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Description	

# Preparation of large thermally stable platinum nanocube by using solvent-thermal reaction

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**We describe the synthesis of single-crystalline Pt nanocube with a large diameter (around 35 nm) using a solvent-thermal reaction in polarity-controlled mixture of 1-butanol, toluene, and *N,N*-dimethylformamide at 185 °C.**

In recent years, artificially modulated nanocrystal-based structures with reduced dimensions have attracted great interest for both potential device applications and for novel physical phenomena. Thermal stability of nanocrystals is important for applications, especially for devices that need annealing or which work at high temperature. At high temperatures, typically above 300 °C, the organic capping layers decompose and the metal nanoparticles can deform and aggregate.<sup>1</sup> As a result, the size, shape and composition of nanoparticles during or after high-temperature reactions could be different from those of pristine nanoparticles. Large-sized Pt nanocrystals show quite high thermal stability, and can reduce shrinkage to some degree under annealing.<sup>2</sup> In this regard, large-sized Pt nanoparticles that are stable at high reaction temperatures are in high demand. However, reports of preparing size-controlled Pt nanocrystals with large-diameter are rare, although there are several research groups who have claimed success with large-sized noble metal cube (with sizes >25 nm), such as Pd nanocube,<sup>3</sup> Ag nanocube,<sup>4</sup> and Au nanocube.<sup>5</sup> Large-sized nanocrystals are rarely formed in Pt, probably due to the high internal strain energy compared with other face-centered cubic (*fcc*) metals.<sup>6</sup> Till now, large Pt nanoparticles are limited to some aggregations of Pt nanoparticles.<sup>7</sup> Recently, Tian

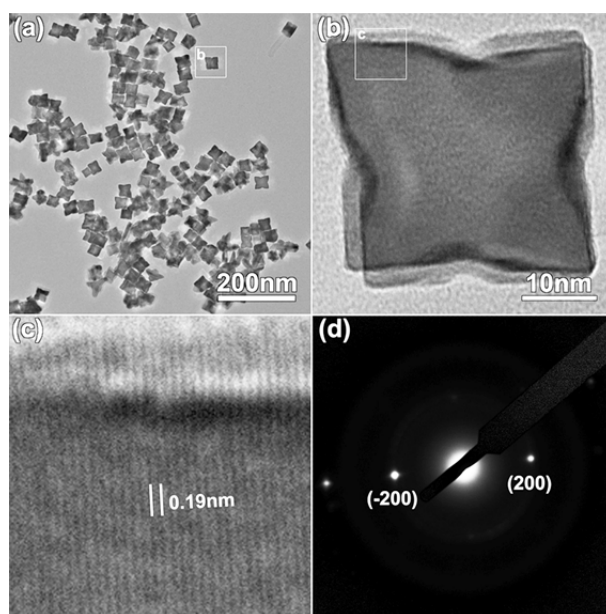
and co-workers reported a breakthrough in the synthesis of large Pt nanocrystals<sup>8</sup> via an electrochemical preparation. The synthesis of large Pt nanocrystals remains a challenge.

In this work, we first describe the synthesis of single-crystalline Pt nanocube with a large diameter (around 35 nm) by using solvent-thermal reaction in the presence of 1-butanol, toluene, and *N,N*-dimethylformamide (DMF) without the aid of foreign metal ions. Solvent-thermal reaction is a quite new synthesis method for metal nanocrystals using low boiling-point (*b.p.*) solvents, and there are a lot of candidates for such a kind of synthesis. Nanocrystals are easy to separate and purify in low *b.p.* solvents. We used a Teflon-lined stainless steel autoclave for the shape-controlled synthesis of Pt nanocrystals at high temperature in mixture of 1-butanol, toluene, and DMF. In this reaction, 1-butanol is a reducer, while toluene and DMF adjust the polarity of the solution. Oleylamine (OA) is a protective agent in this reaction. For a typical reaction, 2 mL platinum(II) acetylacetonate (Pt(acac)<sub>2</sub>, 10 mM in toluene), 0.5 mL acetic acid solution (80 mM in toluene), 1 mL oleylamine solution (0.1 M in toluene), 1 mL 1-butanol, and 2.5 mL *N,N*-dimethylformamide (DMF) were mixed together in a 10 mL Teflon-lined stainless steel autoclave and then heated to 185 °C in a furnace for 16 hours without stirring. The solution was then allowed to cool naturally to room temperature. After that, the solution was centrifuged and the precipitation was washed by ethanol twice. The desired nanocubes (Pt@OA) were obtained as a black powder (45-55% yield). In this reaction, oleylamine can be replaced by another alkylamine, such as dodecylamine.

