_3$, and 2.0 M NaOH solutions were added in the order listed with their amounts specified in Scheme 1. The mixture was sonicated for

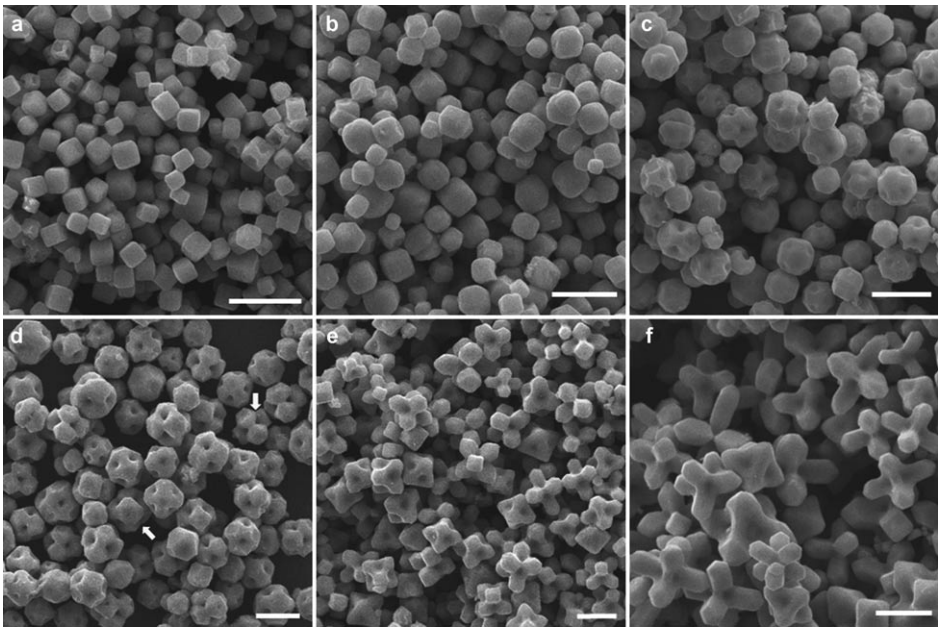


Figure 6. SEM images of the Ag_2O crystals synthesized with molar ratios of $AgNO_3/NH_4NO_3/NaOH$ 1:2:41.8. For the products shown from panels a–f, the volumes of $AgNO_3$ solution added are the same as those used for samples A–F in Scheme 1. The scale bars are equal to 1 μm.

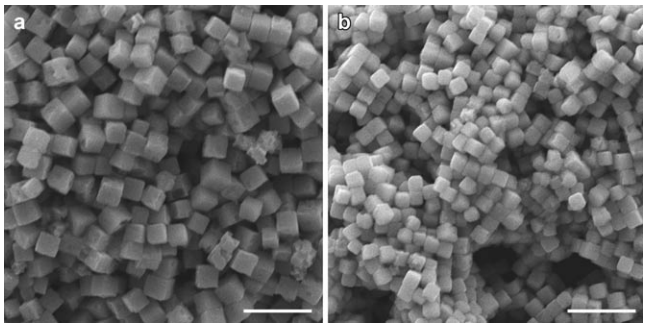


Figure 7. SEM images of the smaller Ag_2O nanocubes synthesized by reducing the volume of $AgNO_3$ solution added. The average nanocube sizes are around a) 300 and b) 200 nm. The scale bars are equal to 1 μm.

10 s, and kept in a water bath at 35 °C for 30 min. Different amounts of 2.0 M NaOH were added to each vial to neutralize hydronium ions released from the dissolution of 0.2 M NH_4NO_3 solution. This pre-added NaOH can more efficiently produce NH_3 from ammonium ions for the formation of $Ag(NH_3)_2^+$ ions. The molar ratio of NH_4NO_3/pre-added NaOH is 1:0.9. Then 1 mL of variable concentrations of NaOH (0.25 to 2.0 M) was added to the mixture. The final molar ratios of $AgNO_3/NH_4NO_3/NaOH$ 1:2:11.8. Different amounts of deionized water were added to each vial in the first step to bring the total solution volume to 6 mL. Upon the addition of this 1 mL of NaOH solution, the solution in the vial immediately turned from colorless to brown. The solution was stirred for 5 min for crystal growth. The samples were centrifuged at 4500 rpm for 3 min. The top solution was removed, and the precipitate was centrifuged twice more in water at 4500 rpm for 3 min to remove unreacted chemicals. Finally the precipitate was dispersed in deionized water (1 mL).

