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# **Preserving the Shape of Silver Nanocrystals**

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### Abstract

Silver nanocrystals with well-controlled shapes have received broad interest owing to their remarkable properties for a variety of applications in areas such as plasmonics, catalysis, and electronics. How to preserve the shape of Ag nanocrystals has become a key issue in realizing the full potential of these applications. Here we provide an account of recent progress in addressing the shape stability of Ag nanocrystals used as colloidal samples. We begin with a brief introduction to the various shape-dependent properties of Ag nanocrystals, followed by a discussion of the general strategies and representative examples that can enhance the shape stability of Ag nanocrystals without compromising their unique properties. Finally, we conclude our discussion with perspective on the challenges in preserving the properties intrinsic to Ag nanocrystals with well-controlled shapes, as well as the possibility to have the strategies extended to other metals.

## **1. Introduction**

Silver (Ag) nanocrystals have received ever-increasing attention owing to their superior properties and widespread use in applications related to photonics, catalysis, sensing, and imaging.<sup>1-9</sup> For most of the applications, it is vital to have a tight control over the geometric shape taken by the nanocrystals because this parameter ultimately determines how they interact with light in a plasmonic device, how they activate chemical species involved in a catalytic reaction, and how they transport electrons through an electronic circuit. A notable example can be found in localized surface plasmon resonance (LSPR), an optical phenomenon that arises from the collective oscillation of conduction electrons upon excitation by the incident light.<sup>7</sup> Among all noble metals, Ag exhibits the best figure of merit in the visible region owing to its favorable electronic structure and the smallest imaginary part of permittivity.<sup>10-12</sup> It is well-established that the geometric shape taken by a Ag nanocrystal can significantly alter the distribution of electrical charges on the surface and thus the wavelengths and intensities of the LSPR peaks. For a Ag nanocube of ca. 40 nm in edge length, its LSPR is dominated by a strong dipole peak located at 430 nm.<sup>13</sup> In comparison, there are two intense LSPR peaks at 370 and 798 nm for a Ag nanorod with a length of ca. 80 nm and a diameter of ca. 20 nm, corresponding to the transverse and longitudinal resonance modes, respectively.<sup>14</sup> The superior plasmonic properties of Ag nanocrystals have contributed to their successful applications in areas related to surface-enhanced Raman scattering (SERS), sensing, and biomedicine.<sup>6-8</sup> As demonstrated in a set of recent studies, Ag nanocubes and their Ag-rich alloy derivatives could be used to detect various organic molecules in the solution phase,<sup>15, 16</sup> track the heterogeneous nucleation in nanocrystal growth,<sup>17,18</sup> and monitor catalytic reactions through in situ SERS fingerprinting.<sup>19,20</sup>

In addition to the plasmonic properties, one can manipulate catalytic activity and/or selectivity of Ag nanocrystals by controlling their shape and thus engineering the types of facets exposed on the surface. To this end, Ag nanocrystals with different shapes have been explored as catalysts for the styrene oxidation and ethylene epoxidation reactions. It was reported that the catalytic activity of Ag nanocubes (with an edge length of *ca*. 50 nm and enclosed by {100} facets) toward styrene oxidation was more than 4 and 14 times higher than those of Ag nanospheres (with a diameter of 50 nm, but enclosed by a mix of {111} and {100} facets) and Ag nanoplates (with an edge length of 200 nm and a thickness of 15 nm, mainly covered by {111} facets), respectively.<sup>21</sup> On the other hand, Ag nanowires mainly enclosed by {100} facets showed a higher selectivity (65% *vs*. 47%)

toward ethylene epoxidation than their spherical counterparts.<sup>4</sup> These findings clearly demonstrate a strong correlation between the catalytic activity and/or selectivity of Ag nanocrystals and their geometric shapes or types of facets expressed on the surface.

Despite the remarkable success in shape-controlled syntheses of Ag nanocrystals, it remains a grand challenge to stabilize and preserve their shapes, especially for those containing sharp corners and edges on the surface. For example, it was reported that Ag triangular nanoplates with sharp corners would be transformed into circular disks when heated in water at 80 °C (Figure 1, A and B).<sup>22</sup> It was also found that Ag nanocubes would evolve into nanospheres if they were subjected to aging in ethylene glycol (EG) at 110 °C (Figure 1, C and D).<sup>23</sup> These and other examples suggest an urgent need to understand the shape instability of nanocrystals made of Ag or other noble metals, and ultimately to come up with effective strategies to preserve their shapes and thus shape-enabled properties sought for a broad range of applications. At the current stage of development, attempts to understand the shape instability of colloidal metal nanocrystals and efforts to preserve the shapes have been met with limited success although nanocrystals with new, complex shapes are constantly reported through the development of advanced protocols. In fact, there is an everincreasing gap between the ability to synthesize colloidal metal nanocrystals with diverse and controllable shapes and the competence to preserve their shapes. This gap has contributed to the disparity between the academic studies and industrial applications of colloidal nanocrystals.

Herein, we review recent progress in enhancing the shape stability of colloidal Ag nanocrystals. We begin with a discussion on the origin of shape instability for Ag nanocrystals, followed by the introduction of two general strategies for preserving the geometric shapes taken by Ag nanocrystals, including encapsulation of the entire nanocrystal and passivation of the most reactive surface sites through the deposition of a second corrosion-resistant metal (M). We then discuss how to experimentally accomplish galvanic-free deposition of M on Ag nanocrystals for the fabrication of Ag@M nanocrystals with a core—shell or core—frame structure. Finally, we use a few case studies to demonstrate the role of the second metal in enhancing the shape stability of Ag nanocrystals exposed to an oxidative environment and/or an elevated temperature. We conclude our discussion with perspective and remarks on future directions in preserving or enhancing the superior properties intrinsic to Ag nanocrystals with controlled shapes.



**Fig. 1** (A, B) TEM images of Ag triangular nanoplates (A) before and (B) after they had been aged in pure water at 80 °C for 9 h. (C, D) TEM images of Ag nanocubes (C) before and (D) after they had been annealed in a PVP/EG solution at 110 °C for 30 min. (A–B) Reproduced with permission from ref 22. Copyright 2015 American Chemical Society. (C–D) Reproduced with permission from ref 23. Copyright 2020 Royal Society of Chemistry.

# 2. The origin of shape instability and mitigation strategies

In this section, we briefly discuss the intrinsic instability of shape-controlled Ag nanocrystals and the possible strategies for mitigating this issue.

# 2.1 What causes the shape of Ag nanocrystals to change?

The shape instability of Ag nanocrystals can be understood from two different angles. From the viewpoint of structure,<sup>24</sup> as illustrated in Figure 2A, most of the shape-controlled nanocrystals are metastable because they are far-from-equilibrium kinetic products determined by local minima in

Gibbs free energy. If these kinetic products are provided with an adequate thermal or kinetic energy, they favor spontaneous transformation into the thermodynamic product corresponding to the global minimum in Gibbs free energy. This driving force is responsible for most of the shape changes reported in literature. For a nanocrystal, the total Gibbs free energy of formation ( $G_{total}$ ) is equal to the sum of bulk and surface free energies, as shown in the following equation:<sup>25</sup>

$$G_{total} = G_{bulk} + \sum (\gamma_i A_i)$$
 Equation (1)

where  $\gamma_i$  is the specific surface energy of different crystallographic facets and  $A_i$  corresponds to the surface area of facets. During shape transformation, at a fixed volume, the term of  $G_{\text{bulk}}$  should remain the same. As such, the change in total Gibbs free energy,  $\Delta G_{\text{total}}$ , will be determined by  $\gamma_i$ and  $A_i$ . For the three low-index facets of a face-centered cubic (*fcc*) nanocrystal, the atoms located on the {111}, {100}, and {110} planes have three, four, and five dangling bonds, respectively. By taking into the consideration of planar density of each facet, it is generally accepted that their specific surface energies should increase in the order of  $\gamma_{\{111\}} < \gamma_{\{100\}} < \gamma_{\{110\}}$ . However, a nanocrystal in the shape of octahedron or tetrahedron, enclosed by the {111} facets on the surface, does not have a minimum  $G_{\text{total}}$  because both of them possess larger surface area to volume ratios and thus higher surface areas relative to the case of a cubic nanocrystal covered by {100} facets. Based on the concept of Wulff construction, the thermodynamically favorable shape of an *fcc* nanocrystal situated in the vacuum is a truncated octahedron enclosed by a mix of {100} and {111} facets, as illustrated by the three-dimensional (3D) model in Figure 2B. In other words, the truncated octahedral nanocrystal possesses a minimum total surface free energy, which is often referred to as the thermodynamic product. In comparison, the Ag nanocrystal with a cubic, octahedral, or tetrahedral shape represents a far-from-equilibrium product favored by kinetics only and it is intrinsically susceptible to shape changes, especially when subjected to an elevated temperature.