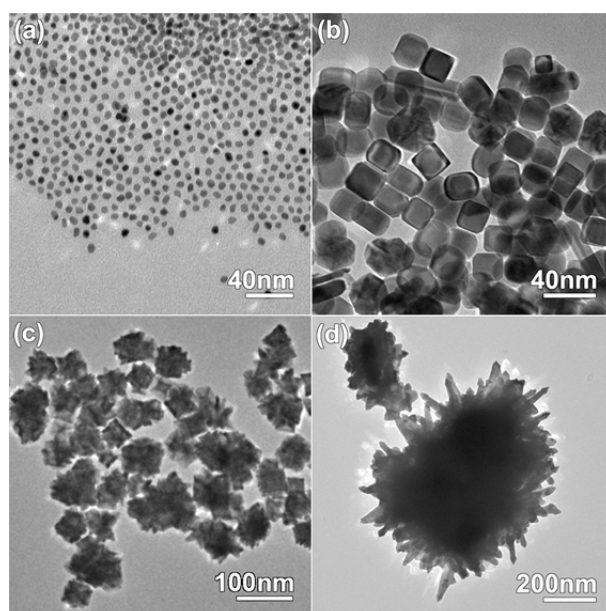
We use TEM to characterize the Pt nanocubes after synthesis. The average diameter is  $35.1 \pm 4.7$  nm, and more than 86% of cube was identified in whole product (Fig. 1a). Figs 1b & 1c are high-resolution TEM images of the nanocube in Fig. 1a. The octopod nanocube indicates overgrowth at the corners. As shown in Fig. 1c, the lattice spacing between the {200} planes, 0.19 nm, is also in agreement with that of bulk Pt crystal. Selected area electron diffraction

(SAED) pattern (Fig. 1d) for an individual nanocube (as shown in Fig. 1b), shows the single-crystal nature of particles, and {200} lattice fringes are parallel to the edges of the cube. The advantage of this technique over other high-temperature synthesis methods is that the formation of nanocubes under alcohol occurs at a slow rate, facilitating the formation of anisotropic and faceted particles by controlling the polarity of solution with DMF and toluene. Furthermore, the shape and size of nanocrystals depend on other different conditions, such as the concentration of surfactant, reagents, synthesis temperature and time. Among the various parameters, the reaction conditions of polarity, temperature and stirred state were found to be critical in controlling particle size and morphology.

According to our previous research, the morphology of nanocrystals was significantly affected by solvent polarity, which may change the interaction between nanoparticles and protective agent and result in anisotropic growth.<sup>9</sup> Without DMF in the reaction system, while keeping other parameters constant, we found that the size and shape are totally different from those shown in Fig. 1. The nanocrystals formed cuboctahedrons without DMF with diameter of  $6.9 \pm 1.5$  nm (Fig. 2a). DMF also can serve as a temporary protective agent for Pt nanocrystals through the interaction between carbonyl amide group and Pt. To clarify how the functional group and the polarity effects the shape, we employed another similar function group with low polarity, *N,N*-dibutylformamide (DBF), to replace DMF in this reaction. As shown in TEM image (Fig. 2d), only multibranch particles<sup>10</sup> with diameter of ca. 500 nm were obtained. That is to say, polarity plays a vital role in the formation of large nanocubes.



**Fig. 1** (a) TEM image of Pt@OA; (b) Close-up of area [b] marked in Fig. 1a; (c) Close-up of area [c] marked in Fig. 1b; (d) Selected area electron diffraction pattern of nanocrystal shown in (b).



**Fig. 2** TEM image of Pt nanocrystals prepared in the same conditions as 35 nm Pt nanocrystal *except* (a) without DMF; (b) with stirring; (c) at 155 °C; and (d) replacing DMF with DBF.

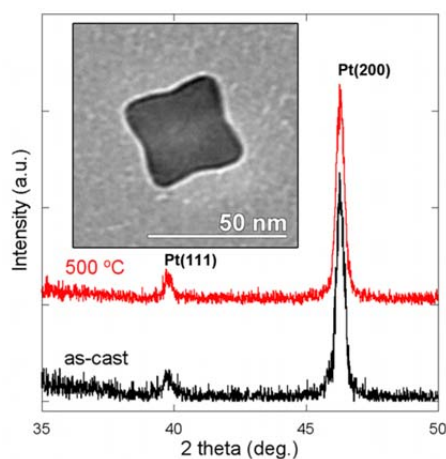
The words 'VIGOROUS STIRRING' frequently appear in synthesis of monodispersed nanocrystal in wet-chemical syntheses. Here we distinguish between two systems; with and without stirring. For the synthesis of large Pt nanocrystals, it is important to decrease the number of Pt nuclei in the reaction system, to induce the Pt atoms to grow directly from the Pt nuclei, so as to form large particles (based on Lamer and Dinegar's theory).<sup>11</sup> However, Pt nuclei seem to form easily due to the high internal strain energy between Pt atoms.<sup>6</sup> In order to control the growth speed, keeping the system in a static state is an efficient way to increase the growth of the Pt nuclei, or to combine the nuclei while reducing the number of nuclei formed.<sup>12</sup> Furthermore, a static system is easy to reach the equilibrium state of atoms and solution. Coincident with the above assumptions, the diameter of Pt nanocubes decreased from 35 nm to 22 nm, as shown in Fig. 2b.

