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Morphology and oxidation state of ALD-grown Pd nanoparticles on TiO_2- and SrO-terminated $SrTiO_3$ nanocuboids

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ABSTRACT

We employ $SrTiO_3$ nanocuboid single crystals with well-defined (001) surfaces that are synthesized to have either a TiO_2- or SrO-terminated surface to investigate the influence of surface termination on the morphology and the chemical property of supported metallic nanoparticles. Using such monodispersed STO nanocuboids allows for practical catalytic reaction studies as well as surface studies comparable to a single crystal model catalyst. Pd nanoparticles were grown by atomic layer deposition, which is able to control the effective coverage, chemical state, and the size of the Pd nanoparticles. The properties of Pd nanoparticles were examined by transmission electron microscopy, X-ray absorption spectroscopy, and X-ray photoemission spectroscopy. The morphology and growth pattern for the Pd nanoparticles supported on the $SrTiO_3$ nanocuboids are shown to depend on the surface termination.

1. Introduction

It is well known that the support oxide in heterogeneous catalysts has a pronounced influence on the physical and chemical properties of supported metal nanoparticles. The support oxide may participate in the reaction directly, introduce charge transfer from/to the nanoparticles, or alter the shape and size of the supported metal nanoparticles. The thermodynamic equilibrium shape of supported metal nanoparticles can be determined by the Winterbottom construction [1], which links the relative surface and interface energies between nanoparticle/support oxide to the equilibrium shape of nanoparticle. The Winterbottom construction governs the degree of truncation of metal nanoparticle by the support, and gives insight into nanoparticle engineering of catalysts with precise control of the morphology.

In order to study the structure–activity relationship, there is a "materials gap" that needs to be filled. Traditional model catalysts used in surface science studies are usually single-crystals, for which the surface-area-to-volume ratio is too small for practical catalytic reactions. Alternatively, the surfaces of support oxides used commercially are usually poorly defined, making it difficult to correlate the measured catalytic effects to the atomic-scale interface and nanoparticle structure. Our approach to minimize the "materials gap" is using a controlled nanoscale support material with well-defined surfaces. $SrTiO_3$ (STO) nanoparticles can be synthesized with distinct faceting [2–5]. Our approach follows previously established work [6–9] utilizing $SrTiO_3$ nanocuboids with low size dispersion and well-defined (001) surfaces as the support material of the catalytic nanoparticles. In this study, TiO_2- and SrO-terminated surfaces of STO nanocuboids [10] are utilized to study the effect of surface termination on the morphology and chemical state of the supported nanoparticles in a way that excludes the intrinsic chemical difference when comparing nanoparticles on support oxides with different bulk compositions.

Pd and Pt are active catalytic metals and both have a lattice constant close to that of STO ($a_{Pd} = 3.89$ Å, $a_{Pt} = 3.92$ Å, $a_{STO} = 3.905$ Å). Earlier studies of Pt and Pd nanoparticles supported on single crystal STO substrates as model systems for investigating properties of the nanoparticles such as morphology [11–18], photolysis performance [19], and interfacial atomic correlations with the STO lattice [11,20–22]. Moving from single crystal to faceted nanoparticle supports, it has been demonstrated recently that Pt/STO nanocuboid catalyst systems have high thermodynamic and sintering resistance due to the strong cube-on-cube epitaxy at the interface [8]. Furthermore, when $SrTiO_3$ nanocuboids are substituted with $Ba_{0.5}Sr_{0.5}TiO_3$ nanocuboids, the Winterbottom truncation of Pt nanoparticles leads to the corresponding change predicted by lattice mismatch and interfacial free energy. As shown earlier, the shape of the Pt nanoparticle can be controlled by the support in a predictable manner [8]. Pd, with similar lattice constants and chemical properties as those of Pt, is expected to show similar behavior.

In this study, Pd deposition was carried out by atomic layer deposition (ALD). It has been recognized that ALD is capable of synthesizing supported transition metal nanoparticles, such as Pd, Pt and Ru on various supports [6,16–18,23–26]. ALD also has the ability to fine tune the amount of metal deposited by the number of ALD cycles. However, the growth of ALD-synthesized metal nanoparticles at the early stage is still poorly understood, especially for the deposition of Pd. Pd/STO samples

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with different numbers of ALD cycles have been prepared in the current study and characterized by transmission electron microscopy (TEM) and X-ray absorption spectroscopy (XAS) to reveal and compare their morphology, chemical state, and local atomic coordination structure.

2. Materials and methods

2.1. Sample preparation

Single crystal $SrTiO_3$ (STO) nanocuboids with well-defined (001) faces were synthesized to have predominantly SrO- or TiO_2-terminated surfaces by acetic acid- [2,3] and oleic acid-assisted methods [4] respectively. The nanocuboids are in the form of a dry, white powder. High resolution transmission electron microscopy (HRTEM) experiments and density function theory (DFT) simulation were previously used to determine the surface termination of the STO nanocuboids [10]. The SrO-terminated STO nanocuboids, synthesized by the steps described in [4], were washed with ethanol then calcined in air at 450 °C for 3 h in order to remove the residual oleic acid ligands. Standard Brunauer–Emmett–Teller (BET) analysis determined that the surface area was 20 m^2/g for the TiO_2-terminated nanocuboids, and 61 m^2/g for the SrO-terminated nanocuboids. The mean edge length for the TiO_2-terminated nanocuboids is 67 nm with a standard deviation (SD) of 12.5 nm; for the SrO-terminated nanocuboids, the mean is 15 nm with 2.8 nm SD. See Fig. S1 in the Supplementary material (SM) for the size distribution histograms and BET analysis.