From the perspective of chemical reactivity,<sup>26</sup> Ag is more susceptible to oxidation or sulfuration at an elevated temperature when compared with other noble metals such as Au, Pd, or Pt. The oxidative etching will be accelerated in the presence of a coordination ligand (*e.g.*, halide ions) for the dissolved Ag<sup>+</sup> ions, leading to oxidative etching. As Ag atoms are continuously dissolved from the surface, the nanocrystal is also expected to evolve into different shapes.

In terms of mechanism, the shape of a Ag nanocrystal can change through two different pathways: atom migration across the surface and oxidative etching (Figure 2C). Surface migration

is a physical process, in which atoms diffuse across the surface of a nanocrystal, typically from corners/edges to side faces, generating a more stable shape with essentially the same volume as the initial nanocrystal but different area proportions for the facets. The kinetics of atom migration is sensitive to temperature and the protection of capping agent, which is, in turn, dependent on its concentration in the suspension medium, solvent, size of the nanocrystal, and temperature. In contrast, oxidative etching is a chemical process, by which an oxidant for Ag and a coordination ligand for the resultant Ag<sup>+</sup> ions convert (partially or completely) the metal nanocrystal into soluble ions, accompanied by changes to both shape and volume of the nanocrystal. In addition to all those parameters related to surface migration, the rate of oxidative etching is sensitive to other factors that include the concentration of metal ions in the suspension medium, as well as the type and concentration of oxidant/reductant.



**Fig. 2** (A) Schematic illustration showing the energy profile diagram for the thermodynamic and kinetic products. (B) Schematic illustration showing the 3-D atomic model of an *fcc* nanocrystal in the equilibrium shape based on the Wulff construction. (C) Two possible pathways for the shape transformation of a Ag nanocrystal, which involve atom migration and oxidative etching, respectively. These two pathways can be differentiated based on the level of metal ions in the suspension medium, as well as preservation *vs.* variation of particle volume. (A) Reproduced with permission from ref 24. Copyright 2015 American Chemical Society.

#### 2.2 How to preserve the shape of Ag nanocrystals?

As expected, one of the most effective strategies to preserve the shape of Ag nanocrystals is to passivate the entire surface with a conformal, ultrathin shell made of a more resistant metal (M: Au, Pt, Pd, Rh, or Ir) for the creation of Ag@M core-shell nanocrystals. When the shell is controlled below 1-2 nm in thickness, the plasmonic properties characteristic of Ag should be largely retained while the shell can significantly enhance the stability of the Ag nanocrystals. As discussed in Section 3.1, a conformal shell of Au could be readily deposited on the surface of Ag nanocubes for the generation of Ag@Au core-shell nanocubes.<sup>27</sup> It was found that even a few atomic layers of Au could effectively protect the underlying Ag atoms from oxidative etching while the plasmonic properties and SERS activity of the original Ag nanocubes were preserved. In general, the oxidative etching of Ag tends to be initiated from a site with the highest surface energy. Taking the commonly used Ag nanocubes as an example, when the {100} facets are capped with poly(vinylpyrrolidone) (PVP), the specific surface energies should decrease in the order of  $\gamma\{110\} > \gamma\{111\} > \gamma\{100\}$ .<sup>28</sup> In turn, the atoms located on the corners and edges, terminated in {111} and {110} facets, respectively, would be more susceptible to oxidative etching and dissolution, resulting in the transformation of nanocubes into nanospheres (see Figure 1D). In this regard, another strategy to mitigate possible shape transformation is to protect the active sites (e.g., corners and edges) on Ag nanocrystals with metal M for the generation of Ag@M core-frame nanocrystals. As discussed in Section 3.2, the Ag@Ir core-frame nanocubes with selected deposition of Ir on the corners and edges could preserve the cubic shape even up to an elevated temperature.<sup>23</sup> In this case, partial decoration of the Ag surface with a different metal can greatly expand the functionality of Ag nanocrystals by integrating the catalytic property of M with the plasmonic property of Ag.<sup>29-31</sup>

### 2.3. How to achieve galvanic-free deposition of M on Ag nanocrystals?

Seeded growth represents a general approach to the synthesis of Ag@M core-shell or core-frame nanocrystals in a solution phase. In general, the M atoms derived from the reduction of M<sup>n+</sup> precursor should be conformally deposited onto the surface of the existing Ag nanocrystals (*i.e.*, the seeds) in a layer-by-layer fashion. However, such a synthesis is often plagued by the possible galvanic replacement reaction between the Ag nanocrystals and the precursor to metal M because of the low reduction potential relative to other noble metals.<sup>26,27</sup> In this process, Ag atoms tend to be oxidized and dissolved into the reaction solution, transforming the Ag nanocrystal into a hollow nanostructure. A simple and effective approach to mitigate the effect of galvanic replacement is to introduce a strong reducing agent into the reaction system.<sup>27</sup> In this case, the M<sup>n+</sup> precursor can be reduced *via* chemical reduction exclusively for the generation of M atoms, followed by their deposition onto the edges, corners, and/or side faces of Ag nanocrystals for the generation of Ag@M core-frame and then core-shell nanocrystals in controllable manner.

Figure 3 compares the two approaches (with two protocols under each approach) for achieving galvanic-free deposition of M on Ag nanocubes. The first strategy can be used to conformally deposit M on the entire surface of a Ag nanocube. In one protocol, M<sup>n+</sup> precursor is titrated into an aqueous mixture of Ag nanocubes, ascorbic acid (H2Asc), PVP, and NaOH under alkaline condition at room temperature.<sup>27,32,33</sup> Because H<sub>2</sub>Asc is neutralized by OH<sup>-</sup> to provide ascorbate monoanion (HAsc<sup>-</sup>) with substantially enhanced reducing power, it is feasible to compete with and suppress the galvanic replacement reaction.<sup>32</sup> As such, the M atoms derived from the reduction by HAsc<sup>-</sup> can be successively deposited on the edges, corners, and side faces of a Ag nanocube to have it transformed into a Ag@M core-shell nanocube. In another protocol, M<sup>n+</sup> precursor is titrated into a suspension of Ag nanocubes in the PVP/EG solution at an elevated temperature.<sup>34</sup> At an elevated temperature, the strong reducing power of EG enables the chemical reduction of M<sup>n+</sup> precursor for the generation of M atoms without the involvement of galvanic replacement. As such, these derived M atoms can also be deposited on the entire surface of a Ag nanocube for the generation of a Ag@M core-shell nanocube. The second strategy involves the deposition of M only onto the edges of a Ag nanocube. In one protocol, both M<sup>n+</sup> and Ag<sup>+</sup> precursors are co-titrated into an aqueous solution containing Ag nanocubes, H<sub>2</sub>Asc, and PVP under acidic condition at room temperature.<sup>35,36</sup> When there are adequate Ag<sup>+</sup> ions in the reaction system, it is feasible to suppress the galvanic replacement reaction between M<sup>n+</sup> precursor and Ag. As such, chemical reduction of the two precursors by H<sub>2</sub>Asc produces M and Ag atoms, followed by their co-deposition onto the edges of the Ag nanocube for the generation of a Ag@M–Ag core–frame nanocube. In another protocol, M<sup>n+</sup> precursor is titrated into a suspension of Ag nanocubes in a PVP/EG solution held at an elevated temperature.<sup>23,37</sup> In this case, the chemical reduction of M<sup>n+</sup> precursor by EG produces M atoms, followed by their deposition on the edges of a Ag nanocube for the generation of a Ag@M core–frame nanocube.



