A new route to synthesis of Ag₂O micro-/nanostructures, including a mixture of cubes, pyramids, triangular plates, pentagonal rods, and bars, has been developed by pulsed excimer laser ablation of bulk silver in water using polysorbate 80 as surfactant. The polysorbate 80 played an important role in the formation of the Ag₂O structures, and similar structures could be obtained in polysorbates 20 and 40 aqueous solutions. We have proposed a mechanism to explain the formation of Ag₂O structures. This laser ablation method provides a unique approach to discover and fabricate new Ag₂O morphologies.

1. Introduction

Silver(II) oxide (Ag₂O) micro-/nanostructures have attracted increasing interest in the past decade for memory applications.¹⁻⁴ Ag₂O is a semiconductor with a band gap in the visible region (2.25 eV).¹ Research has revealed that Ag₂O nanoparticles and thin films could show photovoltaic emission due to photo-induced Ag cluster formation, and this has potential applications for rewritable optical data storage.¹ Recent research also indicated that Ag₂O micro-/nanostructures had shape-dependent antibacterial activity.³ However, only a limited number of approaches have been developed to synthesize Ag₂O particles with well-defined morphologies. Penner et al. reported an electrochemical method to fabricate hopperlike and flowerlike Ag₂O particles by anodizing a Ag wire in a basic solution.² Very recently, Ag₂O cubes, octahedra, and truncated octahedra have been synthesized by a wet-chemical method using AgNO₃, NH₃·3H₂O, and NaOH.³ By a similar method, but changing NH₃ to NH₂NO₃, Lyu et al. also obtained Ag₂O cubes, octahedra, truncated cubes/octahedra, and hexapods.⁴ Development of other synthesis routes to Ag₂O structures is still desired. And since all of the previously reported Ag₂O structures probably evolved from cubic shapes,³⁻⁴ it is wondered whether Ag₂O could grow into other new morphologies.

Herein, we report a laser-based approach to fabricate Ag₂O micro-/nanostructures directly from bulk Ag at room temperature. These structures, including a mixture of cubes, pyramids, triangular plates, pentagonal rods, and bars, were formed by pulsed excimer laser ablation of a Ag target in water with polysorbate 80. The molecular structure of polysorbate 80 is shown in Figure 1A. It is a nonionic surfactant that is very efficient for drug delivery in the brain.⁵ We also found polysorbate 40 and polysorbate 20, which have similar molecular structures as polysorbate 80 as shown in parts B and C of Figure 1, respectively, could serve a qualitatively similar role in this laser-based approach. Pulsed laser ablation in liquid is a method for nanoparticle generation. Laser ablation of Ag has been performed in pure water, aqueous solutions of sodium dodecyl sulfate, or poly(vinylpyrrolidone) (PVP), but only spherical Ag particles were obtained.⁶⁻⁷ This work provides a unique approach to discover and fabricate new Ag₂O micro-/nanostructures such as the triangular plates and pentagonal rods which have not been fabricated by electrochemical and wet-chemical methods.²⁻⁴

2. Experimental Section

In a typical experiment, 0.02 mL of polysorbate 80 (also known as Tween 80) was added into 40 mL of distilled water to make a solution (0.05% v/v) by stirring and ultrasonic treatment. A silver metal target (99.99%, 2 in. in diameter) was placed on the bottom of a glass beaker, which was then filled with the solution. The glass beaker was rotating with speed of ~120 rpm during the laser ablation. The solution was 6 mm in depth. Pulsed laser ablation was carried out with a KrF excimer laser (wavelength 248 nm, pulse width 30 ns) operating at 10 Hz. The laser beam was spatially filtered and focused onto the surface of the target using a lens with focal length of 50 cm. The irradiated area was a circle with diameter of ~1 in. The laser spot was rectangular with a size of about 1.8 × 0.7 mm² and fluence of 8.8 J/cm² (calculated from the pulse energy measured after the focus lens). The fluence was chosen to induce effective ablation yet not too high to cause splashing of the liquid layer. The ablation lasted for 20–80 min. The resulting solution was centrifuged to obtain a precipitate, which was then washed in distilled water, centrifuged, and finally dried at room temperature on glass or silicon substrates and copper grids for X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) analyses.

