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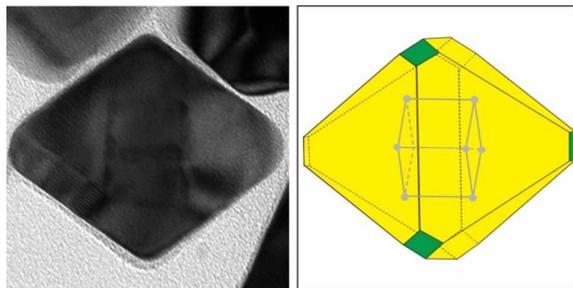
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PdS cubic frames were introduced as markers to monitor the shape evolution of Pd nanocubes to octahedron.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Monitoring the Shape Evolution of Pd Nanocube to Octahedron by PdS Frame Marker

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

We report the use of compounds formed on the surface of nanocrystals as markers to effectively monitor the shape evolution during nanocrystal growth. By labelling the corners and edges of cubic Pd seeds with PdS through sulfuration, we obtain clear insight in their shape transition to octahedrons. This work significantly expands the scope of the marker technique for studying nanoparticle shape evolution.

Considerable attention has recently been directed towards the growth mechanism of nanocrystals due to their lure of exotic and genuinely useful properties promising for a wide range of applications where the nanoscale morphology and topology greatly influence their performance.¹⁻⁶ Most of these studies, however, rely on the use of electron microscopy, which has been recognized as one of the most powerful tools for real-time monitoring nanocrystal growth, for example, in imaging the growth of Pt₃Fe nanorods in solution³ and oriented attachment of Pt nanocrystals.⁴ Although these prior studies have demonstrated the feasibility of tracking nanocrystal growth in real time, it still remains a great challenge to closely monitor what happens to individual particles under systematically varied growth conditions.^{7,8} Before significant improvement in microscopic techniques can be achieved for this purpose, it is still necessary to develop new and practical methods for tracking the growth of nanocrystals under different growth conditions. Recently, we proposed a marker technique, using embedded Au frames as markers, to successfully monitor the growth of Ag nanoplates with the help of transmission electron microscopy.⁵ Later, Mirkin and co-workers used nanoparticles of Au as both seeds and microscopy label to follow the growth of 20-fold twinned icosahedra of Ag.⁶ Although this marker technique has provided insight in the role of particular reaction conditions in controlling nanocrystal growth, the subject of study was only limited to Ag-Au systems.^{5,6} In addition, these limited cases seem to suggest that epitaxial growth of one metal to another one might be a prerequisite of this marker strategy, which may prevent extending it to studying many other nanocrystal systems.

In this work, we report that compounds formed on the surface of nanocrystals can also be effectively used as markers to monitor the shape evolution during the growth of nanocrystals, thus significantly expand the scope of the marker technique for studying nanoparticle shape evolution. More specifically, we describe a new and effective marker to monitor the growth of Pd nanocrystals by labelling the original boundaries of seeds through

site-selective sulfuration. Due to the different coordination numbers, the reactivity of surface atoms at different sites is also different, making it possible to label some particular sites of the original seeds and outline their morphology.⁹⁻¹¹ Taking a cubic nanocrystal for example, the reactivity of different sites is supposed to decrease in the order of corner, edge, and side face.^{12,13} Therefore, we could easily and tightly control the kinetics and degree of sulfuration to label the corner and edge sites of the original cubic seeds. Most interestingly, the sulfuration process, if carried out in controllable way, does not interfere with the subsequent seeded growth, thus allowing the use of sulphide frames as markers to monitor the shape evolution of the nanocrystals.

In a typical synthesis, Pd nanocrystals were used as a model to illustrate our marker strategy. Pd is known as a key component of many catalysts used in industrial processes and commercial devices.¹⁴ When served as a catalyst, the activity and selectivity of Pd nanocrystals have a strong dependence on their shapes,^{12,15-19} making exquisite morphology control a critically important area of study. As clear elucidation of the growth paths can benefit the controlled synthesis of Pd nanocrystals, we apply this new marker technique to monitor the growth of Pd nanocrystals.

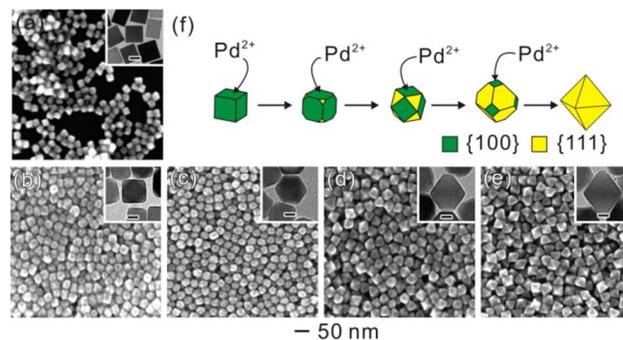


Figure 1. Shape-controlled growth of Pd nanocrystals by using Pd nanocubes as seeds: (a) nanocubes used as seeds; (b) truncated nanocubes; (c) cuboctahedrons; (d) truncated octahedrons; and (e) octahedrons. (f) Schematic illustrating how nanocubes evolved into octahedrons. The insets show TEM images of individual nanocrystals at a higher magnification (scale bars: 10 nm).