**Fig. 3** Schematic illustration showing two approaches to the deposition of M on Ag nanocubes for the generation of Ag@M nanocubes with a core–shell and core–frame structure, respectively. Modified with permission from ref 29. Copyright 2017 American Chemical Society.

## 3. Case studies

In this section, we use a set of examples to demonstrate how to improve the shape stability of Ag nanocrystals by decorating their surface with another metal or a compound. We also discuss the possible mechanisms responsible for the observed improvement in shape stability.

## 3.1 Ag@M core-shell nanocrystals

In contrast to Ag, Au is well known for its strong resistance to oxidation. If a thin layer of Au can be conformally deposited on Ag nanocrystals, the resultant Ag@Au core-shell structures should exhibit enhanced shape stability while preserving the superior plasmonic properties intrinsic to Ag. However, it has been a major challenge to deposit Au on Ag using a colloidal method due to the involvement of galvanic replacement between Ag and the precursor to Au. By introducing a strong reducing agent to suppress the galvanic replacement reaction, we developed a versatile

method to achieve galvanic-free deposition of Au on Ag nanocubes for the fabrication of Ag@Au core-shell nanocubes.<sup>27</sup> In a typical process, aqueous HAuCl<sub>4</sub> was titrated into an aqueous suspension of Ag nanocubes in the presence of H<sub>2</sub>Asc, NaOH, and PVP at room temperature (Figure 4A). When NaOH was used at a pH value of 11.2 for the reaction solution, it could react with H<sub>2</sub>Asc to form sodium ascorbate (NaAsc), a reducing agent. In addition, NaOH could also neutralize the added HAuCl<sub>4</sub> for the formation of AuCl<sub>3</sub>(OH)<sup>-</sup>, AuCl<sub>2</sub>(OH)<sub>2</sub><sup>-</sup>, AuCl(OH)<sub>3</sub><sup>-</sup>, and  $Au(OH)_4^{-,38}$  and all of them have lower reduction potentials than that of  $AuCl_4^{-}$  to significantly decrease the rate of galvanic replacement reaction.<sup>39</sup> In the early stage of a synthesis, it was argued that a small number of Au atoms would still be generated through the galvanic replacement reaction and deposited on the Ag nanocubes at the expense of Ag atoms dissolved from the corners. The resultant Ag<sup>+</sup> ions would react with OH<sup>-</sup> for the creation of Ag<sub>2</sub>O patches at the corners<sup>40</sup> to protect the underlying Ag from further reacting with Au<sup>3+</sup> ions, terminating the galvanic replacement reaction. Under this circumstance, the added Au<sup>3+</sup> ions would be reduced by NaAsc to produce Au atoms, followed by their conformal deposition onto the Ag nanocube in a layer-bylayer manner for the generation of Ag@Au core-shell nanocubes, including the deposition of some Au atoms on the  $Ag_2O$  patches at the corners.

Figure 4, B and C, shows transmission electron microscopy (TEM) images of the Ag nanocubes with an edge length of 38 nm and the corresponding Ag@Au core-shell nanocubes prepared by titrating 0.4 mL of HAuCl<sub>4</sub> (0.1 mM) into the reaction mixture. Figure 4D shows an aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM) image of an individual nanocube shown in Figure 4C. When the nanocube was oriented along the [001] zone axis, the atomic-resolution HAADF-STEM image (the inset in Figure 4D) clearly resolves the arrangements of Au and Ag atoms. According to this image, the conformal shell made of Au had an ultrathin thickness of three atomic layers only. The shape stability of the Ag nanocubes and asprepared Ag@Au core-shell nanocubes was evaluated by following their characteristic LSPR peaks using UV-vis spectroscopy. As shown in Figure 4E, the major LSPR peaks of the Ag and Ag@Au nanocubes were located at 435 and 443 nm, respectively. After aging in 2.3% aqueous  $H_2O_2$  for up to 10 h, the LSPR peak of the Ag@Au nanocubes was shifted to 447 nm while the peak intensity remained essentially the same. In comparison, the LSPR peak of the Ag nanocubes disappeared in 3 min. These results suggest that an ultrathin layer of Au shell of only three atomic layers could significantly improve the shape stability of the Ag nanocubes in 2.3% aqueous  $H_2O_2$ .

In a separate study, it was also found that the Au shell could preserve the shape of Ag nanocubes in 1.0  $\mu$ M aqueous solution of NaHS.<sup>27</sup> It is worth pointing out that the Ag@Au core-shell nanocubes would become vulnerable to oxidation and dissolution if the sample was exposed to an acid. In this case, the acid was able to dissolve the Ag<sub>2</sub>O patches at the corners, lifting off the Au overlayers and thus exposing the underlying Ag atoms. As a result, the Ag in the core could be etched away using 2.3% aqueous H<sub>2</sub>O<sub>2</sub>, transforming the core-shell nanocubes into Au nanoboxes with well-defined openings at the corner sites.<sup>40</sup>

We also demonstrated the defect-assisted deposition of Au on Ag nanocubes for the generation of Ag@Au core-shell nanocubes with Au shells up to eight atomic layers in thickness.<sup>34</sup> As shown in Figure 5A, the new synthetic route relies on the use of EG as both a solvent and a reducing agent. By eliminating the involvement of H<sub>2</sub>Asc, NaOH, and water, the formation of Ag<sub>2</sub>O patches at the corners can be avoided. The synthesis has to be conducted at an elevated temperature to increase the reducing power of EG. In a typical synthesis, aqueous HAuCl<sub>4</sub> was titrated into a suspension of Ag nanocubes in a mixture of PVP and EG at 110 °C. At the early stage, the galvanic replacement between Ag and HAuCl<sub>4</sub> would create voids on the side faces of the Ag nanocube due to the dissolution of Ag atoms in the form of Ag<sup>+</sup> ions through oxidation. Since the defectlined sites were high in surface energy, they would become the active sites for the co-deposition of Ag and Au atoms derived from the co-reduction of Ag<sup>+</sup> and Au<sup>3+</sup> ions, filling the defects while providing atoms to the entire surface through diffusion for the generation of a nanocube comprised of a Ag core and a Au-Ag alloy shell. Since the initially formed Au-Ag alloy shell was enriched in Au, it could protect the underlying Ag from oxidation and thus terminate the galvanic replacement reaction. In the following step, Au atoms would be generated via chemical reduction of HAuCl<sub>4</sub> by EG for their continuing deposition on the nanocubes for the generation of Ag@Au core-shell nanocubes.

Figure 5B shows the TEM image of a sample prepared with the use of 1.0 mL HAuCl<sub>4</sub> (0.1 mM). Compared with the original Ag nanocubes, the average edge length was increased from 37.5  $\pm$  1.3 nm to 39.7  $\pm$  1.5 nm, confirming the deposition of Au shells. Figure 5C shows the TEM image of the resultant nanostructures after the sample in Figure 5B had been incubated in 30% H<sub>2</sub>O<sub>2</sub> for up to 12 h. There was essentially no change to the shape or morphology, indicating much improvement in shape stability for the nanocubes. Figure 5D shows the HAADF-STEM image recorded from one of the nanocubes in Figure 5B. The contrast between Ag and Au confirms that

the particle was indeed comprised of a Ag core and a Au shell. In addition, the defects (marked by the dotted black line) on the side faces of the Ag nanocube can also be identified. This result supports the argument that Au atoms would be deposited to fill the defect sites first before the conformal deposition of Au could occur across the entire surface of a nanocube. Figure 5E shows the atomic-resolution HAADF-STEM image recorded from a nanocube oriented along the [001] zone axis, indicating a Au shell of three atomic layers in thickness. In fact, the thickness of the Au shell can be readily tuned by controlling the amount of HAuCl<sub>4</sub> added into the reaction system. Figure 5F shows HAADF-STEM image of another nanocube prepared using 4.0 mL HAuCl<sub>4</sub>, together with atomic-resolution image in Figure 5G. In this case, the Au shell was increased to eight atomic layers in thickness. As expected, the as-obtained Ag@Au core-shell nanocubes exhibited excellent shape stability in the EG/PVP solution when aged in air at 110 °C while the Ag nanocubes would be transformed into Ag nanospheres (see Figure 1D).



