Supporting Information

3D AgCl Microstructures Selectively Fabricated via a Cl⁻-Induced Precipitation from [Ag(NH₃)₂]⁺

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Figure S1. Low magnification SEM micrographs show uniformity of the selectively precipitated 3D AgCl microstructures. The uniform structures indicate a well separation between the nucleation and growth period. The figure labels are associated with those in Figure 2. The scale bars are 10 μm.
The theoretical yield calculation

The theoretical yield of the precipitated AgCl microstructures was calculated based on the solubility constant ($K_{sp}$) of AgCl and complex formation constant ($K_f$) of Ag$^+$ and NH$_3$.

\[
\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \quad ; \quad K_{sp} = 1.77 \times 10^{-10} \quad (1)
\]

\[
\text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons [\text{Ag(NH}_3)_2]^+ (aq) \quad ; \quad K_f = 1.6 \times 10^7 \quad (2)
\]

\[
\text{AgCl(s)} + 2\text{NH}_3(aq) \rightleftharpoons [\text{Ag(NH}_3)_2]^+ (aq) + \text{Cl}^-(aq) \quad ; \quad K = \frac{K_{sp} \times K_f}{2} = 2.83 \times 10^{-3} \quad (3)
\]

Although AgCl is sparingly soluble in water ($K_{sp} = 1.77 \times 10^{-10}$), its solubility increases in an ammonia solution. Since the water soluble [Ag(NH$_3$)$_2]^+$ complex with a strong affinity of NH$_3$ towards Ag$^+$ ($K_f = 1.6 \times 10^7$) was solubilized in an NH$_4$OH rich medium, a relatively high Cl$^-$ concentration is necessary to induce a precipitation of AgCl crystals.

Initial concentrations of [NH$_4$OH] = a M, [Ag$^+$] = b M, [Cl$^-$] = c M. Due to the relatively high $K_f$, all Ag$^+$ is assumed forming into the water soluble complex, thus [Ag(NH$_3$)$_2]^+$ $\approx$ b M. As a result, the final concentration of [NH$_4$OH] = (a-2b) M.

\[
\text{AgCl(s)} + 2\text{NH}_3(aq) \rightleftharpoons [\text{Ag(NH}_3)_2]^+ (aq) + \text{Cl}^-(aq)
\]

Initial concentration: - (a-2b) b c
Change: x 2x -x -x
Final concentration: x [(a-2b)+2x] (b-x) (c-x)

Based on the above relationship,

\[
K = \frac{[\text{Ag(NH}_3)_2]^+ ] \times [\text{Cl}^-]}{[\text{NH}_3]^2}
\]

\[
2.83 \times 10^{-3} = \frac{(b-x) \times (c-x)}{(a-2b + 2x)^2}
\]

By solving for x, the precipitation yield $= \frac{x}{b} \times 100\%$

The following figures show theoretical yield of the studied system.
Figure S2. Theoretical yield of AgCl precipitates from a solution containing Ag$^+$, Cl$^-$, and NH$_4$OH. The yield is given in terms of concentration of each reactant. Under the employed conditions, nearly 100% of AgCl was precipitated. Note, the concentration of NH$_4$OH was always lower than 0.3 M.
Figure S3. SEM micrographs show structural evolution of 6x4pAgCl from octahedral seeds in Cl⁻-rich environment. Initially, the short cubic pods in Figure S3A grew out from the six square tips of the octahedral seed. However, in Cl⁻-rich environment, the growth along <111> directions was predominantly promoted. 3, 4 As a result of the constraint imposed by the growth environment, four pods grew out of the {111} corners of each pods. The twenty four short pods in Figure S3B then further grew in the Cl⁻-rich environment. Finally, 6x4pAgCl was obtained when an octahedral seed was growth in a Cl⁻-rich environment (Figure S3C). The scale bars are 1 µm.

Figure S4. SEM micrographs show structural evolution of 8x3pAgCl from cubic seed in NH₄OH-rich environment. In contrast to those in Figure S3, the short pods in Figure S4A grew out from the eight triangular tips of the cubic seed. However, in an NH₄OH-rich environment, the growth along <100> directions was promoted. Three square pods grew out of the tip of the eight short pods (Figures S4A-B). The twenty four square pods the further grow along <100> directions in the growth environment with high concentration of NH₄OH (Figure S4C). The scale bars are 1 µm.
Figure S5. High magnification SEM micrographs of pods in selected 3D AgCl microstructures: (A) triangular pods of 8pAgCl, (B) triangular fishbone of 8pAgCl with fishbone pods, (C) square pods of 6pAgCl, and (D) square pods of 6pAgCl with 4-blade arrowhead pods.

