

# Selective Epitaxial Growth of Silver Nanoplates\*\*

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The properties of metal nanocrystals (NCs) are determined not only by their size, composition, and structure (for example, solid vs. hollow) but also by their shape, which controls how atoms are arranged and coordinated on the surface.<sup>[1,2]</sup> Noble-metal NCs with controlled shapes may exhibit unique crystal-facet-dependent properties, as demonstrated in a number of applications, such as surface-enhanced Raman scattering (SERS)<sup>[3–7]</sup> and catalysis.<sup>[8–10]</sup> As the shapes of noble-metal NCs are usually defined by polyhedra enclosed by {111} and {100} facets,<sup>[11]</sup> manipulating the evolution of these low-index planes is essential to shape control. Although there has been a comprehensive discussion of shape-controlled synthesis in terms of several metallic systems,<sup>[12]</sup> such as platinum,<sup>[13]</sup> palladium,<sup>[14,15]</sup> gold, and silver,<sup>[16–18]</sup> it still remains a challenge to produce noble-metal NCs enclosed by low-index facets experimentally, along with a deep understanding of their formation mechanisms.

Zeng and Xia have now demonstrated a facile approach to control the facet-dependent growth (lateral vs. vertical) of triangular Ag nanoplates (Figure 1).<sup>[19]</sup> To minimize the influence of nucleation processes, pre-synthesized Ag triangular NCs were used as seeds to investigate epitaxial growth in a solution system. The key finding in this work was the selectivity of a capping ligand with different affinities towards {111} and {100} facets; that is, citrate anchors more strongly on {111} than {100} facets, whereas poly(vinyl pyrrolidone) (PVP) binds more strongly to {100} than {111} facets of Ag nanoplates. In particular, sodium citrate (Na<sub>3</sub>CA), as a citrate source, stabilizes the {111} facets of Ag nanoplates with a crystal growth direction parallel to the top (bottom) plane, resulting in the formation of Ag thin plates with increasing lateral dimensions. In contrast, PVP favors the {100} facets and promotes growth along vertical orientation, producing thicker Ag plates. With successive rounds of epitaxial growth, it was demonstrated that the edge length (defined as the

longest distance across a plate) and thickness of the Ag nanoplates could be increased from (45 ± 15) nm to (5.0 ± 0.5) μm and from (5.0 ± 0.5) nm to nearly 200 nm, respectively, by confining the growth to a lateral or vertical mode. During a vertical growth process capped by PVP, Ag nanoplates underwent a truncation process and changed from triangular to a nearly circular shape then finally reached a truncated right bipyramid with increasing area ratio of {100} to {111} facets. In contrast, in the lateral mode, the growth was more favorable for the formation of Ag thin plates with large area ratio of {111} to {100} when Na<sub>3</sub>CA was presented. It is also worth pointing out that such a selective growth could actually be successively repeated many times without losing the control of its morphology.

As both growth modes were performed under the same synthetic conditions except for the use of a different capping agent, the epitaxial growth rate of Ag between two successive rounds of deposition was also estimated from the volume change. It was found that the PVP-mediated growth rate was about eight times that involving citrate in vertical growth, whereas the former was approximately one seventieth of the latter in lateral growth. Overall, PVP provided a much lower growth rate than citrate did. This observation is consistent with a previous argument on the growth of Ag octahedra,<sup>[20]</sup> indicating that the catalytic activity of the pre-existing Ag atoms on the side faces should be higher than those located on the flat top (or bottom) surfaces of Ag nanoplates.

Importantly, this work also demonstrated a promising application in amplifying and tuning SERS signals. It was suggested that the SERS signals from Ag or Au NCs could be further augmented when a thin layer of metal is used as the substrate.<sup>[5–7]</sup> It was further predicted that there should be a strong correlation between the SERS enhancement factors (EFs) and the thickness of the metal substrate.<sup>[21]</sup> The as-prepared Ag nanoplates with controllable lateral dimensions, as ideal SERS underlying substrates, were subsequently employed in supporting 55 nm Ag nanospheres functionalized with 1,4-benzenedithiol in the SERS study.<sup>[19]</sup> The data indicated a sixfold intensity of the SERS signal at 1564 cm<sup>−1</sup> with increasing the thickness of Ag plates (substrates) from 18 nm to 55 nm when their edge length was fixed at about 400 nm, whereas further increase of their thickness (up to 100 nm) results in little enhancement of the SERS EF. On the contrary, increase of the edge length from about 0.5 μm to 1 (or 2) μm only doubles the intensity of the same SERS signal while the thickness was kept at about 20 nm. More importantly, the investigation showed that generally the SERS EF

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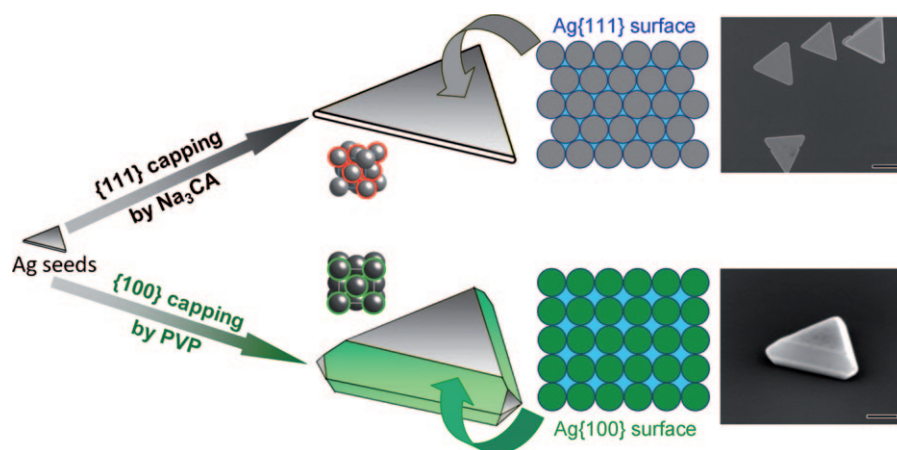
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**Figure 1.** Epitaxial growth of Ag nanoplates by two capping modes. Scale bars: Upper image: 500 nm, lower image: 200 nm.

of Ag nanospheres could be enhanced by five to thirty times when such Ag nanoplates were used for replacing a silicon wafer substrate.

The new synthesis strategy described herein has a high potential impact and could enable many other advanced applications. If a technology in epitaxial growth of a Pt-based alloy on {111} top/bottom facets of Ag nanoplates (either chemically or electrochemically) can be further developed, for instance, this method may create a novel avenue to challenge activity-enhanced cathode catalysts in fuel cells by bearing in mind that the {111} facets of some platinum bimetals, such as  $\text{Pt}_3\text{Ni}\{111\}$ ,<sup>[8,10]</sup> have an extremely high oxygen-reduction catalytic performance.

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