**Fig. 4** (A) Schematic illustration showing the transformation of a Ag nanocube into a Ag@Au core-shell nanocube by titrating HAuCl<sub>4</sub> into an aqueous suspension of Ag nanocubes in the presence of H<sub>2</sub>Asc, NaOH, and PVP at room temperature. (B, C) TEM images of (B) Ag nanocubes and (C) Ag@Au nanocubes. The insets in (B, C) are the corresponding magnified TEM images. (D) HAADF-STEM image taken from a Ag@Au nanocube where the Au shell was three atomic layers in thickness. The inset in (D) is the corresponding atomic-resolution HAADF-STEM image along [001] zone axis with a scale bar at 2 nm. (E) UV-vis spectra of the Ag nanocubes and Ag@Au nanocubes before and after mixing with 2.3% aqueous H<sub>2</sub>O<sub>2</sub> for 10 h. Reproduced with permission from ref 27. Copyright 2014 American Chemical Society.



Fig. 5 (A) Schematic illustration showing the synthesis of Ag@Au core-shell nanocubes by titrating HAuCl<sub>4</sub> into a mixture of Ag nanocubes, PVP, and EG at 110 °C. (B, C) TEM images of (B) the sample prepared with 1.0 mL HACl<sub>4</sub> (0.1 mM) and (C) the resultant nanostructures after etching the sample with 30% aqueous  $H_2O_2$  for 12 h. (D-G) HAADF-STEM images of two samples prepared by reacting Ag nanocubes with (D, E) 1.0 and (F, G) 4.0 mL of HACl<sub>4</sub>. Reproduced with permission from ref 34. Copyright 2019 American Chemical Society.

In addition to Ag nanocubes, Xia and co-workers demonstrated the deposition of Au on Ag nanowires for the generation of Ag@Au core-shell nanowires by following the protocol described in Figure 4A.<sup>41</sup> Although the morphology of the core-shell nanowires was essentially identical to the pristine Ag nanowires (Figure 6, A and B), an ultrathin Au shell could be resolved by elemental mapping using energy dispersive spectroscopy (EDS) (the inset in Figure 6B). The Ag nanowires and the as-prepared Ag@Au nanowires were then subjected to different oxidative environments to compare their shape stability by monitoring changes to the LSPR peaks. As shown by the UVvis spectra in Figure 6, C and D, the characteristic LSPR peaks of the pristine Ag nanowires and the Ag@Au nanowires remained at the same positions, but their intensities decreased by ca. 30% and 15%, respectively, when the samples were aged in O<sub>2</sub>-saturated water. These results indicate that both the Ag and Ag@Au nanowires were able to resist oxidation by the O<sub>2</sub> dissolved in pure water. However, their responses to other oxidative environments such as aqueous H<sub>2</sub>O<sub>2</sub> (0.85 M) or aqueous Fe(NO<sub>3</sub>)<sub>3</sub> (up to 1 mM) differed significantly. Specifically, the LSPR peak of the Ag nanowires disappeared when the sample was aged in aqueous  $H_2O_2(0.85 \text{ M})$  or aqueous  $Fe(NO_3)_3$ , indicating the complete dissolution of Ag due to oxidative etching. In comparison, the LSPR peak of the Ag@Au nanowires remained at the same position while the LSPR peak intensity dropped by ca. 3% and 33% after incubation in aqueous H<sub>2</sub>O<sub>2</sub> and Fe(NO<sub>3</sub>)<sub>3</sub>, respectively, for 1 h. These results confirmed no substantial change to the morphology as a result of the effective protection of Ag nanowires by the ultrathin Au shell.

In another study, Ko and co-workers used the protocol described in Figure 4A to synthesize Ag@Au core-shell nanowires.<sup>42</sup> The as-obtained core-shell nanowires exhibited superb electrical conductivity and enhanced chemical and electrochemical stability when compared with Ag nanowires. Specifically, they evaluated the stability of the nanowires by measuring their electrical conductivity under ambient conditions. It was found that the resistance of the electrodes made of Ag@Au nanowires with a Au shell of 3 or 5 nm in thickness would increase slowly over 4 weeks, whereas the electrode comprised of pristine Ag nanowires showed a much faster degradation rate. Most of the nanowires became disconnected after 4 weeks, leading to electrical failure. In contrast, the Ag@Au core-shell nanowires were able to maintain their original structure, confirming the improved electrode stability under ambient conditions when there was an ultrathin Au shell on the Ag nanowires. The electrochemical stability was also examined by cyclic voltammetry (CV) test using a typical three-electrode measurement method in an aqueous Na<sub>2</sub>SO<sub>4</sub> electrolyte with

Ag/AgCl reference electrode and Pt counter electrode. During the CV test, the Ag nanowires were oxidized to release Ag<sup>+</sup> ions directly into the electrolyte solution, leading to an irreversible reaction in the electrode material and thus significant current drop. In comparison, the electrode consisting of Ag@Au core-shell nanowires preserved typical rectangular CV curves for good electrodes with oxidation and corresponding reduction peak at reverse voltage scan state without rapid current drop even at the 50th cycle. Moreover, the Au shell was not destructed during the CV electrochemical test, while the pristine Ag nanowires were damaged and disconnected.

In addition to the demonstration of Ag@Au core-shell nanocubes and nanowires with enhanced shape stability, Yin and co-workers reported how to improve the shape stability of Ag nanoplates by galvanic-free deposition of Au on their surface.<sup>43</sup> Specifically, Ag@Au nanoplates were prepared by adding an aqueous solution containing HAuCl<sub>4</sub>, KI, and PVP into a mixture of H<sub>2</sub>Asc, PVP, diethylamine, and Ag nanoplates. Because the use of KI could decrease the reduction potential of AuCl<sub>4</sub><sup>-</sup> by complexation with I<sup>-</sup> ions, the galvanic replacement between the newly formed Au<sup>3+</sup> complex and Ag could be effectively mitigated. In addition, diethylamine could be unselectively adsorbed on the entire surface of Ag nanoplates to help eliminate possible etching while the Au atoms derived from the chemical reduction by H<sub>2</sub>Asc could be uniformly deposited on the entire surface of Ag nanoplates for the creation of a core-shell structure. The as-obtained core-shell nanoplates exhibited excellent stability in 2.1% aqueous H<sub>2</sub>O<sub>2</sub>, phosphate buffer solution, aqueous NaCl, and phosphate-buffered saline (PBS) solution. Based on the literature search, the conformal deposition of Au has also been successfully extended to Ag nanocrystals with other shapes or morphologies, including cuboctahedra,<sup>19</sup> decahedra,<sup>44</sup> pentagonal rods,<sup>44</sup> and irregularly-shaped nanoparticles,<sup>45,46</sup> for the fabrication of Ag@Au core-shell nanostructures with enhanced shape stability.



**Fig. 6** (A, B) TEM images of (A) Ag nanowires and (B) Ag@Au core–shell nanowires. The inset in (B) is the corresponding EDS elemental mapping of Ag and Au in a Ag@Au nanowire with a scale bar of 10 nm. (C, D) UV–vis spectra of (C) Ag nanowires and (D) Ag@Au nanowires before and after etching with O<sub>2</sub>-saturated pure water, aqueous  $H_2O_2$ , and aqueous Fe(NO<sub>3</sub>)<sub>3</sub>, respectively. Reproduced with permission from ref 41. Copyright 2017 Royal Society of Chemistry.