The triangular pod in 8pAgCl is originated by the $<111>$ growth out of the triangular tips of a cube in the Cl$^-$-rich environment. The formation of fishbone triangular pod in 8pAgCl is the result of the competitive $<111>$ growth along the pot length at a relatively high concentration of Cl$^-$. Similarly, the formation of square pod in 6pAgCl is the result of the $<100>$ growth out of the square tip of an octahedron in NH$_4$OH-rich environment. The square pods with 4-blade arrowhead in 6pAgCl were formed at a relatively high NH$_4$OH concentration. The thick square pods is due to a rapid growth in $<100>$ directions along the pod length at an extremely high NH$_4$OH concentration.
Figure S6. Schematic drawing shows facets and growth directions of 3D AgCl microstructures from cubic and octahedral seeds.\textsuperscript{5, 6} The cubic seed consists of six \{100\} facets, eight \{111\} corners and twelve \{110\} edges. The octahedral seed consists of eight \{111\} facets, six \{100\} corners and twelve \{110\} edges. The 8pAgCl develops from cubic seed via a preferential growth along <111> directions in the Cl\textsuperscript{-}-rich environment. On the other hand, the 6pAgCl develops from octahedral seed via a preferential growth along <100> directions in the NH\textsubscript{4}OH-rich environment.
Figure S7. (A) XRD patterns of precipitated 3D AgCl microstructures. (B) The plot of intensity ratios of (111) and (200) peaks. The XRD patterns confirm that all precipitates are pure AgCl.
**Figure S8.** XRD patterns of (A) as synthesized 6pAgCl with 4-blade arrowhead pods, (B) after a 28-minute irradiation, and (C) after a partial reduction by L-ascorbic acid (L-AA). The standard XRD patterns of Ag and AgCl were added for comparison.

**Figure S9.** Low magnification and high magnification SEM micrographs of 3D AgCl microstructures after the 20-min irradiation by a xenon arc lamp: (A) 8pAgCl with triangular fishbone pods, (B) octahedron, (C) caged octahedron, and (D) 6pAgCl with 4-blade arrowhead pods. The high magnification SEM micrographs reveal isolated silver nanoparticles (AgNPs) on AgCl surface after the irradiation. The SEM results agree with the visual observation as the white precipitates turned black after the 20-minute irradiation.
Figure S10. Degradation kinetics of methyl orange (MO) by 6pAgCl with 4-blade arrowhead pods under a visible-light irradiation. All 10-cyclic tests were conducted consecutively using the same catalyst. The catalyst was thoroughly cleaned with DI water before performing the next catalytic test. The experimental conditions (weight of catalyst, concentration and volume of analyte, and irradiation condition) are the same as those of Figure 8.

Figure S11. Degradation kinetics of methyl orange (MO) by 8pAgCl with triangular fishbone pods under a visible-light irradiation. All 10-cyclic tests were conducted consecutively using the same catalyst. The catalyst was thoroughly cleaned with DI water before performing the next catalytic test. The experimental conditions (weight of catalyst, concentration and volume of analyte, and irradiation condition) are the same as those of Figure 8.
6pAgCl with 4-blade arrowhead pods

A: as prepared  
B: 1\textsuperscript{st} time  
C: 10\textsuperscript{th} time

8pAgCl with triangular fishbone pods

A: as prepared  
B: 1\textsuperscript{st} time  
C: 10\textsuperscript{th} time

**Figure S12.** SEM micrographs show structural change of catalyst: (A) virgin, (B) after the 1\textsuperscript{st} test cycle, and (C) after the 10\textsuperscript{th} test cycle. The scale bars are 10 µm and 0.5 µm (insert).
Figure S13. EDS spectra and EDS maps of 6pAgCl with 4-blade arrowhead pods (A) virgin (B) after the 1st and (C) after the 10th cycle photocatalytic decomposition of MO. The elemental contents of Ag and Cl were further employed for the calculation of Ag/Cl ratio (shown in Table S1).

Table S1. Elemental composition (Ag and Cl) of 6pAgCl with 4-blade arrowhead pods measured by EDS technique.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (%atom)</th>
<th>Ag : Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ag</td>
<td>Cl</td>
</tr>
<tr>
<td>Virgin AgCl microstructure</td>
<td>51.27</td>
<td>48.73</td>
</tr>
<tr>
<td>After the 1st exposure</td>
<td>52.93</td>
<td>47.07</td>
</tr>
<tr>
<td>After the 10th exposure</td>
<td>56.84</td>
<td>43.16</td>
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**Figure S14.** Degradation kinetics of 10 mg/L methylene blue (MB) by 6pAgCl with 4-blade arrowhead pods under a visible-light irradiation. All cyclic tests were conducted consecutively using the same catalyst. The catalyst was thoroughly cleaned with DI water before performing the next catalytic test. The experimental conditions (weight of catalyst, volume of analyte, and irradiation condition) are the same as those of Figure 8.

**Figure S15.** Degradation kinetics of 10 mg/L methylene blue (MB) by 8pAgCl with triangular fishbone pods under a visible-light irradiation. All cyclic tests were conducted consecutively using the same catalyst. The catalyst was thoroughly cleaned with DI water before performing the next catalytic test. The experimental conditions (weight of catalyst, volume of analyte, and irradiation condition) are the same as those of Figure 8.
References


