

# Shape control of Pd-based nanocrystals via quasi-solid-state reactions

Lei Zhang,<sup>a,b</sup> Gang Xie,<sup>b</sup> Junfeng Hui,<sup>a,b</sup> Biao Xu,<sup>a</sup> Guolei Xiang,<sup>a</sup> and Xun Wang<sup>\*a</sup>

<sup>a</sup> Department of Chemistry, Tsinghua University, Beijing, 100084 P. R. China, Fax: 8610-62792791; Tel:8610-62792791;

E-mail: wangxun@mail.tsinghua.edu.cn

<sup>b</sup> College of Chemistry and Materials Science, Northwest University, Xi'an, 710069, P. R. China.

**Chemicals.** Ethanol, formamide, ethylene glycol, acetone, PVP(K-30,  $M_w \approx 58000$ ), PdCl<sub>2</sub>, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, citric acid, were analytical grade and purchased from Beijing Chemical Reagent Company

**Synthesis of Pd nanocube.** Mix 10mg PdCl<sub>2</sub> with 75mg PVP in a mortar by grinding, then add 20mg KI, keep grinding until the color of the powder change to brownish black. Transfer the mixture to a glass surface plate and inject 100ul formamide, grind it to paste-like. The sample was heated at 150°C directly, annealed for 4h and cooled to room temperature. The material was redispersed in ethanol. The resultant solution was centrifuged at 10000 rpm for 10 min. The precipitate was washed with ethanol for three times to get the Pd nanocube.

**Synthesis of Pd-Pt dendritelike nanocrystal and Pd-Pt cube nanocrystal.** keep the same procedure as synthesis of Pd nanocube but 10mg H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O was added with 10mg PdCl<sub>2</sub>. Anneal the sample at 150°C for 1h, 2h and 4h respectively to get pure Pd-Pt dendrite-like nanocrystal, the mixture of Pd-Pt dendrite-like with cube nanocrystal and pure Pd-Pt cube nanocrystal. But if shorten the anneal time to 5 min only clusters were formed.

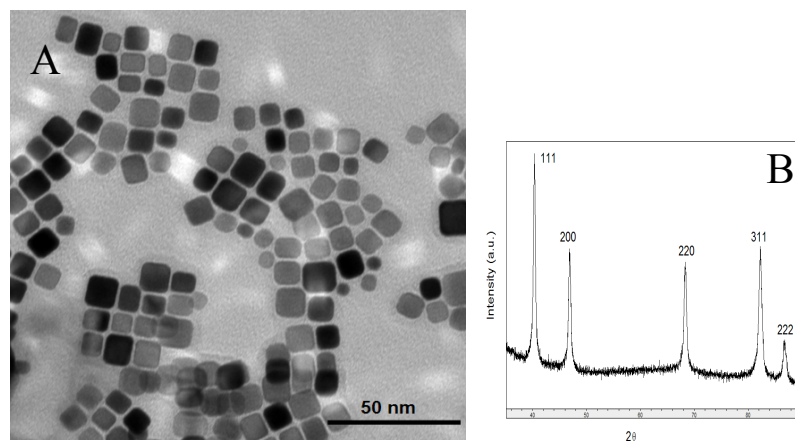
**Synthesis of Pd-Pt truncated octahedron nanocrystal, Pd-Pt octahedron nanocrystal and Pd-Pt dendrite-like nanocrystal.** Keep the same procedure as synthesis of Pd nanocube but 10mg H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O was added with 10mg PdCl<sub>2</sub> and KI was omitted. Anneal the sample at 120°C for 4h for the preparation of nanocrystals with the shape of truncated octahedron. If the temperature was 150°C, the resultant nanocrystals were with the shape of octahedron. Increase the amount of the H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O to 30mg with other conditions unchanged. We got Pd-Pt dendrite-like nanocrystals.

**Synthesis of Pd octahedron nanocrystal with the average size of 5 nm and 10 nm.** Keep the same procedure as synthesis of Pd nanocube but replaced the formamide by EG with the same amount and 20 mg citric acid substituted for KI. The size of the nanocrystal was related to the ratio of PdCl<sub>2</sub> and PVP. When 10mg PdCl<sub>2</sub> and 35mg PVP was involved Pd octahedron nanocrystal with the average size of 5 nm was prepared. Increase the amount of PdCl<sub>2</sub> to 20mg the size change from 5nm to 10nm.