#### 3.2 Ag@M core-frame nanocrystals

Although coating the entire surface of Ag nanocrystals with a shell made of a more resistant metal M can greatly enhance its shape stability, it inevitably alters the surface composition and thus void the catalytic properties associated with Ag. It may also dampen the plasmonic properties intrinsic to Ag when the shell becomes too thick. Because the oxidation and thus shape degradation of Ag nanocrystals is often initiated from the edges and corners with higher surface free energies than that of side faces, it is also possible to preserve the shape of Ag nanocrystals by passivating these vulnerable sites with metal M in the form of Ag@M core–frame nanocrystals. In one study, we demonstrated the galvanic-free deposition of a Pd-Ag alloy on the edges of Ag nanocubes.<sup>36</sup> In

a typical process, Na<sub>2</sub>PdCl<sub>4</sub> and AgNO<sub>3</sub> were co-titrated into an aqueous suspension of Ag nanocubes in the presence of H<sub>2</sub>Asc and PVP at room temperature (Figure 7A). When the molar ratio of AgNO<sub>3</sub> to Na<sub>2</sub>PdCl<sub>4</sub> was greater than 0.5, the galvanic replacement reaction between Ag and Na<sub>2</sub>PdCl<sub>4</sub> could be retarded due to the sufficient involvement of Ag<sup>+</sup> ions to push this reaction backward. In this case, co-reduction of Na<sub>2</sub>PdCl<sub>4</sub> and AgNO<sub>3</sub> byH<sub>2</sub>Asc produced Pd and Ag atoms for their co-deposition onto the edges and then corners of Ag nanocubes to produce Ag@Pd-Ag core-frame nanocubes. Figure 7B shows the sample prepared by co-titrating 0.1 mL of Na<sub>2</sub>PdCl<sub>4</sub> (0.2 mM) and AgNO<sub>3</sub> (0.1 mM) for each precursor solution. The absence of pits on the nanocubes suggests that the galvanic replacement reaction between Ag and Na<sub>2</sub>PdCl<sub>4</sub> was rather limited. After the etching of this sample with aqueous H<sub>2</sub>O<sub>2</sub>, Figure 7C shows the formation of cubic nanoframes with small openings at the corner sites. When the titration volume was increased to 0.2 mL, Figure 7, D and E, shows the resultant nanostructures before and after etching with aqueous  $H_2O_2$ , respectively. As the amounts of the precursors were increased, cubic nanoframes with thicker ridges and filled corners were formed. Collectively, these results indicate that the co-deposition of Pd and Ag was initiated at the edges and then extended to corners. In addition, the formation of cubic nanoframes after etching with aqueous H<sub>2</sub>O<sub>2</sub> suggests that the Pd atoms being deposited on the edges and corners of Ag nanocubes could survive in an oxidative environment. In principle, the co-titration methodology can also be applied to synthesize Ag@M-Ag (M: Au, Pt, Ir, Rh, and Ru) core-frame nanocrystals. When the reduction potential of  $M^{n+}$  is higher than that of PdCl<sub>4</sub>-, the lower limit of molar ratio between AgNO3 and Mn+ should be increased effectively to include sufficient Ag<sup>+</sup> ions to suppress the galvanic replacement reaction.<sup>35</sup> It has been demonstrated that such core-frame nanocubes with integrated plasmonic and catalytic properties on the same particle can serve as a bifunctional probe for analyzing M-catalyzed reactions by SERS.<sup>19, 20, 36</sup>



**Fig. 7** (A) Schematic illustration showing the synthesis of Ag@Pd-Ag core–frame nanocubes by co-titrating Na<sub>2</sub>PdCl<sub>4</sub> and AgNO<sub>3</sub> into an aqueous suspension of Ag nanocubes in the presence of H<sub>2</sub>Asc and PVP. (B, C) TEM images of the nanocubes obtained by setting the co-titration volume of AgNO<sub>3</sub> (0.1 mM) and Na<sub>2</sub>PdCl<sub>4</sub> (0.2 mM) to 0.1 mL (B) before and (C) after etching with aqueous H<sub>2</sub>O<sub>2</sub>. (D, E) TEM images of the nanocubes obtained by increasing the co-titration volume of AgNO<sub>3</sub> (0.1 mM) and Na<sub>2</sub>PdCl<sub>4</sub> (0.2 mM) to 0.2 mL (D) before and (E) after etching with aqueous H<sub>2</sub>O<sub>2</sub>. The scale bars in the insets are 20 nm. TEM images reproduced with permission from ref 36. Copyright 2015 American Chemical Society.

Another approach to depositing metal M on the edges of Ag nanocrystals is to titrate M<sup>n+</sup> into a mixture of Ag nanocrystals and PVP in EG at an elevated temperature. Figure 8A shows a synthesis involving the titration of Na<sub>3</sub>IrCl<sub>6</sub> at 110 °C. It was argued that the Ir atoms derived from the reduction of Na<sub>3</sub>IrCl<sub>6</sub> by EG could be preferentially deposited on the edges of Ag nanocubes, leading to the formation of Ag@Ir core-frame nanocubes.<sup>23</sup> Figure 8, B and C, shows TEM images of the original Ag nanocubes and the sample prepared by titrating 0.1 mL of Na<sub>3</sub>IrCl<sub>6</sub> (2 mM) into the reaction system. When compared with the original Ag nanocubes, the corners of the asprepared Ag-Ir nanocubes were sharpened, indicating the deposition of Ir onto the edges and then corners. To further confirm the deposition of Ir on the Ag nanocubes, inductively-coupled plasma mass spectrometry (ICP-MS) was used to obtain an Ir to Ag atomic ratio of 11:165 for the Ag@Ir nanocubes. UV-vis spectroscopy was also used to evaluate the shape stability of the Ag nanocubes and as-prepared Ag@Ir nanocubes by monitoring their LSPR peaks. Specifically, the sample was incubated in PVP/EG solution at 110 °C, followed by the collection of UV-vis spectra at different time points of 5, 10, and 30 min, respectively. Figure 8D shows that the major LSPR peak of the Ag nanocubes was continuously blue shifted from 448 nm to 434, 425, and 415 nm, respectively. The shoulder peaks located at 390 and 352 nm, associated with the sharp corners and edges of nanocubes, also decreased in intensity. The TEM image confirms the transformation of the Ag nanocubes to nanospheres after 30 min (the inset in Figure 8D). In contrast, Figure 8E shows that the major LSPR peak of the Ag@Ir nanocubes showed little change in peak position over 30 min, indicating an enhancement in shape stability. This result is also supported by the TEM image of the sample after aging at 110 °C for 30 min (the inset in Figure 8E). It is worth mentioning that a similar protocol has also been extended to synthesize Ag@Rh core-frame nanocubes with enhanced shape stability by titrating Na<sub>3</sub>RhCl<sub>6</sub> into a mixture of Ag nanocubes, PVP, and EG at 110 °C.37



**Fig. 8** (A) Schematic illustration showing the synthesis of Ag@Ir core–frame nanocubes. (B, C) TEM images of (B) original Ag nanocubes and (C) Ag@Ir nanocubes prepared by the titration of 0.1 mL Na<sub>3</sub>IrCl<sub>6</sub> (2 mM). (D, E) UV–vis spectra recorded from suspensions of (D) the Ag nanocubes and (E) the Ag@Ir nanocubes before and after thermal annealing in a PVP/EG solution at 110 °C for different periods of time. The insets in (D, E) are the corresponding TEM images of the resultant nanostructures after thermal annealing for 30 min. The scale bars are 50 nm. Reproduced with permission from ref 23. Copyright 2020 the Royal Society of Chemistry.