Temperature plays two roles in this system, 1) to induce thermal decomposition of Pt precursor in the presence of alcohol, and 2) to enhance the solubility of large nanocubes in solution. For thermal decomposition, high temperature tends to result in fast reduction. We have proved that Pt(acac)<sub>2</sub> can be reduced in our system even at 145 °C. It is well known that slow reduction benefits the formation of large nanoparticles. Interestingly, after decreasing the reaction temperature from 185 °C to 155 °C, we could not get larger nanocubes, but some attached nanostructures, where small nanocrystals attached to the surface of large ones (Fig. 2c). A plausible reason is that high temperature enhances the solubility of nanocubes in a homogeneous system. However, the large Pt nanoparticles precipitate out at low temperature, and the remaining Pt precursor becomes new nuclei which grow into particles, then adsorb on the previous ones, as shown in Fig. 2c.

For large nanoparticles, their dispersion in solution remains a big issue, because of strong interparticle interaction at room temperature. Traditionally the dispersion of particles with

polymeric protective agent has been studied for over 50 years, and was found to be a delicate balance among energies such as van der Waals force, electric double layers, entropy.<sup>13</sup> PVP is commonly used as protective agent for silver, palladium, and platinum. The analysis indicates the carbonyl group can attach to the Pt surfaces due to chelated interaction. In our experiment, we use a 2.0 % PVP (w/v) solution in ethanol to replace oleylamine by sonication for 30 mins, and the nanocubes (Pt@PVP) were precipitated by additional acetone. The precipitate was redissolved into ethanol and precipitated by acetone again. Thermogravimetry analysis shows the weight loss of Pt@OA and Pt@PVP to be 2.46 % and 6.14%, respectively. The Pt nanocube did not precipitate out in ethanol with a concentration of 0.1 mg/mL after being kept at room temperature for one month. The individual nanocubes by TEM observation also indicated Pt@PVP does not aggregate in polar solution after ligand exchange.

The thermal stability of Pt nanocube on SiO<sub>2</sub> has been investigated using XRD and TEM. We directly fabricate Pt nanocubes on silicon substrate by drop-cast. The large nanocubes tend to have face-to-face deposition, because it is energetically the most favorable. After annealing at 500 °C for 5 min by rapid thermal annealing (RTA) as shown in Fig. 3, the peaks retain a high intensity ratio of (200) to (111) with same full width at half maximum (FWHM). The slightly increased intensity at (111) originates from thermal wetting, as explained previously by Yang and co-workers.<sup>1</sup> We used TEM to check thermal stability. TEM samples were prepared on gold grid coated with silica support film (Structure Probe, Inc.), then annealed at 500 °C or 600 °C in air for 5 mins. As shown in Fig. 3 inset, Pt nanocube did not change its shape at 500 °C after heat treatment in air, while at 600 °C the temperature induced wetting of Pt on SiO<sub>2</sub> (Data not shown), which can be attributed to the interfacial mixing of Pt and SiO<sub>2</sub> and the resulting negative interface energy. This fact indicates that large Pt nanocube shows high thermal stability even when annealed at 500 °C in air on SiO<sub>2</sub> substrate.



**Fig. 3** XRD pattern of Pt nanocubes by drop-cast: black (as drop-cast); red (after RTA at 500 °C for 5 minutes). Inset is the TEM image of Pt nanocube after annealing at 500 °C for 5 minutes on TEM grid with silica support film.

## Conclusions

In summary, we synthesized single-crystalline Pt nanocube with a large diameter (around 35 nm) using a solvent-thermal reaction in the presence of DMF. Solvent-thermal reaction provides a new synthesis method for metal nanocrystals, even when using low boiling-point solvents. The experiment indicates that controlled polarity, temperature and stirring conditions play vital roles in large cube synthesis. Changing the protective agent from oleylamine to PVP induces high solubility of Pt nanocubes in polar solvent. This Pt nanocube shows good stability at 500 °C, which can serve as an electrode in nanodevices, such as PZT memory in our current research by a liquid process.<sup>14</sup>



## Notes and references

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