Synthesis of Ag_2O octapods: To synthesize Ag_2O octapods, a similar preparation procedure to that described above was used. A mixture of deionized water (4.739 mL), 0.2 M NH_4NO_3 solution (0.125 mL), 0.1 M $AgNO_3$ solution (0.125 mL), and 2.0 M NaOH solution (11.25 μL) was sonicated for 10 s, and kept in a water bath at 35 °C for 30 min. Then 0.5 M NaOH solution (1 mL) was added and the resulting mixture was stirred for 5 min. The final molar ratios of $AgNO_3/NH_4NO_3/NaOH$ 1:2:41.8.

Surface property examination: For the examination of comparative surface properties of several Ag_2O nanostructures synthesized (i.e., cubes, octahedra, hexapods, and octapods), the entire centrifuged precipitate was dispersed in 10 mL of 10 mg L^{-1} aqueous methylene blue or methyl orange solution in a vial. UV/Vis absorption spectra of the samples were taken before and after every 10 min of stirring for up to 60 min by transferring the solution to a cuvette.

Instrumentation: SEM images of the synthesized Ag_2O crystals were obtained by using a JEOL JSM-7000F scanning electron microscope. TEM characterization was performed on a JEOL JEM-2100 electron microscope operating at 200 kV. XRD patterns were collected by using a Shimadzu XRD-6000 diffractometer with $Cu_{K\alpha}$ radiation. UV/Vis absorption spectra

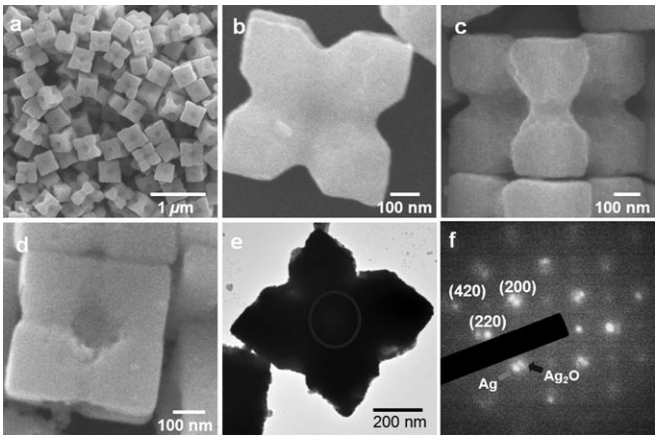


Figure 8. a) SEM image of the Ag_2O octapods synthesized. b and c) SEM images of a single Ag_2O octapod viewed along the [100] and [110] directions. d) SEM image of an octapod that is less developed. e) TEM image of an octapod viewed along the [100] direction. f) SAED pattern recorded over the circled region in panel e. Ag diffraction spots are also observed due to prolonged irradiation of the particle with a focused electron beam.

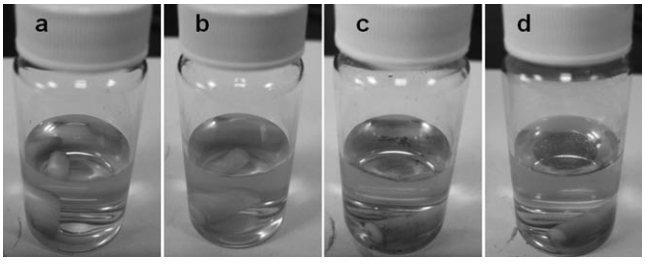


Figure 9. Photographs of the methylene blue solutions taken after dispersing the Ag_2O octapods (a), cubes (b), octahedra (c), and hexapods (d) for 60 min with stirring.

were recorded on a Jasco V-570 spectrophotometer. Diffuse reflectance spectra were obtained on the same Jasco V-570 spectrophotometer equipped with an integrating sphere.

Acknowledgements

We thank the National Science Council of Taiwan for the support of this work (grant NSC 98–2113M-007-005-MY3).

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Received: March 4, 2010
Revised: July 1, 2010
Published online: October 19, 2010

