

## Shape-Controlled Synthesis of Palladium Nanocrystals

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### ABSTRACT

In a solution-phase synthesis, the final shape taken by a nanocrystal is determined by the twin structures of seeds and the growth rates of different crystallographic facets. Here, the maneuvering of these factors in an aqueous system to achieve shape control for Pd nanocrystals is discussed. L-ascorbic acid, citric acid, and poly(vinyl pyrrolidone) are tested for manipulating the reduction kinetics, with citric acid and Br<sup>-</sup> ions used as capping agents to selectively promote the formation of {111} and {100} facets, respectively. The distribution of single-crystal versus multiple-twinned seeds can be further manipulated by employing or blocking oxidative etching. The shapes obtained for the Pd nanocrystals include truncated octahedron, icosahedron, octahedron, decahedron, hexagonal and triangular plates, rectangular bar, and cube. The ability to control the shape of Pd nanocrystals provides a great opportunity to systematically investigate their catalytic, electrical, and plasmonic properties.

### 1. INTRODUCTION

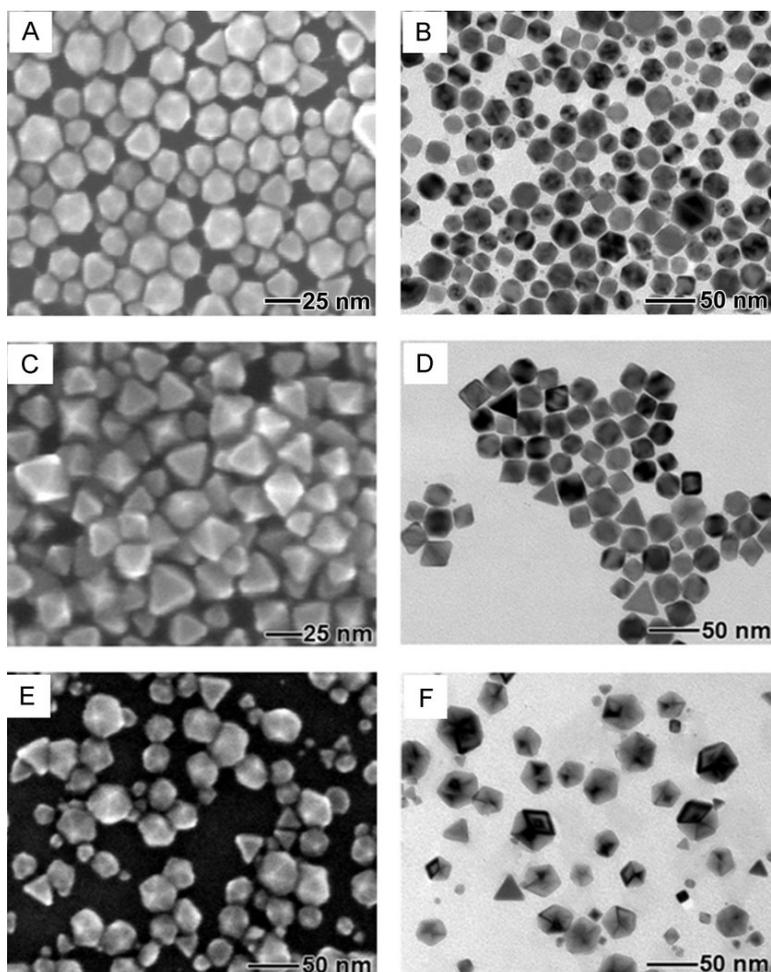
Palladium is a key catalyst invaluable to many industrial processes; notable examples include hydrogenation/dehydrogenation reactions, low-temperature reduction of automobile pollutants, and petroleum cracking. It has also demonstrated remarkable performance in hydrogen storage at room temperature and atmospheric pressure. In organic chemistry, a large number of carbon-carbon bond forming reactions such as Suzuki, Heck, and Stille coupling all depend on catalysts based upon Pd(0) or its compounds. It has been shown that the activity and selectivity of a catalyst can be greatly enhanced by the use of nanocrystals enclosed by specific crystal facets that are intrinsically more active for a particular reaction. Since the facets exposed on a nanocrystal are determined by its shape, an exquisite shape control of Pd nanocrystals is therefore highly desired for tailoring their catalytic properties and also a prerequisite for high performance in various catalytic applications.

A water-based synthesis of metal nanocrystals provides a number of merits such as simplicity, convenience, and the potential for large-scale production. Here we present the facile water-based synthesis of Pd nanocrystals with a rich variety of

shapes including truncated octahedron, icosahedron, octahedron, decahedron, hexagonal and triangular thin plates, rectangular bar, and cube.