In our prior work, we have shown that Pd octahedrons can be prepared by selective deposition of Pd atoms onto {100} facets of Pd nanocubes,²⁰ which were pre-synthesized according to a procedure we developed before.²¹ As can be seen in Figure 1, a shape transition from cube to octahedron can be observed by

controlling the ratio of Pd precursor to the seed in the reaction. This growth mechanism can be further confirmed by more TEM images of the obtained nanocrystals in each stage (Figure S1). Similar shape transformation path from cube to octahedron has also been observed in many other metals (e.g., Ag and Au).^{22,23} Although this kind of growth path has been extensively studied by characterizing the products at different reaction times or different precursor amounts, it is still challenging to unambiguously define the growth pathway due to the difficulty in differentiating the seeds from the final products. In addition, the low resolution of SEM and the difficulties in defining 3D projections in TEM images also restrict systematic growth mechanism studies of Pd nanocrystals, making it difficult to truly recognize the relationship between growth orientations of the seed and the final nanocrystals. Although some studies have proposed that the catch-and-see method can give us an image of shape evolution during the nanostructure growth, more in-depth study is necessary to fully comprehend its underlying causes and mechanisms.

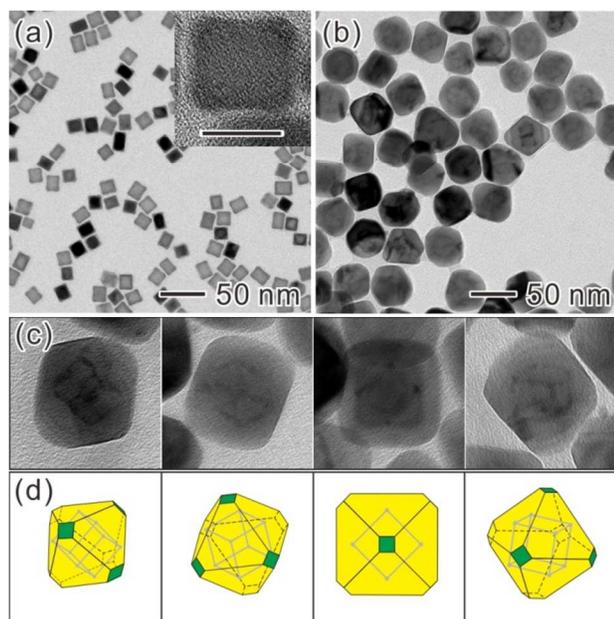


Figure 2. Monitoring the shape evolution of Pd nanocrystals from cube to octahedron by using sulfurized Pd nanocubes as seeds: (a) TEM images of sulfurized Pd nanocubes used as seeds; (b) TEM images of as-prepared Pd octahedrons marked with PdS frames; (c) TEM images of Pd octahedrons viewed from different directions; and (d) their corresponding models. The inset in (a) shows the TEM image of sulfurized Pd nanocubes at a higher magnification (scale bars: 10 nm).

To acquire a better understanding of the overgrowth of Pd nanocubes, we have developed a straightforward but informative marker experiment by using partially sulfurized Pd nanocubes as a new marker. In a typical experiment, the Pd nanocubes were firstly sulfurized by polysulfide (Na_2S_x), and then used as seeds for the subsequent overgrowth to octahedrons. As an important sulfuration reagent, Na_2S_x has ever been used for the selective sulfuration of Ag nanocrystals.²⁴ By appropriately sulfurizing the Pd nanocrystal with Na_2S_x , we can outline the original boundaries (edges and corners) of the Pd nanocrystal (inset in Figure 2a). Owing to the difference in electron-scattering efficiencies

