

Morphological changes in Ag nanocrystals triggered by citrate photoreduction and governed by oxidative etching†

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The shape of a nanocrystal undergoes significant changes in response to variations in the surrounding environment. In this communication, it has been demonstrated that introduction of citric acid into the system of Ag nanocubes can trigger their shape evolution into nanospheres.

Mastery over the geometrical shape of a nanocrystal enables control of its properties and enhances its usefulness for a given application.¹ For instance, the shape of a Au or Ag nanocrystal plays the most important role in determining the number, position, and intensity of localized surface plasmon resonance (LSPR) modes.² The shape of a nanocrystal is largely defined by facets on surface, despite other parameters such as twin defects. To date, use of capping agents has been demonstrated as the most versatile approach to tailoring surface facets. Capping agents can preferentially bind to specific facets and thus manipulate the growth rates of different facets. A typical example is the use of citrate in the synthesis of Ag nanocrystals where citrate molecules promote {111} surface facets and favor the formation of {111}-enclosed shapes—octahedrons and prisms.³

Despite the success in shape control, preserving the shape of nanocrystals represents another grand challenge. Extensive studies have shown that the shape of a metal nanocrystal can undergo dynamic (and sometimes reversible) changes in response to variations in the surrounding environment. As capping agents are likely to remain on the surface of a nanocrystal and stabilize its shape, their removal (or reduction in coverage) may lead to changes in the shape of a nanocrystal, while also potentially providing a novel and facile way to access new nanocrystal shapes if controlled appropriately.

Herein it is reported that Ag nanocubes undergo a significant morphological change while their capping agent, poly(vinyl pyrrolidone) (PVP) is replaced with citric acid. This work catches our attention that one should never overlook the power of a minor change in a conventional synthesis, as well as illustrates what parameters we should pay attention to in order to preserve the shape of Ag nanocubes. In-depth investigations

also shed light on the mechanisms which are intimately and intricately linked in this system. The findings about this shape evolution, on the other hand, enable a high-yield synthesis of Ag nanospheres with tunable surface plasmonic properties. As compared to etching approach,⁴ this method avoids introducing etchant solution (thus potentially other metal impurities) and allows a ligand exchange and charge modification on nanocrystal surface. Note that direct growth approach can also generate Ag nanospheres but only works for sizes below 25 nm.⁵ The method presented here proves applicable to different sizes (Fig. S1†), as versatile as the etching approach.

In this work, single-crystal Ag nanocubes with sharp corners and edges were used as starting materials and mixed with citric acid in aqueous solution under ambient conditions. Fig. 1 shows TEM and SEM images of Ag nanocrystals sampled at different stages from a reaction performed in the presence of room light. The starting materials of Ag nanocubes were synthesized by following a solution-phase process with PVP as a capping agent to promote {100} facets.⁵ The images (Fig. 1a and b) show that the starting nanocrystals have a cubic profile with well-defined corners and edges. As the reaction proceeded, the nanocubes first became more rounded (Fig. 1c and d) and then transformed into spheres

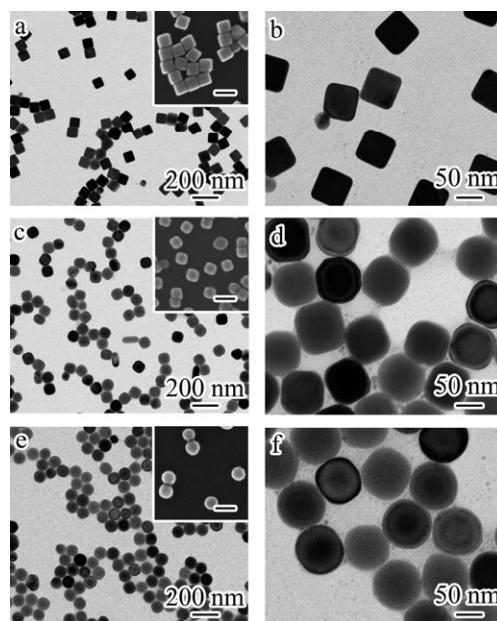


Fig. 1 TEM images of Ag nanocrystals formed during a morphological evolution: nanocubes as starting materials (a and b); truncated nanocubes formed after reaction for 30 min (c and d); and nanospheres formed after reaction for 120 min (e and f). The insets of (a), (c) and (e) show SEM images of corresponding samples (scale bar represents 100 nm).