# 3.3 Ag@Ag<sub>2</sub>S nanocrystals

As demonstrated in Section 3.2, the decoration of M on the active sites of Ag nanocrystals could enhance the shape stability. A similar strategy to preserve the shape of Ag nanocrystals is to deactivate these high-energy sites *via* sulfuration.<sup>22</sup> In a typical synthesis, an aqueous suspension

of triangular Ag nanoplates was mixed with aqueous polysulfide  $(Na_2S_x)$  solution (Figure 9A). The sulfuration initiated from the corners of Ag nanoplates and then progressed toward the central region with time, leading to the concurrent shrink of Ag region. The success of this reaction relies on the use of  $Na_2S_x$  that was prepared in advance by reacting sulfur powders with  $Na_2S$  aqueous solution at 80 °C for 12 h. As such, it is possible to instigate the reaction between Ag and Na<sub>2</sub>S<sub>x</sub> to produce Ag<sub>2</sub>S. On the other hand, because  $S_x^{2-}$  only diffused into Ag lattice very slowly due to its larger size compared to monomeric S and S<sup>2-</sup>, the kinetics and degree of sulfuration could be readily manipulated. Figure 9, B-E, shows TEM images that decipher the evolution of the original Ag nanoplates to Ag@Ag<sub>2</sub>S nanoplates at different time points of reaction. Compared to the Ag nanoplates, the area of Ag<sub>2</sub>S expanded from corners to central region with the reaction time. To evaluate the stability of the Ag nanoplates before and after decorating with Ag<sub>2</sub>S at corner sites, the samples were re-dispersed in water and aged at 80 °C. Figure 9F shows TEM image of the resultant products after the Ag nanoplates were aged for 9 h, indicating their transformation into round disks. In comparison, once the corner sites had been converted to Ag<sub>2</sub>S, Figure 9G shows that the Ag@Ag<sub>2</sub>S nanoplates could maintain their morphology under the same aging condition. Again, UV-vis spectroscopy was used to monitor the shape transformation. Figure 9H shows that the major LSPR peak of the Ag nanoplates was blue shifted by 300 nm while the peak of the Ag@Ag<sub>2</sub>S nanoplates did not show any change to its intensity and position, confirming the TEM observations. Remarkably, the sulfuration methodology was also successfully extended to the fabrication of Ag@Ag<sub>2</sub>S nanocubes.<sup>22</sup> Similar to the case of Ag nanoplates, sulfuration reaction occurred from the most vulnerable corners of Ag nanocubes for the creation of Ag<sub>2</sub>S at all corner sites. When benchmarked against Ag nanocubes, these Ag@Ag<sub>2</sub>S nanocubes showed great shape stability at 100 °C even after aging in water for 12 h. Collectively, this study revealed that converting the corners of Ag nanocrystals to Ag<sub>2</sub>S could effectively improve their shape stability in water held at an elevated temperature.



**Fig. 9** (A) Schematic illustration showing the transformation of a nanoplate from Ag to Ag@Ag<sub>2</sub>S *via* sulfuration at room temperature. (B–E) TEM images of (B) the Ag triangular nanoplates and the as-prepared Ag@Ag<sub>2</sub>S nanoplates after sulfuration for (C) 1, (D) 5, and (E) 20 min, respectively. (F, G) TEM images of the (F) Ag nanoplates and (G) Ag@Ag<sub>2</sub>S nanoplates after being aged at 80 °C for 9 h. (H) UV-vis spectra recorded from aqueous suspensions of the Ag and Ag@Ag<sub>2</sub>S nanoplates before and after aging at 80 °C for 9 h in water, respectively. Reproduced with permission from ref 22. Copyright 2011 American Chemical Society.

# 4. Conclusions

Owing to their superior properties, Ag nanocrystals with well-controlled shapes have received considerable research interest and potential applications in many areas, including plasmonics, SERS, electronics, and catalysis. However, our ability to optimize and maintain the performance of these nanocrystals is intrinsically plagued by their shape instability. As such, it is essential to develop strategies to preserve the shape of Ag nanocrystals in an oxidative or/and corrosive environment. In most cases, the high energy sites on Ag nanocrystals, such as corners and edges, could become the vulnerable sites for the dissolution of Ag atoms in the form of Ag<sup>+</sup> ions, leading to the deterioration of original shape. In principle, the passivation of these vulnerable sites on Ag nanocrystals with a more corrosion resistant metal or compound could enhance the shape stability while sustaining the intrinsic properties of Ag nanocrystals. In this review article, we introduce two major strategies to improve the shape stability of Ag nanocrystals, including several synthetic approaches for the galvanic-free deposition of a second metal M on Ag nanocrystals for the creation of core-shell or core-frame structures. We then showcase a series of examples to illustrate the enhancement in shape stability of Ag nanocrystals using a shell or frame composed of a more corrosion resistant metal M or compound. Despite recent success, it remains a challenge to achieve the full potential of Ag nanocrystals stabilized using a core-shell or core-frame structure. Here we highlight a short list of major challenges and potential solutions correspondingly.

(1) Preserving the properties intrinsic to Ag nanocrystals. As discussed in Sections 2 and 3, both core-shell/frame structures, comprised of a Ag nanocrystal core and a more corrosion resistant shell/frame, could be obtained by controlling the synthesis process, especially by suppressing the galvanic replacement reaction between the precursor(s) to the shell/frame element(s) and Ag nanocrystals. These structures are able to protect the Ag core from etching and preserve the shape in corrosive environments. The preservation of shape is a prerequisite for protecting the intrinsic properties of Ag nanocrystals. In addition to the shape stability, the composition and thickness of the shell/frame on Ag surface are crucial parameters for keeping the intrinsic properties of Ag nanocrystals, because of the plasmonic damping effect typical of the shielding element on Ag. For example, compared with Ag cuboctahedra, the SERS activity did not change much at all upon the deposition of Au on their surfaces to form Ag@Au cuboctahedra with less than 10 Au atomic layers on ridges, when 1,4-benzenedithiol (1,4-BDT) was used as a probe molecule.<sup>19</sup> It was also reported that Ag@Au core-shell nanocubes with 3 Au atom

layers on side faces provided comparable SERS intensity to Ag nanocubes for 1,4-phenylene diisocyanide (1,4-PDI), but the peak intensity decreased when the Au shell was thickened.<sup>34</sup> In another study, when one monolayer of Ir atoms was deposited on the edges and corners of Ag nanocubes, the Ag@Ir nanocubes also showed comparable SERS intensity at a laser excitation at 532 nm for most of the characteristic peaks of 2,6-dimethylphenyl isocyanide (2,6-DMPI), while weak  $v_{NC(Ir)}$  and  $v_{NC(Ag)}$  band peaks were observed because of the weak coupling between the conduction electrons of Ir and visible light and its damping effect on Ag nanocubes.<sup>23</sup> Similarly, when a small amount of Pd or both Pd and Ag atoms was deposited and confined on the edges of Ag nanocubes, the Ag@Pd and Ag@Pd-Ag nanocubes showed comparable SERS intensity for 1,4-BDT, but the characteristic peaks intensity decreased with increase in Pd and Pd-Ag ridge thickness.<sup>36</sup> Altogether, it is feasible to protect the intrinsic plasmonic properties of Ag nanocrystals by properly selecting the elements and exquisite tuning the thickness of the shell/frame. However, there is still a lack of criteria to guide the composition and structure design for preserving the intrinsic properties of Ag nanocrystals.

(2) Strategies to enhance the properties of Ag nanocrystals. In addition to enhancing the shape stability and preserving the intrinsic properties of Ag nanocrystals, the deposition of a different metal on the surface also brings in a great opportunity to enhance their properties and extend their scope of application. As discussed before, the Au shell deposited on Ag cuboctahedra preserved the intrinsic SERS activity from 1,4-BDT at an excitation of 532 nm.<sup>19</sup> On the other hand, the Ag@Au core-shell cuboctahedra exhibited the significantly enhanced SERS signal collected from 1,4-BDT when excited at 785 nm. For example, the intensity of the peak assigned to benzene ring mode was increased by 15-fold relative to Ag cuboctahedra. Moreover, the deposition of Au on Ag cuboctahedra combined the excellent SERS activity with the catalytic activity of Au, which was successfully used as SERS substrate for *in situ* monitoring the reduction of 4-NTP to 4-ATP by NaBH<sub>4</sub>. The enhancement in SERS activity and combination of SERS and catalytic activity were also reported by other groups.<sup>47-49</sup>

Apart from the deposition of a different metal on Ag nanocrystals, alloying has been demonstrated as an effective approach to combine the plasmonic property of Ag with the stability of another metal M. In one study, Figure 10A outlines a route that produces fully alloyed Ag/Au nanospheres by sequential deposition of Ag and SiO<sub>2</sub> on Au nanoparticles, followed by annealing at an elevated temperature and removal of the SiO<sub>2</sub>.<sup>50</sup> Figure 10, B–E,

shows TEM images of corresponding intermediate nanoparticles at different stages of the synthesis. The chemical and thermal stability of the as-prepared Ag/Au alloy nanoparticles was evaluated by benchmarking against Ag nanoplates using UV-vis spectroscopy. Figure 10F shows that the LSPR peak of Ag nanospheres with a size of *ca*. 22 nm disappeared when they were exposed to a mixture containing H<sub>2</sub>O<sub>2</sub> and NH<sub>4</sub>OH. In contrast, for the Ag/Au alloy nanospheres that were annealed at 900 and 930 °C, Figure 10, G and H, shows the UV-vis spectra of these two samples before and after their exposure to the same corrosive solution for more than 24 h, respectively. It was argued that 930 °C was a critical annealing temperature, above which highly stable Ag/Au alloy nanospheres were obtained for their potential applications in many plasmonic fields with great stability involving corrosive agents.