We also performed the experiments with different polysorbate 80 concentrations (0%, 0.01%, 0.25%, and 1.25% v/v) while keeping the same ablation time to 20 min and further used ethanol/water mixed solvent (V_ethylene=V_water = 1:3) with 0.05% v/v polysorbate 80. For comparison, we also performed the laser ablation in aqueous solutions of polysorbate 20 (0.05% v/v), polysorbate 40 (0.05% v/v), Triton X-100 (0.05% v/v), and PVP.

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3. Results and Discussion

3.1. Ag₂O Cubes and Other Morphologies. Figure 2 shows the XRD pattern of the products prepared by KrF excimer laser ablation of a Ag target in water with polysorbate 80 (0.05% v/v) for 80 min. The relatively strong peaks can be indexed into cubic Ag₂O (PCPDF No. 75-1532), but peaks from face-centered cubic (fcc) Ag (PCPDF No. 87-0719) are present, indicating that laser ablation also produced Ag particles. Figure 3A shows a typical SEM image of the products revealing that they consist of a large quantity of cubes with edge lengths varying from 400 nm to 1 μm. Figure 3B shows the SEM image with higher magnification and further shows that the cubes have square facets. It is interesting that the products contain hollow cubes such as the one with a broken shell shown in Figure 3C. Besides cubes, spheres, pyramids, triangular plates, and rods can be also observed as shown in Figure 3D–H. The spheres are mainly Ag, and the other morphologies are Ag₂O as indicated by their different stabilities under electron irradiation which will be discussed later. Similar Ag nanostructures, especially triangular plates and rods (wires), have stimulated enormous research activity. The cross section of the Ag₂O rods have a pentagonal shape as shown in Figure 3G, the same as the Ag nanowires synthesized by the polyol process. However, the ends of the rods are bounded by 10 facets, which are different from the Ag nanowires bounded by five {111} facets. The existence of these nanostructures

Figure 1. Molecular structures of (A) polysorbate 80, (B) polysorbate 40, and (C) polysorbate 20.

Figure 2. Typical XRD pattern of the products fabricated by laser ablation of Ag in aqueous solution of polysorbate 80 (0.05% v/v).

Figure 3. SEM images of (A) products fabricated in aqueous solution of polysorbate 80 (0.05% v/v) for 80 min, (B) image with higher magnification, (C) a hollow cube, (D, E) triangular plates, (F) sphere, pyramid, and rods, and (G, H) rods.
indicates that the water–polysorbate 80 system is promising for the discovery of new Ag₂O nanostructures.

3.2. Stabilities of Ag₂O Particles. The Ag₂O cubes and other structures are very sensitive to electron beam irradiation. Figure 4A shows a SEM image of a collection of a cube, a rod, and a sphere. After irradiation by the electron beam for 2 min, another image was taken as shown in Figure 4B. It can be observed that a number of nanoparticles appear on the surfaces of the cube and the rod. Then the electron beam was focused onto the two areas marked by the rectangles for 2 min. As a result, the cube and rod were partially decomposed into smaller nanoparticles, but the sphere was almost unaffected (Figure 4C). The phenomenon is more apparent under transmission electron microscopy. Parts A and B of Figure 5 are two sequential TEM images with a temporal interval of 10 s, and the structure of the triangular plate and cubes have remarkably transformed into aggregates of nanoparticles. Figure 5C shows the TEM image of the nanoparticles with higher magnification; the diameters of the nanoparticles range from 30 to 80 nm. The corresponding SAED pattern indicates that the nanoparticles are Ag and Ag₂O (Figure 5D). The Ag resulted from the decomposition of Ag₂O under electron irradiation. A similar phenomenon was observed in single crystalline Ag₂O cubes synthesized by chemical reactions. Large numbers of nanoparticles of several nanometers could be produced on the surface of the Ag₂O cubes under a focused electron beam for several seconds. This phenomenon has not been previously reported in Ag cubes and nanoparticles, and it is considered that the spheres in the products are mainly Ag, although they may contain thin oxide shells and the other particles are Ag₂O. The instabilities of Ag₂O particles under electron beam irradiation are probably due to the irradiation-induced heating effects. It is known that Ag₂O tends to decompose into Ag under thermal treatment, and the total decomposition begins at ∼360 °C.