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† Electronic supplementary information (ESI) available: Detailed experimental procedures; comparison by volume for Ag nanocrystals in shape evolution; TEM images of 40 nm Ag nanocubes in the presence of citric acid; TEM images of the samples treated with acetoacetate, sodium citrate or ascorbic acid instead of citric acid; TEM images of the samples in the absence of light or with the exclusion of oxygen from the system; SERS spectra of Ag nanocubes and nanospheres; specifications of light source and glassware. See DOI: 10.1039/c0cc03799k

(Fig. 1e and f). The resulting Ag nanocrystals displayed an almost perfectly circular profile under TEM and retained their high level of monodispersity throughout the transformation process. The nanocubes had a diameter of 58.5 ± 2.7 nm, and the nanospheres had a slightly bigger diameter of 61.6 ± 3.3 nm, calculated from measurements of 200 particles. A comparison by volume shows a significant volume shrinkage in the Ag nanocrystals after the shape evolution (Table S1†).

The slight increase in particle diameter indicates that the morphological transformation does not simply result from a similar etching process to the reported case.⁴ Instead an atomic addition step should be involved, attributed to this diameter growth. Citric acid as the only chemical added into the system is hypothesized to play an important role in the generation of new Ag atoms. It has been reported separately by Mirkin and Brus research groups that citrate can be degraded to acetoacetate through a photoreaction when irradiated with a light source with wavelengths centered at 550 ± 20 nm.⁶ To investigate whether a similar photochemical process occurred in this system, the reaction solution at different stages was measured with ¹H NMR spectroscopy after removing Ag nanoparticles and evaporating water. From the NMR spectra (Fig. 2), one can see that the intensity of the four resonance peaks between δ 2.60 and 2.90 assigned to citric acid decreased as the reaction proceeded. Three new resonances appeared at δ 1.8–2.1 and became stronger simultaneously, which can be indexed to the formation of acetoacetate. These results reveal that citric acid served as a photo-reductant in the reaction. To evaluate the role of photoreduction in shape evolution, we have performed several control experiments. When light was excluded from the system, Ag nanocubes preserved their sharp corners and edges when they were stored in the presence of citric acid for 24 h (Fig. S2†), indicating that the morphological change was triggered by light (specifications for light source and glassware, see Fig. S8†). As acetoacetate instead of citric acid was directly used in the reaction, the shape of Ag nanocubes was remained unchanged no matter whether or not the light was present in the system (Fig. S3†). It excludes the possibility that photodegradation product actually caused the shape changes.

Photoreduction plays an important role in atomic addition on nanocrystal surface; however, it is worth pointing out that etching is the predominant process in the system. It is believed that oxidative etching (by oxygen dissolved in solution) dissolved some surface atoms (*e.g.*, at corners and edges) into

silver ions and made the nanocubes severely truncated. This dissolution, on the other hand, provided Ag precursor for the photoreduction. To assess the importance of etching in this system, the Ag nanocubes were kept in an aqueous solution of sodium citrate that also has the function of photoreduction instead of citric acid. Fig. S4† shows that the Ag nanocubes could still evolve into nanospheres, but progress was much slower. The sample only reached the stage of truncated nanocubes after 2 h of reaction, and completion of entire transformation required 8 h. The main difference caused by sodium citrate is PH value of reaction system. It has been demonstrated that the presence of acid can facilitate oxidative etching process as the potential of oxygen reduction is increased from 0.401 V to 1.229 V depending on the concentration of acid.⁷ The contribution of oxidative etching was further confirmed by the experiment by excluding the oxygen from the system in an inert atmosphere where no significant shape change could be observed (Fig. S5†). These experiments show that transformation progress is closely related to etching ability.

Taken together, two key and competitive processes are responsible for the transformation from nanocubes to nanospheres: oxidative etching enhanced by the acidity of citric acid to remove atoms from surface, and photoreduction by citric acid to bring freshly formed atoms onto surface. The changes in particle shapes clearly show that the locations for etching should be different from atomic addition sites. Fig. 3 illustrates a transformation mechanism from nanocubes to nanospheres. From the view of thermodynamics, spherical shapes (or Wulff polyhedrons) enclosed by a mix of {111} and {100} facets are most favored in order to minimize total surface energies.⁸ In the synthesis of Ag nanocubes, PVP was used as a capping agent to promote {100} surface facets thanks to its preferential binding to {100}.⁹ In this case, the order of surface free energies of different facets was altered by introduction of molecules onto specific facets to meet the lowest total energies. In this system, the coverage of PVP on nanocube surface was greatly reduced (or totally removed) when citric acid was introduced to the system, as determined by surface-enhanced Raman spectroscopy (SERS) and zeta-potential measurements (Fig. S6†). As a result, the surface energies of nanocubes were no long low to make them favorable by thermodynamics, resulting in a transformation towards the thermodynamically favored form—spherical shape. Specifically the oxidative etching by oxygen that was enhanced by the acidity of citric acid selectively removed more active atoms from corners and even edges, which enlarges coverage of {111} facets on surface. Although oxidative etching always occurs in

