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Size-Controlled Palladium Nanocubes for Carbon Monoxide Oxidation

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Metal nanocrystals (NCs) are of particular interest due to their special properties and applications in catalysis, electronics, sensing, photonics, imaging, and biomedicine [1]. For catalytic reactions, the activity and selectivity of metal NCs may strongly depend on their size and shape [2]. Because of their importance for many industrial applications, synthesis of size- and shape-controlled Pd NCs has attracted much attention in recent years [3]. We report here the synthesis and characterization of cubic Pd NCs with controllable sizes in the range of 6-18 nm. The catalytic performance of the synthesized cubic Pd NCs for CO oxidation was also investigated.

Cubic Pd NCs with different sizes were synthesized by manipulating the rate of reduction of the Pd precursor. In a typical process, 8.0 ml of an aqueous solution containing poly-vinyl-pyrrolidone (PVP) and different amounts of KBr and KCl was put in a 20 ml vial and pre-heated in air under magnetic stirring at 80 ^{o}C for 10 min. Then, 3.0 ml of an aqueous solution containing Na_2PdCl_4 (57 mg, Aldrich) was added. After capping the vial, the reaction was allowed to proceed at 80 ^{o}C for 3 h. The product was separated by centrifugation and washed with water to remove excess PVP. TEM images were obtained using a Philips 420 transmission electron microscope operated at 120 kV. A JEOL 2200FS (scanning) transmission electron microscope (STEM/TEM) equipped with a CEOS Co. aberration corrector for the probe-forming lenses, which provides a nominal resolution of about 0.07 nm [4], was employed to analyze the detailed structural information of the cubic Pd NCs.

Figure 1 shows TEM images of the synthesized cubic Pd NCs with average sizes of 6, 10 and 18 nm, respectively. The Pd cubes are all single crystals and consist of predominantly {100} facets. To elucidate the detailed surface atomic arrangement of the Pd NCs, sub-Ångström resolution high-angle annular dark-field (HAADF) images were obtained. Figure 2 shows a representative HAADF image of such a cubic Pd NC oriented along the [001] zone axis, clearly revealing the atomic arrangement of the{001} and {111} surfaces. The shape of the Pd NC is in fact a truncated cube with small {111} and large {001} surfaces. The image also shows that both the {001} and {111} surfaces are atomically flat. However, the HAADF image reveals that the {001} and {111} surfaces probably contain atomic-height islands, depressions, and probably atomic steps and kinks. The presence of these atomic-scale surface features may have an effect on the catalytic performance of these Pd NCs. In order to study the catalytic behavior of the cubic Pd NCs with different sizes, we performed a series of catalytic tests for CO oxidation. Figure 3 shows the turnover frequency (TOF) of the Pd NCs, clearly revealing that the TOF of the 6-nm Pd NCs is approximately 3 and 10 times higher than that of the 10- and 18-nm Pd NCs, respectively. Our results indicate that the size and shape of noble metal nanoparticles have significant effect on their catalytic performance [5].

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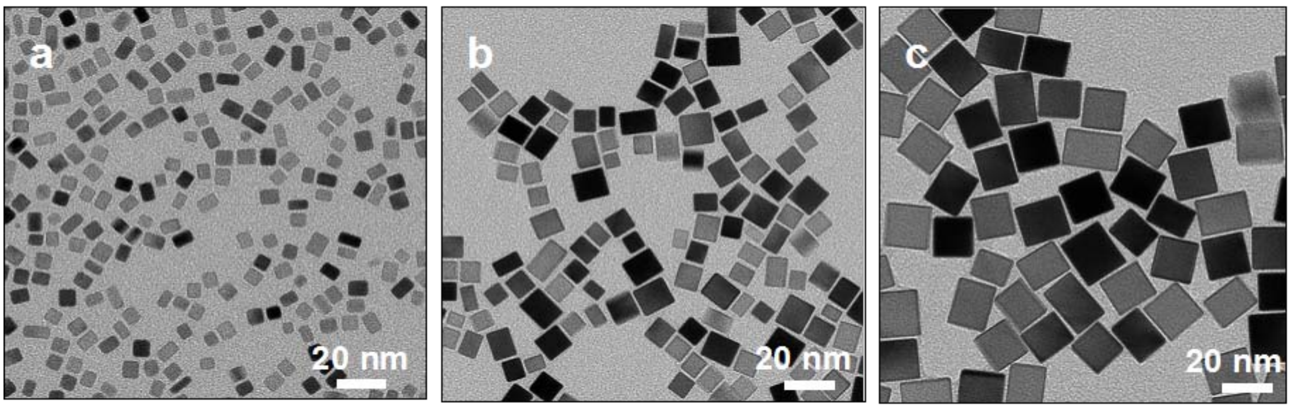
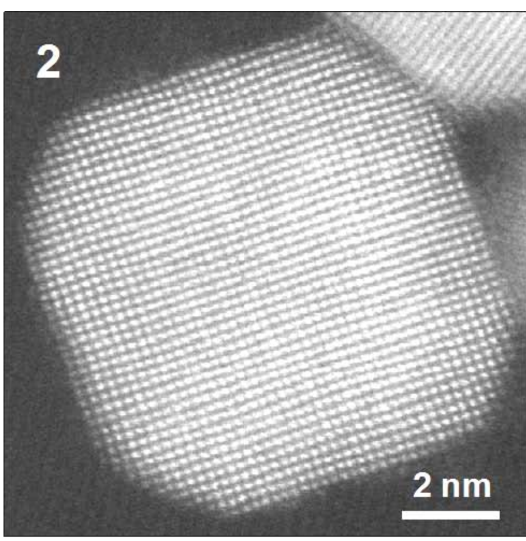


FIG.1. TEM images of cubic Pd nanocrystals with different sizes: 6 nm (a), 10 nm (b) and 18 nm (c).



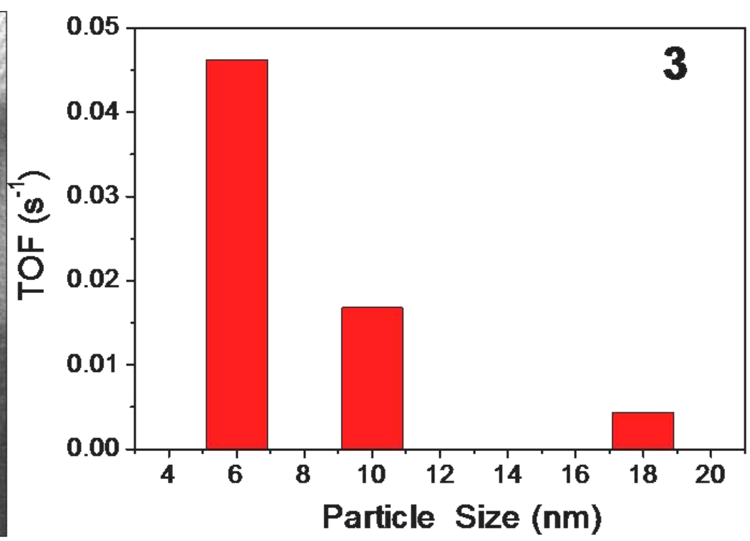


FIG.2. High-resolution HAADF-STEM image of a cubic Pd nanocrystal oriented along the [001] zone axis, clearly revealing the surface atomic arrangement of the {001} and {111} surfaces.

FIG.3. Turnover frequency (TOF) of CO conversion at 140°C over supported cubic Pd nanocrystals with different sizes. The TOF was calculated on the basis of CO molecule per surface Pd atom.

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