In addition, the Ag nanoparticles encapsulated in SiO<sub>2</sub> and TiO<sub>2</sub> shells also showed enhanced shape stability, and they have been applied to enhance the light-harvesting capability of solar cells and device performance because of their exceptional LSPR property.<sup>51,52</sup> In one report, Ag@SiO<sub>2</sub> core-shell nanocubes were synthesized by adding NH<sub>4</sub>OH and tetraethyl orthosilicate (TEOS) into a suspension of Ag nanocubes in ethanol.<sup>51</sup> The Ag@SiO<sub>2</sub> nanocubes with a SiO<sub>2</sub> shell of ca. 5 nm thick were spin-coated onto the poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS) film to fabricate CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>-based perovskite solar cells (PSCs). The SiO<sub>2</sub> layer on Ag nanocubes prevented direct contact between Ag serving as anode here with the photoactive layer in the PSCs, which solved the problem of exciton quenching loss at the surface of Ag nanocubes by substantially decreasing the charge recombination on Ag surface. The incorporation of Ag@SiO<sub>2</sub> nanocubes with optimized concentration increased the short-circuit current density  $(J_{sc})$ , open-circuit voltage  $(V_{oc})$ , and fill factor (FF) of the device with enhancement factors of 11.7%, 1.5%, and 18.1%, respectively. Moreover, the introduction of Ag@SiO2 nanocubes also reduced the hysteresis of the PSCs. The performance enhancement was attributed to a strong electromagnetic field at a peak of ca. 460 nm for the Ag nanocubes, leading to light absorption improvement of the high-energy zone and thereby enhanced opto-to-electron conversion efficiency of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> in this region. Finally, the protection from the ultrathin SiO<sub>2</sub> shell effectively avoided exciton/carrier recombination at the surface of Ag nanocubes, which contributed to the charge transportation and extraction in the device and thereby better performance. In another study, thin TiO<sub>2</sub> shell also enhanced the stability of Ag nanoparticles and prevented recombination of photoelectrons with dye and electrolyte on the surface of Ag nanoparticles at the same time.<sup>52</sup> The incorporation of these Ag@TiO<sub>2</sub> nanoparticles was able to improve the power conversion efficiency while reducing photoanode thickness of dye-sensitized solar cells (DSSCs). These results indicate that the deposition of SiO<sub>2</sub> and TiO<sub>2</sub> enhanced the properties of Ag nanoparticles and expanded their scope of applications in the area of solar cells.

(3) Extension to other metals. For Ag nanocrystals, when their vulnerable sites are covered and protected from corrosive agents, either by a shell or a frame made of a more corrosion resistant metal or compound, the shape stability could be significantly enhanced, resulting in preserved properties and enhanced applications. In principle, the stability of nanocrystals made of other metals could also be improved by protecting their vulnerable sites with a more stable element or compound. For instance, compared with pure Pd nanocubes, Pd@Rh core-frame nanocubes could maintain cubic shape up to high temperatures.<sup>53</sup> Even when annealing at 500 °C for 1 h, the shape of Pd@Rh core-frame nanocubes did not experience significant change due to the deposition of Rh (with a much higher melting point than Pd) on corners and edges. In contrast, Pd nanocubes quickly evolved into nanospheres and even started to fuse together at the same temperature. Because Rh has a higher activation energy than Pd for self-surface diffusion, the Rh atoms deposited on the corners and edges provide a higher energy barrier to melting the surface of Pd@Rh core-frame nanocubes. Likewise, the Pd@Pt icosahedra with a Pt shell of 2.7 atomic layers on the surface exhibited excellent thermal stability with well-preserved shape under heating in a TEM up to 300 °C for 30 min.<sup>54</sup> These Pd@Pt icosahedra also exhibited excellent catalytic activity and durability towards the oxygen reduction reaction (ORR). Even for Au nanoparticles, atomistic simulations demonstrated that the Au@Pt core-shell structure could enhance the thermal stability and maintain the shape of Au nanostructure up to a high temperature.<sup>55</sup> The thermal stability increases with increasing the thickness of Pt shell. Similar to Ag@SiO<sub>2</sub> and Ag@TiO<sub>2</sub>, Au@TiO<sub>2</sub> and Au@SiO<sub>2</sub> core-shell nanoparticles are thermal stable up to 400 °C in air and could serve as effective shell-isolated SERS substrates.56

Altogether, core-shell/frame structure is effective in protecting the relatively unstable Ag nanocrystals by passivating their vulnerable sites with a more stable metal or compound. This strategy can also be extended to other metals, which would not only enhance the shape stability but also preserve or even improve their intrinsic properties. Furthermore, the introduction of another metal or compound can even bring in new capabilities, extending these nanostructures to

novel applications. Despite the major progress, there are still a number of challenges needed to be addressed. Firstly, it is not easy to precisely control the synthesis of core-frame/shell nanostructure, during which the Ag cores are likely to be etched to a certain extent due to the possible involvement of galvanic replacement. Secondly, the frame/shell consisting of too many atomic layers inevitably deteriorates the intrinsic properties of Ag nanocrystals while thin frame/shell can only enhance the shape stability to a certain extent, which may not meet our requirements. As such, we may still have to compromise the performance of these nanostructures in many applications. Thirdly, to our knowledge, only a limited number of metals and compounds have been used for stabilizing Ag nanocrystals, which may limit the scope of applications. It is hoped that these challenges can be solved in the future and the concepts and case studies presented in this review could serve as a good reference for other researchers dealing with the shape instability of metal nanocrystals.



**Fig. 10.** (A) Schematic illustration showing the preparation of a Ag-Au alloy nanosphere from a Au nanoparticle through immediate steps involving deposition of Ag and SiO<sub>2</sub>, annealing, and SiO<sub>2</sub> removal. (B–E) TEM images of (B) Au nanoparticles, (C) Au@Ag core/shell nanoparticles, (D) Au@Ag@SiO<sub>2</sub> nanoparticles, and (E) Ag/Au alloy nanospheres corresponding to the schematic images at different stages in (A). (F–H) UV–vis spectra of (F) Ag nanospheres, (G) Ag/Au alloy nanospheres annealed at 900 °C and (H) Ag/Au alloy nanospheres annealed at 930 °C before and after etching in a mixed solution of hydrogen peroxide and ammonia. Reproduced with permission from ref 50 at https://pubs.acs.org/doi/10.1021/ja502890c. Further permissions related to the material excerpted should be directed to the American Chemical Society.

# **Conflicts of interest**

There are no conflicts to declare.

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# References

- 1 Z. Fan, and H. Zhang, Acc. Chem. Res., 2016, 49, 2841-2850.
- 2 S. A. Maier, P. G. Kik, H. A. Atwater, S. Meltzer, E. Harel, B. E. Koel, and A. A. G. Requicha, *Nat. Mater.*, 2003, **2**, 229–232.
- 3 S. Linic, P. Christopher, and D. B. Ingram, Nat. Mater., 2011, 10, 911–921.
- 4 P. Christopher, and S. Linic, J. Am. Chem. Soc., 2008, 130, 11264–11265.
- 5 P. K. Jain, X. Huang, I. H. El-Sayed, and M. A. El-Sayed, Acc. Chem. Res., 2008, 41, 1578– 1586.
- 6 J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao, and R. P. Van Duyne, *Nat. Mater.*, 2008, 7, 442–453.

7 A. J. Haes, C. L. Haynes, A. D. McFarland, G. C. Schatz, R. P. Van Duyne, and S. Zou, *MRS Bulletin*, 2005, **30**, 368–375.