3.3. Effects of Polysorbate 80. To study the role of polysorbate 80 on the formation of Ag₂O particles, we performed the ablation in water with different concentrations of polysorbate 80 (0–1.25% v/v). In pure water, only Ag nanoparticles with weak oxidation could be obtained. Figure 6A shows the TEM image of the nanoparticles, and the corresponding SAED pattern is shown in Figure 6B, which mainly contains diffraction spots from Ag although weak spots from Ag₂O could be also observed. In the aqueous solution of 0.01% polysorbate 80, Ag₂O particles could form, but many Ag spheres also exist as shown in Figure 6C. Some of the spheres are hollow due to laser-induced bubbles. Figure 6D shows the SEM image of a typical hollow particle with a broken shell. 0.05%–0.25% concentrations are acceptable for the fabrication of Ag₂O particles (Figure 6E–H), and these concentrations are higher than the critical micelle concentration (CMC) of polysorbate 80, which is ∼0.01% v/v. It is observed that the cubes tend to coalesce into bars with the increasing of the polysorbate 80 concentration. Some bars are pointed out by the arrows in Figure 6H. Even higher concentrations (∼1.25%) will increase the viscosity of the solution and attenuate the laser beam largely decreasing the ablation efficiency.

It is clear that the polysorbate 80 played a critical role in the formation of Ag₂O micro- and nanostructures. And then it is expected that other polysorbates, such as polysorbate 40 and polysorbate 20, which have similar molecular structures as polysorbate 80, should play a similar role. This inference can be verified by the SEM images of products fabricated in 0.05% polysorbates 20 and 40 aqueous solutions as shown in parts A and B of Figure 7, respectively, in which similar cubes and other structures can be observed. For comparison, we performed the laser ablation in 0.05% Triton X-100 aqueous solution. The molecular structure of Triton X-100, which is another widely used nonionic surfactant with CMC of 0.012%, is shown in Figure 8A. Figure 8B shows the SEM image of the products. Only spheres can be obtained, and some of the spheres are hollow such as the one indicated by the arrow. We further performed the laser ablation in aqueous solution of PVP (20 mg/mL). PVP is a capping agent that could promote the formation of Ag cubes in polyol synthesis. However, the products are still spheres as shown in Figure 8C. Figure 8D shows the XRD patterns of the products, indicating that particles fabricated in Triton X-100 solution are partially oxidized Ag and those fabricated in PVP solution are Ag.

Oxidation of metal nanoparticles generated by laser ablation in water or water solutions is usually inherent due to the soluble oxygen or reaction of the metal with water, but generally only Ag/Ag2O core/shell particles would be obtained. The pulsed laser ablation of Ag target in liquid generated Ag clusters that could nucleate and grow into Ag particles, such as the Ag nanoparticles produced in pure water and the Ag spheres in aqueous solution of Triton X-100, and the surface of these particles could be oxidized. However, the well-defined morphologies of Ag2O particles indicate that they should crystallize from Ag2O clusters. One hypothesis to the formation of Ag2O clusters is that the oxygen atoms in polysorbate 80 may trigger the process. The polysorbate 80 molecule has a carbonyl group (C=O) and oxygen atoms in the polyethylene groups. Study has shown that the oxygen in carbonyl group could induce an image dipole on Ag cluster surface resulting in positive polarization, which may promote the oxidation of Ag in a reactive environment. However, the PVP contains more C=O units but does not result in the formation of Ag2O particles. The formation of Ag2O particles is less related to the oxygen in polysorbate 80. Another scenario considers the charge transfer during the formation of Ag2O. Our recent study shows that Ag+ ions are also generated during pulsed excimer laser ablation of bulk Ag in aqueous solutions from laser-produced plasma and/or due to photoionization of Ag clusters, which can be described as

\[ Ag^0 \xrightarrow{hv} Ag^+ (aq) + e^- \] (1)

The dissociative electron may recombine with the Ag+ ion to form a Ag atom or attach to a water molecule:

\[ H_2O + e^- \rightarrow OH^- + H \] (2)

Then Ag2O will form by the reaction:

\[ 2Ag^+ (aq) + 2OH^- \rightarrow Ag_2O(s) + H_2O \] (3)

The polysorbate 80 micelles dispersed in water are considered to promote reaction 2 and limit the recombination of Ag+ ions with dissociative electrons, and thus Ag2O clusters could form.

