Shape controlled synthesis of palladium nanocrystals by combination of oleylamine and alkylammonium alkylcarbamate and their catalytic activity[†]

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The shape of Pd nanocrystals (NCs) can be controlled by combination of oleylamine (OAm) and alkylammonium alkylcarbamate (AAAC), and Pd spheres, tetrahedra and multipods have been synthesized. The multipods and tetrahedra are much more active than the spheres for hydrogenation reactions.

Shape and size controlled synthesis of noble metal nanocrystals (NCs) has attracted much attention due to the fact that the shape and size of NCs play crucial roles for their properties.¹ Palladium (Pd) is widely used as catalyst for different reactions, such as hydrogenation and dehydrogenation reactions, carbon–carbon bond formation reactions, petroleum cracking reactions, and harmful gas conversion. It can also be used in other fields such as hydrogen storage and gas-sensing. Pd NCs with different sizes and shapes have been prepared. For example, some solution methods have been developed to synthesize Pd NCs using strong surface ligands, and nearly spherical monodisperse NCs were obtained.² Other Pd nanostructures have also been reported, such as polyhedra³ (including tetrahedra^{3/}), nanorods,^{4a,b} nanowires,^{4c} leaflike structure.^{4d}

Oleylamine (OAm, Scheme S1) is one of the most commonly used ligands for the synthesis of noble metal NCs. However, spherical NCs and 1-D nanostructures⁵ are usually obtained, and there is still lack of shape control over noble metal NCs except Pt.⁶ Recently, Tilley and co-workers synthesized successfully branched Pd nanostructures using the mixture of OAm and oleic acid as the ligands.⁷ Sun and co-workers⁸ reported OAm-mediated synthesis of nearly monodisperse spherical Pd NCs, and the supported Pd NCs showed excellent activity and stability for formic acid oxidation under fuel cell reaction conditions. Despite these achievements, development of new routes to synthesize Pd NCs of novel structures and studying their functions is still an interesting topic.

It is well known that amines can react with CO₂ to form AAAC.⁹ In this work, we first prepared AAAC by reaction of CO₂ and OAm at ambient conditions in toluene (Scheme S1). The formation of AAAC was confirmed by FTIR and ¹³C-NMR techniques (Fig. S1 and S2). Pd NCs were synthesized in toluene at 60 °C using palladium(II) acetylacetonate (Pd(acac)₂) as

the precursor and borane-*tert*-butylamine complex (BTB) as the reductant in the presence of OAm, AAAC or AAAC/OAm mixtures. The detailed experimental procedures are given in Supporting Information.

Fig. S3 and Fig. 1A, D and F show the TEM images of the Pd NCs obtained at different AAAC/OAm weight ratios (0/10, 3/7, 5/5, 6/4, 7/3, 8/2, 9/1 and 10/0). At AAAC/OAm weight ratios of 0/10 and 3/7, polycrystalline particles were formed, which originated from random aggregation of Pd spherical particles of *ca*. 3 nm, as can be known from the TEM and HRTEM images in Fig. S3A to S3C. At the AAAC/OAm weight ratios of 1/10, 2/8, and 4/6 (data not shown), the size and morphology of the Pd NCs were similar to those prepared at AAAC/OAm weight ratios of 0/10 and 3/7. At the AAAC/OAm weight ratio of 5/5, nearly monodisperse polycrystalline spherical Pd NCs of about 3 nm were obtained (Fig. 1A, Fig. S3D), indicating that addition of AAAC could prevent the aggregation of Pd NCs. A long range ordered superlattice was fabricated by the nearly monodisperse spherical NCs, which



Fig. 1 TEM images of the Pd NCs obtained at AAAC/OAm weight ratios of 5/5 (A), 7/3 (D), and 10/0 (F). (B) TEM image of the superlattice formed by the spherical NCs in (A). (C) Selected area electron diffraction pattern in (A). (E) HRTEM image of NC in (D) (inset: Fast Fourier transformation image). (G) HRTEM image of NC in (F). All the samples above were synthesized at 60 °C for 10 min.

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showed very narrow size distribution (Fig. 1B). Formation of metallic Pd(0) was confirmed by SAED pattern (Fig. 1C).