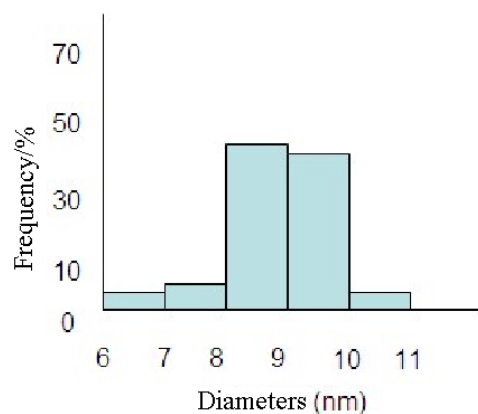
**Formation of clusters.** For all the preparation if short the heating time to 5 min or less only small nanoparticles were obtained in the solution after centrifugation. Then add enough acetone to the up solution for precipitation to get the Pd-based small nanoparticles.

**Instruments.** The size and morphology of the core-shell nanocrystals were probed by transmission electron microscopy (TEM; JEOL JEM 1200EX working at 100 kV), and high-resolution transmission electron microscopy (HRTEM; Tecnai G2 F20 S-Twin working at 200kV) equipped with an X-ray energy dispersive spectrometer (EDS). TEM samples were prepared as follows: A small amount of obtained product was dispersed in ethanol. One drop of

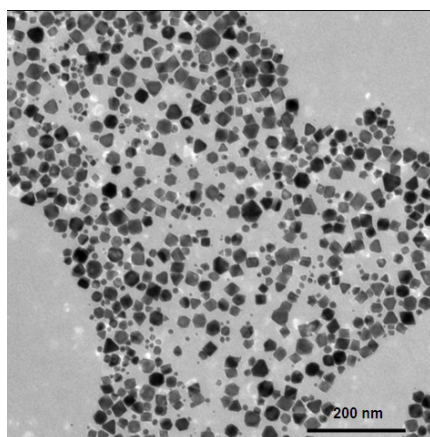
the resulting suspension was deposited on carbon-coated Cu grids, and the solvent was then evaporated at room temperature in the air. Powder X-ray diffraction (XRD) measurement of the products was carried out on a Bruker D8 Advance X-ray powder diffractometer with Cu K $\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ).