between PdS and Pd, the PdS frame can be differentiated from the Pd nanocrystals, making it an ideal candidate for monitoring the stepwise transformation of the Pd nanocubes into other nanocrystals that differ in shape and internal structures. Figure 2a shows the TEM images of Pd nanocubes after sulfuration. From the TEM image, it is clear that the cubic shape of nanocrystals is well maintained. With careful observation, we can further find that the cubic nanocrystals exhibit a darker contrast in the shell area, indicating the formation of PdS nano-frames on the edges and corners of Pd nanocubes. Then, these sulfurized Pd nanocubes were used as seeds for the subsequent overgrowth to octahedrons. The subsequent growth strictly followed the same growth condition of our prior work.²⁰ After the overgrowth, all of the cubic nanocrystals were transformed into octahedrons, as shown in Figure 2b. The successful synthesis of Pd octahedrons implies that the sulfurized Pd nanocubes show the same growth manner during the overgrowth of Pd nanocubes. Different from the normal octahedrons, a cubic frame can be clearly observed inside each prepared octahedron, which can be indexed as PdS frame. The presence of PdS nano-frames as markers inside Pd octahedrons provides us significant insights based on TEM observations (Figure 2b) and elemental mapping (Figure S2) during growth. The TEM images obtained from the octahedrons viewed from different angles (Figure 2c) and their corresponding models (Figure 2d) have further shown the orientation relationships between the original cubic seeds and the resultant octahedrons. As can be seen, the growth of octahedrons was obviously induced by the cubic seeds, and with the same orientations of the Pd nanocubes. Based on the above results, the growth was found to follow isotropic epitaxial growth model, although the Pd nanocubes were divided by the sulfide corners and edges. As we have demonstrated in our previous work, the formation of Pd octahedrons was resulted from the deposition of Pd atoms selectively onto the {100} facets. Although the corners ($\langle 111 \rangle$ direction) and edges ($\langle 110 \rangle$ direction) were sulfurized by Na_2S_x , thus hindering the deposition of Pd atoms onto these two sites, the growth of octahedrons is still favoured.

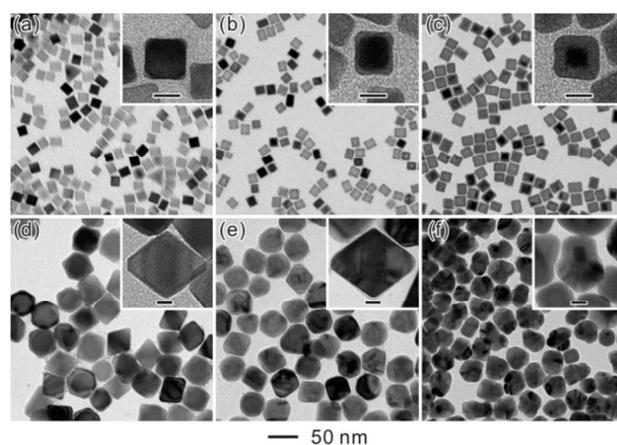


Figure 3. (a-c) TEM images of sulfurized cubic seeds with different volume of Na_2S_x : (a) 250 μl ; (b) 750 μl ; (c) 5 ml; and the corresponding products (d-f). The insets show TEM images of individual nanocrystals at a higher magnification (scale bars: 10 nm).

As aforementioned, the formation of Pd octahedrons was resulted from the deposition of Pd atoms onto Pd(100) facets, and the formation of PdS on the surface of Pd nanocubes can hinder

this deposition. Therefore, in order to give a good view of PdS markers inside the Pd octahedrons, it is important to control the degree of sulfuration. To this end, we further tuned the addition of polysulfide (Na_2S_x), which was used as sulfuration reagent in our experiment. TEM and HRTEM images were used to characterize the sulfuration ratio of Pd nanocubes (Figure S3). The results were summarized in Figure 3. With a low concentration of Na_2S_x (0.05 mM), the PdS nano-frames were difficult to be observed due to the weak signal, as shown in Figure 3a and d. Slightly increasing the concentration to 0.15 mM can result in the proper sulfuration of cubic seeds, with corners and edges being sulfurized and $\{100\}$ facets stay unchanged. However, if further increasing the concentration of Na_2S_x to 1.0 mM, the original Pd cubic seeds would be extensively sulfurized, even the $\{100\}$ surface of Pd nanocubes. In this case, the growth of products can't be induced by the original cubic seeds any more, since the Pd nanocubes were fully encapsulated inside the PdS shells, and only irregular Pd nanocrystals with many twin planes inside can be formed due to the large lattice mismatch between Pd and PdS. Due to the energy minimization, Pd deposition only happens preferentially on $\{100\}$ facet without PdS rather than edge when the amount of Pd precursor is very small, resulting in the formation of truncated nanocubes (Figure S4). So, it is therefore very important to control the proper ratio of sulfuration. Accordingly, there is a critical amount of Na_2S_x needed to sulfide the edges and corners. When the amount of Na_2S_x introduced into the reaction was less than the critical value, the edge of the cube could not be fully replaced by PdS, resulting in the weak signal of the PdS nano-frames markers in the final octahedrons (Figure 3d). When the amount of Na_2S_x was higher than the critical value, the $\{100\}$ surfaces of Pd nanocubes would be also sulfurized thus the ratio between the growth rates along $\{100\}$ and $\{111\}$ directions was changed, resulting in the formation of Pd nanocrystals with irregular shapes (Figure 3f).