On further increasing the weight ratio of AAAC/OAm to 6/4, some triangular-like NCs could be observed in the TEM image (Fig. S3E), and the triangular-like NCs became the dominant morphology when the weight ratio of AAAC/OAm increased to 7/3 (Fig. 1D). HRTEM characterization indicated that these triangular-like NCs were actually in truncated tetrahedral shape with four {111} facets exposed (Fig. 1E).¹⁰ Time resolved study showed that the growth process of the tetrahedra was finished in 2 min (Fig. S4), and the size and morphologies of the Pd NCs did not change significantly in the following 8 min of heating treatment at 60 °C. At the AAAC/ OAm weight ratios of 8/2 and 9/1 deformed tetrahedra and slightly branched NCs were formed, respectively, as shown in Fig. S3. Fig. 1F showed that in the AAAC/toluene system (without OAm), Pd multipods were generated: mostly I- and V-shaped bipods, less commonly T- and Y-shaped tripods. HRTEM images showed that the legs of these multipods had many stacking faults, and the overall direction of these zig-zag shaped legs was approximately along the $\langle 111 \rangle$ (Fig. 1G and S5). The morphology of the multipods was very different from that of the aggregated Pd particles prepared at AAAC/OAm weight ratios of 0/10 and 3/7 (Fig. S3). Many kinds of multipod-shaped NCs have been reported, most of which are II-VI semiconductors (e.g., ZnO, ZnSe, ZnS, CdS, CdSe, CdTe),^{11a} but only few reports were about noble metals (e.g. Pd, Pt, Au).^{5b,7,11b-d} A survey of the literature revealed that most of the reported multipod-shaped NCs were constructed by several single crystalline legs. Interestingly, the morphology of the Pd multipods synthesized in this work was quite unusual, and plenty of stacking faults existed in these legs. Time dependent study showed that the structures were formed in 40 s, as shown in Fig. S6, revealing that the structures might be derived from the 1-D overgrowth of the twinned nuclei, which was due to fast reaction rate, which will be discussed in the following section.

The morphology of the synthesized Pd NCs was affected mainly by two factors. One was the nucleation and growth rate, the other was the aggregation manner of the NCs. On the one hand, increasing the ratio of AAAC/OAm resulted in more rapid formation of the Pd NCs, as indicated by faster color change of the solution in the experiment, leading to the acceleration of the nucleation and growth process of the Pd NCs. It is known that -NH₂ group can complex with many metal ions by coordination. AAAC, which is a salt formed from one CO₂ and two OAm molecules (Scheme S1), should have weaker coordination ability, and the Pd(II) complex is less stable. Therefore, addition of CO2 can increase the reduction rate of the Pd(II) ions significantly. In the AAAC system, the overhigh reaction rate of the Pd precursor and nucleation rate resulted in kinetically controlled growth manner,^{7,12} and multipods with many stacking faults and surface steps were formed. On the other hand, increasing the ratio of AAAC/OAm could prevent the aggregation of Pd NCs, as discussed above. As in many cases of NCs synthesis, aggregation of the product would take place if OAm was used alone,⁶ which is probably due to poor steric protecting ability of OAm. Here AAAC possesses two long alkyl chains, and



Scheme 1 Schematic illustration of nucleation and growth process of Pd NCs at different AAAC/OAm ratios.

was supposed to provide stronger steric protection over the NCs. These factors finally resulted in the formation of multipods with zig-zag surfaces. At the AAAC/OAm ratio of 7/3 nearly monodisperse Pd NCs, mainly tetrahedra, were formed. The formation of the tetrahedra can be attributed to the intermediate growth manner between kinetically controlled and thermodynamically controlled growth, mainly because the reduction rate of the metal precursor was between that of the kinetic control and thermodynamic control. The slow nucleation and growth rate at AAAC/OAm = 5/5 led to a thermodynamically controlled growth manner and the protecting ability of the AAAC and OAm mixture is strong enough to prevent the NCs from aggregation, resulting in nearly monodisperse spherical Pd NCs. Further decreasing the ratio of AAAC/OAm would result in the aggregation of the spherical NCs because the ligands cannot stabilize the spherical NCs effectively. A schematic illustration of the nucleation and growth process of the Pd NCs at different AAAC/OAm weight ratios is given in Scheme 1.