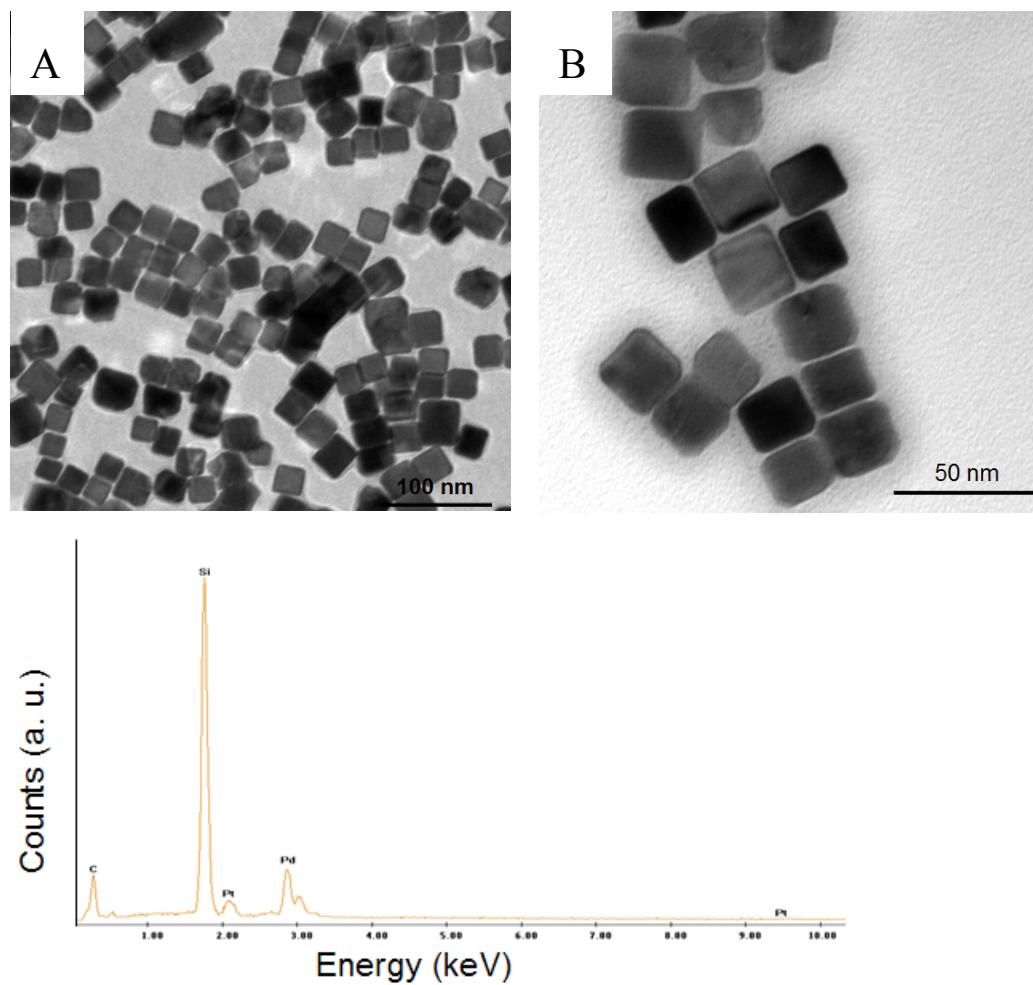
C



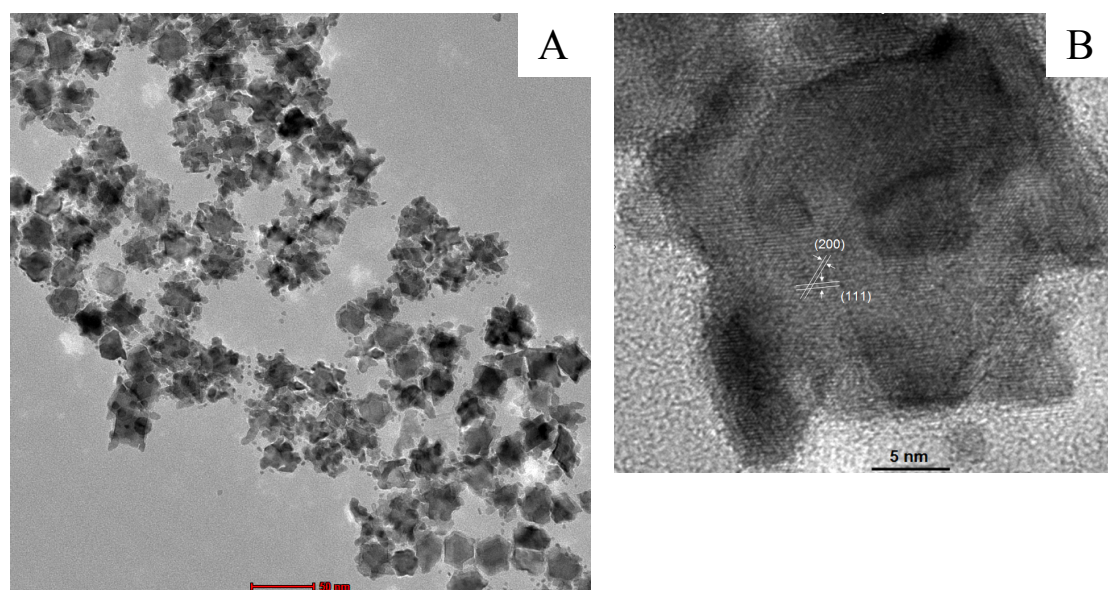
**Fig. S1.** TEM (A) and XRD (B) of Pd nanocube (C) Histogram of particle sizes distribution of Pd nanocubes



**Fig. S2.** TEM image of Pd nanocrystals prepared without KI



**Fig. S3.** (A) TEM image of cubic Pd-Pt. (B) Enlarged TEM image of cubic Pd-Pt. (C) EDX spectrum of cubic Pd-Pt.



**Fig. S4.** (A and B) Typical TEM image of Pd-Pt dendrite-like nanocrystals and corresponding HRTEM image.