The oxygen in the Ag2O occupies the (1/4, 1/4, 1/4) interstitial sites of the fcc lattices constructed by Ag. Further nucleation and growth of the Ag2O clusters result in the formation of cubes and other structures. The existence of these structures, especially the triangular plates and rods, indicates that the fcc lattices of Ag still influence the growth of the Ag2O particles. Similar morphologies have been observed in Ag nanostructures, and great efforts have been devoted to elucidate their growth mechanisms.

The typical facets that construct the surface of Ag nanostructures are {100}, {110}, and {111}, and the free energies are \( \gamma_{[110]} > \gamma_{[100]} > \gamma_{[111]} \). Ag cubes are bounded by {100} facets, and

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this is also the case for Ag2O cubes.\(^3,16\) The triangular facets of Ag plates are often composed of \{111\} facets and the side surfaces of Ag pentagonal rods are bounded by \{100\} facets, and studies have suggested that Ag plates and rods have twinned crystal structures.\(^8,22\) These facts provide clues for further structural analysis of Ag2O crystals. Unlike the previous syntheses of Ag2O crystals in basic solutions,\(^2\)\(^\text{-}4\) the polysorbate 80 solutions used in our experiments are nearly neutral and provide mild environments for the crystallization of Ag2O. The crystallization process should be based on the thermodynamic principle of surface free energy minimization, although it could be disturbed by thermal fluctuations during ablation. That may be the reason that why new Ag2O morphologies can be observed in our experiments, and the observations will be useful for further theoretical and experimental investigations.

3.4. Ag Nanonetworks. We further found that the polysorbate 80 aqueous solutions could be modified to generate Ag nanonetworks by adding ethanol into the solution. Figure 9A,B shows the SEM and TEM images of the products fabricated by excimer laser ablation of Ag in ethanol/water mixture (\(V_\text{ethanol} : V_\text{water} = 1 : 3\)) solution of 0.05% polysorbate 80. Besides Ag2O particles, Ag nanonetworks can be observed in the products. Figure 9C shows a magnified image of the nanonetworks connected by nanoparticles and nanowires. These nanonetworks did not show morphology change under electron beam irradiation. The polysorbate 80 is still important for the formation of the nanonetworks. Figure 9D shows a TEM image of products fabricated in the ethanol/water mixture without polysorbate 80 and Pt nanonetworks in aqueous solution of SDS,\(^23,24\) but Ag nanonetworks fabricated by this method have not been reported before. Ethanol/water mixtures have microscopic phase separation at the cluster level.\(^25\) The existence of ethanol clusters will decrease the possibility of Ag oxidation by water and promote the formation of Ag nanoparticles. The Ag nanoparticles were dispersed in the solution and may be heated by subsequent laser irradiation. The polysorbate 80 is an organic surfactant with lower thermal conductivity than that of water. Therefore, the photothermal effect of Ag nanoparticles surrounded by polysorbate 80 micelles is more significant, resulting in jointing of encountered Ag nanoparticles and finally the formation of networks.\(^23,24\)

4. Conclusions

We have developed a pulsed laser ablation method to directly fabricate a mixture of Ag2O cubes, pyramids, triangular plates, pentagonal rods, and bars from bulk Ag in polysorbate 80 aqueous solutions at room temperature. Polysorbate 80 played an important role in the formation of Ag2O micro-/nanostructures, and similar structures could also form in polysorbates 20 and 40 aqueous solutions. The Ag2O particles were metastable under electron beam irradiation and tended to decompose into Ag nanoparticles. The polysorbate 80 aqueous solutions can be modified to generate Ag nanonetworks by the addition of ethanol. At the current stage, the pulsed laser ablation in liquid method could not achieve the controlled synthesis of uniform Ag2O particles, and Ag spheres that may have oxidized surfaces will also form due to the inhomogeneous environment produced by the laser ablation. This method has shown the ability to fabricate novel Ag2O micro-/nanostructures, beyond the traditional chemical methods, and it is expected to be further extended to discover new morphologies.