8 X. M. Qian, X. H. Peng, D. O. Ansari, Q. Yin-Goen, G. Z. Chen, D. M. Shin, L. Yang, A. N. Young, M. D. Wang, and S. M. Nie, *Nat. Biotechnol.*, 2008, **26**, 83–90.

9 Y. Ge, X. Duan, M. Zhang, L. Mei, J. Hu, W. Hu, and X. Duan, *J. Am. Chem. Soc.*, 2018, **140**, 193–199.

- 10 X. L. Lozano, C. Mottet, and H-Ch. Weissker, J. Phys. Chem. C, 2013, 117, 3062-3068.
- 11 M. Rycenga, C. M. Cobley, J. Zeng, W. Li, C. H. Moran, Q. Zhang, D. Qin, and Y Xia, *Chem. Rev.*, 2011, **111**, 3669–3712.
- 12 S. Link, and M. A. El-Sayed, J. Phys. Chem. B, 1999, 103, 8410-8426.
- 13 Q. Zhang, W. Li, L. Wen, J. Chen, and Y. Xia, Chem. Eur. J., 2010, 16, 10234–10239.
- 14 M. Luo, H. Huang, S.-I. Choi, C. Zhang, R. R. da Silva, H.-C. Peng, Z.-Y. Li, J. Liu, Z. He,

- and Y. Xia, ACS Nano, 2015, 9, 10523–10532.
- 15 S. Shi, Y. Zhang, J. Ahn, and D. Qin, Chem. Sci., 2020, 11, 11214–11223.
- 16 T.-H. Yang, J. Ahn, S. Shi, and D. Qin, ACS Nano, 2021, 15, 14242–14252.
- 17 Y. Zhang, J. Liu, J. Ahn, T.-H. Xiao, Z.-Y. Li, and D. Qin, ACS Nano, 2017, 11, 5080-5086.
- 18 Y. Wu, and D. Qin, J. Am. Chem. Soc., 2018, 140, 8340-8349.
- 19 J. Zhang, S. W. Winget, Y. Wu, D. Su, X. Sun, Z.-X. Xie, and D. Qin, *ACS Nano*, 2016, *10*, 2607–2616.
- 20 J. Li, Y. Wu, X. Sun, J. Liu, S. A. Winget, and D. Qin, ChemNanoMat, 2016, 2, 786–790.
- 21 R. Xu, D. Wang, J. Zhang, and L. Li, Chem. Asian J., 2006, 1, 888-893.
- 22 J. Zeng, J. Tao, D. Su, Y. Zhu, D. Qin, and Y. Xia, Nano Lett., 2011, 11, 3010-3015.
- 23 P. Wang, J. Ahn, R. Gao, and D. Qin, Nanoscale, 2020, 12, 20859-20867.
- 24 Y. Xia, X. Xia, and H.-C. Peng, J. Am. Chem. Soc., 2015, 137, 7947-7966.
- 25 I. V. Markov, Crystal Growth for Beginners: Fundamentals of Nucleation, Crystal Growth and Epitaxy, 1st ed.; World Scientific: Singapore, 1995.
- 26 X. Xia, Y. Wang, A. Ruditskiy, and Y. Xia, Adv. Mater., 2013, 25, 6313-6333.
- 27 Y. Yang, J. Liu, Z.-W. Fu, and D. Qin, J. Am. Chem. Soc., 2014, 136, 8153-8156.
- 28 X. Xia, J. Zeng, L. K. Oetjen, Q. Li, and Y. Xia, J. Am. Chem. Soc., 2012, 134, 1793-1801.
- 29 Y. Wu, X. Sun, Y. Yang, J. Li, Y. Zhang, and D. Qin, Acc. Chem. Res., 2017, 50, 1774–1784.
- 30 Y. Zhang, Y. Wu, and D. Qin, J. Mater. Chem. C, 2018, 6, 5353-5362.
- 31 S. Shi, and D. Qin, Angew. Chem., Int. Ed., 2020, 59, 3782-3792.
- 32 X. Sun, Y. Yang, Z. Zhang, and D. Qin, Chem. Mater., 2017, 27, 4014–4021.
- 33 X. Sun, X. Yang, Y. Zhang, Y. Ding, D. Su, and D. Qin, Nanoscale, 2017, 9, 15107–15114.
- 34 L. Zhang, Y. Zhang, J. Ahn, X. Wang, and D. Qin, Chem. Mater., 2019, 31, 1057–1065.
- 35 X. Sun, and D. Qin, J. Mater. Chem. C, 2015, 3, 11833-11841.
- 36 J. Li, J. Liu, Y. Yang, and D. Qin, J. Am. Chem. Soc., 2015, 137, 7039-7042.
- 37 Y. Zhang, J. Ahn, J. Liu, and D. Qin, Chem. Mater., 2018, 30, 2151-2159.
- 38 S. Wang, K. Qian, X. Bi, and W. Huang, J. Phys. Chem. C, 2009, 113, 6505-6510.
- 39 D. V. Goia, and E. Matijević, A Physicochem. Eng. Aspects, 1999, 146, 139–152.
- 40 X. Sun, J. Kim, K. D. Gilroy, J. Liu, T. A. F. König, and D. Qin, *ACS Nano*, 2016, **10**, 8019–8025.
- 41 M. Yang, Z. D. Hood, X. Yang, M. Chi, and Y. Xia, Chem. Commun., 2017, 53, 1965–1968.

- 42 H. Lee, S. Hong, J. Lee, Y. D. Suh, J. Kwon, H. Moon, H. Kim, J. Yeo, and S. H. Ko, *ACS Appl. Mater. Interfaces*, 2016, **8**, 15449–15458.
- 43 C. Gao, Z. Lu, Y. Liu, Q. Zhang, M. Chi, Q. Cheng, and Y. Yin, *Angew. Chem. Int. Ed.*, 2012, 51, 5629–5633.
- 44 N. Murshid, I. Gourevich, N. Coombs, and V. Kitaev, *Chem. Commun.*, 2013, **49**, 11355–11357.
- 45 Y. Cao, R. Jin, and C. A. Mirkin, J. Am. Chem. Soc., 2001, 123, 7961-7962.
- 46 J. Yang, J. Y. Lee, and H.-P. Too, J. Phys. Chem. B, 2005, 109, 19208–19212.
- 47 H. Jing, Q. Zhang, N. Large, C. Yu, D. A. Blom, P. Nordlander, and H. Wang, *Nano lett.*, 2014, 14 3674–3682.
- 48 J. Huang, Y. Zhu, M. Lin, Q. Wang, L. Zhao, Y. Yang, K. X. Yao, and Y. Han, J. Am. Chem. Soc., 2013, 135, 8552–8561.
- 49 W. Xie, and S. Schlücker, Chem. Commun., 2018, 54, 2326-2336.
- 50 C. Gao, Y. Hu, M. Wang, M. Chi, and Y. Yin, J. Am. Chem. Soc., 2014, 136, 7474-7479.
- 51 X. Ma, B. Ma, T. Yu, X. Xu, L. Zhang, W. Wang, K. Cao, L. Deng, S. Chen, and W. Huang, ACS Appl. Energy Mater., 2019, 2, 3605–3613.
- 52 J. Qi, X. Dang, P. T. Hammond, and A. M. Belcher, ACS Nano, 2011, 5, 7108–7116.
- 53 N. Lu, J. Wang, S. Xie, S. Y. Xia, and M. J. Kim, Chem. Commun., 2013, 49, 11806-11808.
- 54 X. Wang, S.-I. Choi, L. T. Roling, M. Luo, C. Ma, L. Zhang, M. Chi, J. Liu, Z. Xie, J. A. Herron, M. Mavrikakis, and Y. Xia., *Nat. Commun.*, 2015, **6**, 7594.
- 55 Y.-H. Wen, R. Huang, C. Li, Z.-Z. Zhu, and S.-G. Sun, J. Mater. Chem., 2012, 22, 7380-7386.
- 56 T. Hartman, and B. M. Weckhuysen, Chem. Eur. J., 2018, 24, 3733-3741.



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