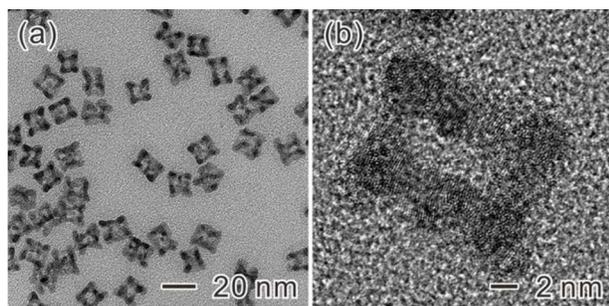


Figure 4. (a,b) TEM images of PdS cubic nano-frames obtained by selectively etching the Pd cores via the galvanic replacement.

In order to further prove the successful partial sulfuration of Pd nanocubes, we used PtCl_6^{2-} ions to react with sulfurized Pd nanocubes.²⁵ As reported, Pd atoms on $\{100\}$ facets of Pd nanocubes can selectively react with PtCl_6^{2-} ions via the galvanic replacement reaction. Therefore, when $\{100\}$ facets of Pd nanocubes were exposed to PtCl_6^{2-} ions, it will slowly disappear and finally only cubic frames can be obtained. Figure 4 shows the TEM images of sulfurized Pd nanocubes after the galvanic replacement reaction. Obviously, only cubic frames can be observed after the reaction, implying that the Pd nanocubes were successfully partially sulfurized. In comparison, no reaction will

occur when the surface of Pd nanocubes was fully sulfurized. HRTEM further confirms that the resulted cubic frames were PdS without Pt deposited on it.

Figure 5 shows the TEM images of Pd nanocrystals with different reaction times. Upon the increase of the reaction time, the sulfurized Pd nanocubes slowly grew larger and the shape changed from cube to truncated cube, cuboctahedron, and finally octahedron, undergoing a similar shape transition and ultimately transforming into a $\{111\}$ -faceted octahedron as we have reported previously.²⁰ During this growth process, we can clearly see that the cubic seeds always appeared at the centre of the as-prepared nanocrystals, implying concentric overgrowth of Pd nanocubes to octahedrons.

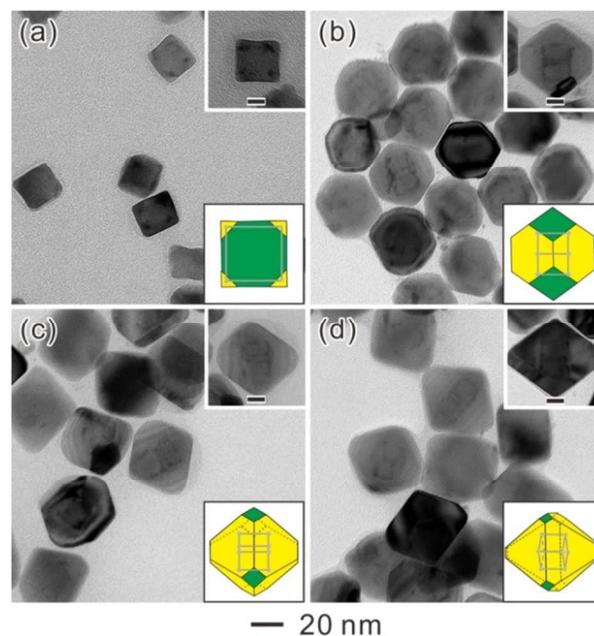


Figure 5. TEM images of marker Pd octahedrons obtained at different reaction times: (a) 30 min, (b) 60 min, (c) 90 min, and (d) 180 min. The insets show TEM images of individual nanocrystals at a higher magnification (scale bars: 10 nm).

Conclusions

In summary, we have presented a new marker technique which uses embedded PdS frames to define the original boundaries of Pd nanocubes after growing to octahedrons. Based on the orientations of the inner frame and surrounding Pd, it is apparent that the shape transformation from a Pd cube to an octahedron is caused by the preferential deposition of Pd onto the $\{100\}$ facets of the cubic seeds. For the first time, this work reveals that a compound resulting from surface reactions can be used as an effective marker for monitoring the growth of nanocrystals, and thus greatly expands the scope of the marker technique to many other metals (e.g., Au, Ag, Pd, and so on).

Acknowledgements

We are grateful for the “start-up fund”, “the Fundamental Research Funds for the Central Universities”, and the support to the Center for Materials Chemistry provided by Xi’an Jiaotong University. Yin also thanks the U. S. National Science Foundation (DMR-0956081) for partial support of this research.

Notes and references

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