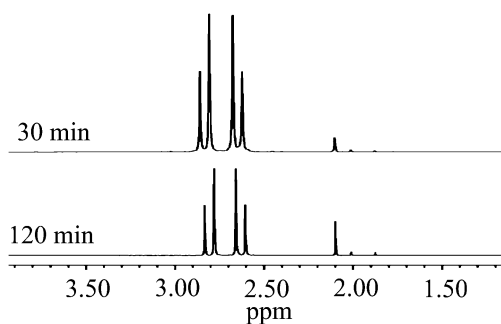


Fig. 2 ¹H NMR spectra taken from reaction solution during the photochemical transformation from Ag nanocubes to nanospheres.

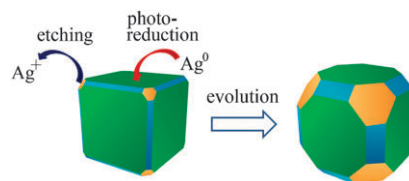


Fig. 3 Schematic illustration for the transformation mechanism from Ag nanocubes to nanospheres. Note that the rate of etching is much higher than that of photoreduction. The green, orange and blue colours represent {100}, {111} and {110} facets, respectively.

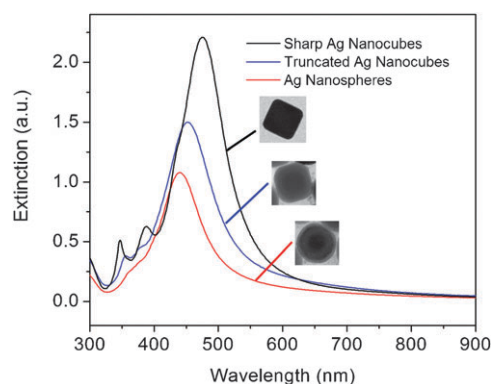


Fig. 4 UV-vis spectra of Ag nanocrystals formed at different stages, showing the tuning of surface plasmonic properties.

the system with oxygen, the transformation from Ag nanocubes into nanospheres takes at least 1 month at room temperature in the case that no other process is involved. One of the major obstacles to hinder the oxidative etching is the protection of Ag atoms by capping agents on surface. However, in the present case, photoreduction by citric acid could largely consume the Ag ions generated from etching process, break the equilibrium between Ag atoms and ions, and facilitate oxidative etching at the beginning of reactions. Once etching started (*i.e.*, the surface atoms at corners and edges were dissolved), it would not be held back by capping agents any more. The photoreduction by citric acid generated fresh Ag atoms which were then added to {100} facets due to the unique capping function of citric acid on {111} facets.³ The contribution of capping effect of citric acid was verified by the experiment with ascorbic acid instead of citric acid (Fig. S7†). As suggested by volume shrinkage in the shape evolution, oxidative etching should be much faster than photoreduction. Thus overall, the evolution from nanocubes into nanospheres is governed by the oxidative etching, but needs to be activated by the photoreduction of citric acid for a relatively fast transformation. It is worth mentioning that the size and shape of nanospheres could be well maintained even after the sample was stored in citric acid solution for more than one month, providing a way to preserve the shape of Ag nanospheres.

The morphological transformation allows us to tune the surface plasmonic properties of Ag nanocrystals. As nanocrystals turned more rounded, a strong dipole peak gradually blue-shifted from 476 nm to 439 nm (Fig. 4). This blue-shift is mainly due to less charge separation caused by high symmetry in particle shape.¹⁰ On the other hand, weak dipole (a weak peak at 348 nm) and quadrupole (a shoulder centered at 389 nm) resonances disappeared, when the shape transformed from

low-symmetric cube to high-symmetric sphere. The changes in surface plasmonic features also confirm the formation of highly symmetric nanospheres.

In conclusion, morphological evolution of Ag nanocubes into nanospheres has been observed when capping agent of PVP is replaced by citric acid. Citrate photoreduction has been demonstrated to trigger this transformation from cubic to spherical shapes, and the entire shape evolution is governed by oxidative etching. This work provides important information about how the shape of nanocrystals can be preserved by controlling specific parameters. It also offers a new method for synthesizing single-crystal Ag nanospheres with well-defined shape, size and dispersity at high yields.

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