Citral¹³ (structure shown in Scheme S2) and cyclohexene hydrogenation were carried out to test the catalytic properties of the Pd NCs with different morphologies shown in Fig. 1 and Fig. S3. The NCs were supported onto silica gel (Fig. S7A), and the OAm and/or AAAC ligands were cleaned by acetic acid and ethanol washing.⁸ FTIR analysis showed that the ligands adsorbed on the Pd NCs could be removed after washing with acetic acid and ethanol (Fig. S7). Fig. S7 also indicates that the supported Pd NCs still kept their primary morphologies and dispersed well on the support.

The results of hydrogenation reactions for citral and cyclohexene are shown in Table S1 and Fig. 2, respectively. Spherical Pd NCs are commonly used to catalyze the hydrogenation reactions. The results of the reactions catalyzed by the aggregates from spherical Pd NCs (prepared at AAAC/OAm = 0/10), spherical Pd NCs (prepared at AAAC/OAm = 5/5), and the Pd/C catalysts with spherical Pd NCs of 3–8 nm¹⁴ are also presented in the table for comparison. As can be known from Table S1 and Fig. 2, the multipods and tetrahedral NCs were much more active than the spherical NCs for both reactions. The activity followed the order: multipods > tetrahedral > spheres > aggregates. Since the aggregated Pd NCs prepared without using AAAC (Fig. S3) were composed of randomly attached spheres and lost part of their surfaces, they exhibited even lower activity



Fig. 2 Cyclohexene hydrogenation results for different shaped Pd NCs: (a) Pd-spheres, (b) Pd-tetrahedra, (c) Pd-multipods (cyclohexene, 2 mmol; Pd, 5×10^{-5} mmol; 313 K; H₂, 4 MPa).

than the spherical NCs. While taking into account that the spherical NCs possessed the smallest size, it was quite interesting that they showed much lower activity compared to the multipods and tetrahedra. This should be mainly ascribed to the difference of surface structures of the Pd NCs. As is known, surface defects including atomic steps and edges often lead to higher catalytic activities.¹⁵ Since the spherical Pd NCs resulted from a thermodynamically controlled growth process, they exhibited the most stable surface, which disfavored high performance in catalysis. On the contrary, the multipods were generated via a kinetically controlled growth process, which resulted in plenty of surface defects (as shown in Fig. 1G and Fig. S5), leading to the highest catalytic activity. In the case of tetrahedra, they were obtained under the condition between thermodynamic growth and kinetic growth, leading to less surface defects on surfaces compared to the multipods, and the activity was between those of spheres and the multipods. It is worth mentioning that the TOF for the hydrogenation of cyclohexene catalyzed by the multipods could be as high as $160\,000 \text{ h}^{-1}$, as was known from the data in Fig. 2.

Furthermore, the catalytic performance of the multipod Pd NCs for citral hydrogenation was also studied in supercritical CO_2 , which is a typical green solvent.¹⁴ As shown in Table S1, CO_2 pressure had a pronounced influence on the citral conversion. In the CO_2 pressure range of 0 to 10 MPa, the citral conversion increased with increasing pressure, whereas the conversion was reduced on increasing the pressure from 10 MPa to 12 MPa. The reason may be that CO_2 influenced the reaction in two opposite ways: firstly, it facilitated H₂ to approach the Pd NCs, and therefore accelerated the reaction; secondly, it diluted citral and slowed the reaction. The overall influence depended on which factor was predominant.

In conclusion, various morphologies of Pd NCs, including spheres, tetrahedra and multipods with plenty of surface defects, could be synthesized by changing the ratio of AAAC/OAm used. The multipods and tetrahedra have much higher catalytic activity than commonly used spherical Pd NCs for the hydrogenation of citral and cyclohexene. Furthermore, since OAm is one of the most important ligands in the synthesis of various kinds of NCs, including semiconductor NCs and noble metal NCs, we believe that OAm and AAAC is an excellent combination for shape controlled synthesis of many other NCs.

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