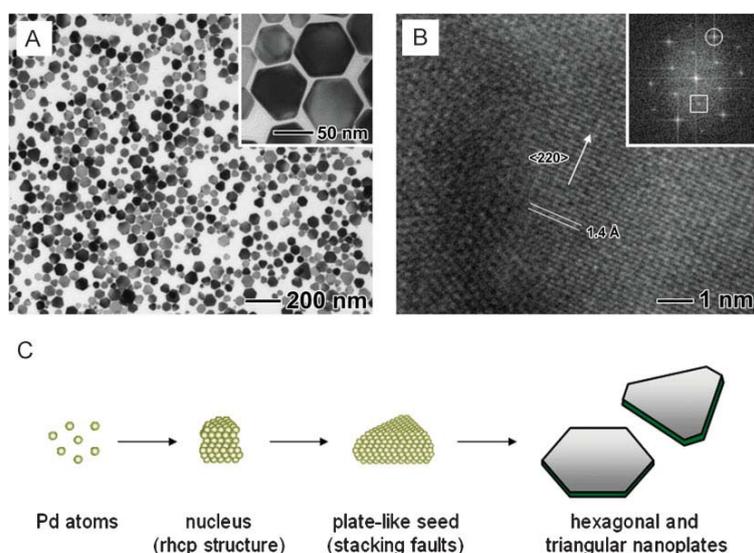
## 2. SHAPE-CONTROLLED PALLADIUM NANOCRYSTALS

Citric acid can be introduced into the reaction. Interestingly, citric acid (or citrate ions) can serve as not only a reducing agent but also a capping agent to stabilize these structures thanks to its strong binding to the {111} facets of Pd. In addition, these species can effectively block oxidative etching by competing with oxygen adsorption onto the Pd surface or exhausting the adsorbed oxygen atoms. In this way, it becomes possible to produce Pd icosahedrons and decahedrons. More specifically, the shape of the final Pd nanocrystals can be controlled by varying the concentrations of  $\text{Na}_2\text{PdCl}_4$  and citric acid to selectively produce Pd icosahedrons, octahedrons, and decahedrons whose surface is covered by the {111} facets as shown in Fig 1.



**Fig. 1.** SEM and TEM images of Pd icosahedrons, octahedrons, and decahedrons.

If the reduction becomes considerably slow, both nucleation and growth may deviate from a thermodynamically controlled pathway. This type of synthesis is known as a kinetically controlled process, and the final nanocrystal shape typically deviates from those favored by thermodynamics (i.e., structures with higher free energies). In one case, thin plates with hexagonal and triangular shapes can be formed, with both top and bottom faces covered by the  $\{111\}$  facets. In practice, kinetically controlled synthesis can be achieved by substantially slowing down the reduction rate. For this purpose, PVP can be used as an ideal reducing agent thanks to its weak reducing power, thereby enabling a kinetic control over both nucleation and growth. Figure 2 shows Pd nanoplates synthesized by heating an aqueous solution containing  $\text{Na}_2\text{PdCl}_4$  and PVP at 100 C for 3 h. The product mainly consists of nanoplates (> 90%) with both hexagonal and triangular shapes and sizes in the range of 50–80 nm. Most of the triangular nanoplates have truncated corners. In the HRTEM image, the fringes can be seen and indexed as  $\{220\}$  of fcc Pd. The FT pattern is composed of spots with a six-fold rotational symmetry, indicating that the top and bottom faces of Pd nanoplates are enclosed by the  $\{111\}$  planes. The spots circled and squared can be indexed to the  $\{220\}$  and forbidden  $1/3\{422\}$  reflections, respectively. Observation of the forbidden spots associated with  $1/3\{422\}$  diffractions suggests that planar defects such as stacking faults are present in the  $\{111\}$  plane perpendicular to the electron beam.



**Fig. 2.** TEM images of Pd nanoplates

### 3. CONCLUSIONS

We have demonstrated the capability and feasibility of using a water-based system for the high-yield production of Pd nanocrystals with a rich variety of shapes,

including truncated octahedrons, icosahedrons, octahedrons, decahedrons, hexagonal and triangular thin plates, rectangular bars, and cubes. The success of this approach depends on a number of parameters such as the reduction kinetics, oxidative etching, and surface capping. These parameters could be combined to provide an effective route to maneuver both the twin structures of seeds and the surface facets, which are two key factors in determining the final shape of a nanocrystal.

#### 4. REFERENCES

- [1] B. Lim, M. Jiang, J. Tao, P. H. C. Camargo, Y. Zhu, Y. Xia, *Adv. Func. Mater.*, 2009,19, 189-200.