The Pd ALD process was conducted in a viscous-flow ALD reactor [27]. Before ALD growth, both TiO_2-STO and pre-treated SrO–STO nanocuboids were heated in the ALD reactor at 200 °C for 10 min in nitrogen gas to equilibrate the temperature of the STO nanoparticles. This was followed by ozone treatment at 200 °C for 30 min to remove surface carbon. Pd(II) hexafluoroacetylacetonate ($Pd(hfac)_2$) and formalin (HCHO) were used as the precursors in the ALD process [23]. The reactant exposures lasted 300 s for each precursor, and nitrogen purges of 300 s were performed in between each precursor exposure and after the last exposure. After ALD processing, the samples were removed from the reactor and cooled in air. Samples were prepared with 1, 5, 10, and 20 cycles (denoted as 1c, 5c, 10c and 20c) of Pd ALD grown on the TiO_2-terminated STO nanocuboids, and with 1c, 5c, and 10c of Pd on the SrO-terminated nanocuboids. The Pd/STO samples were in the form of a dry powder, with a gray-scale color gradient that was darker for increased cycles of Pd.

2.2. Characterizations

2.2.1. Morphology and loading of Pd

The morphology of the as-deposited Pd/STO samples was examined by a JEOL 2100F TEM. The sizes and shapes of a large representative group of Pd nanoparticles for the 5c and 10c samples were measured using the ImageJ software [28].

The atomic percentage ratio between Pd and Sr of the Pd/STO samples was measured by both inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray fluorescence (XRF). The ratio was

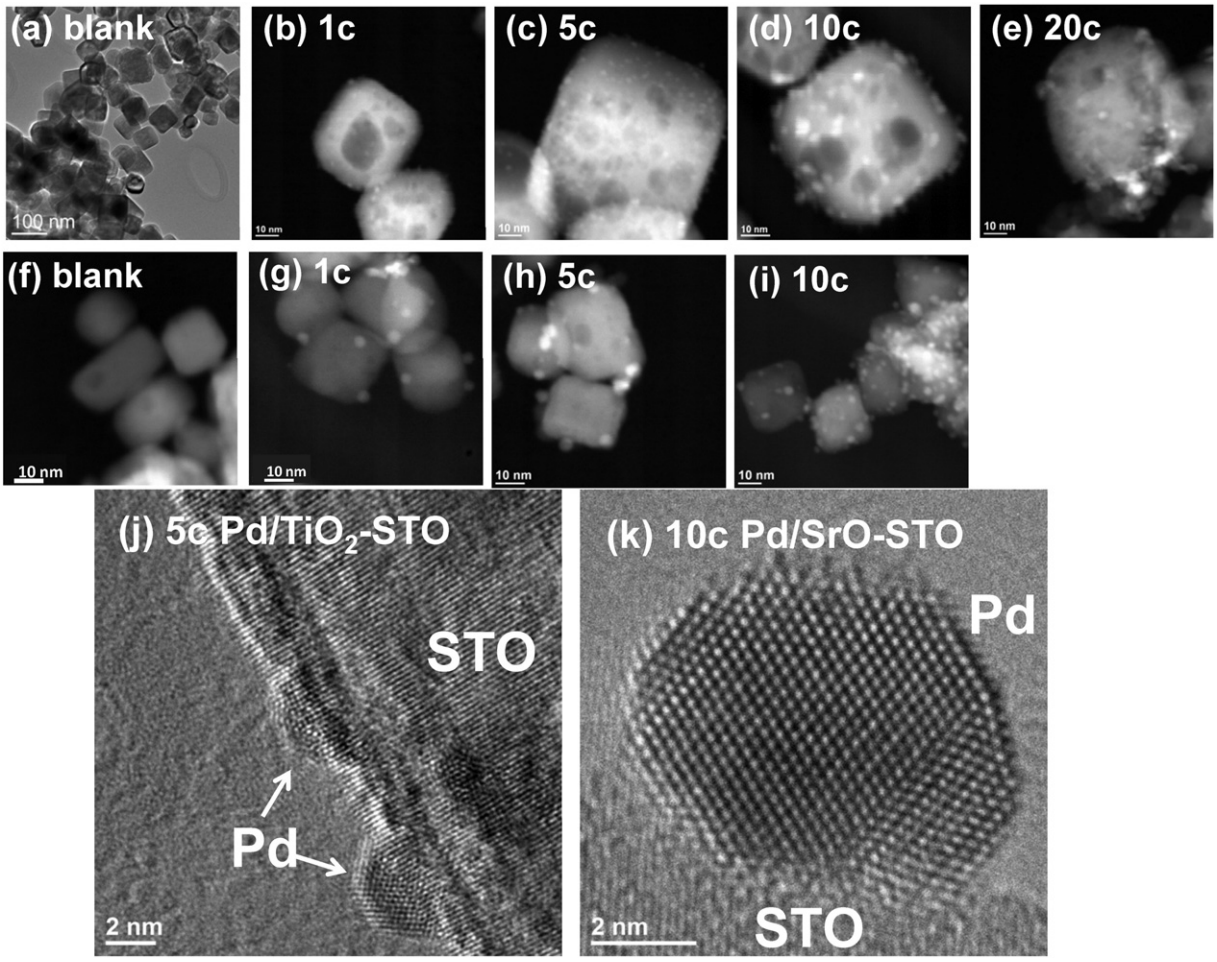

Fig. 1. TEM and HAADF images of TiO_2-terminated (a–e) and SrO-terminated $SrTiO_3$ (f–i) nanocuboids before and after ALD Pd deposition. Pd nanoparticles can be clearly seen from the images. HRTEM images in (j) and (k) show the details of the facetted Pd nanoparticles on TiO_2-terminated and SrO-terminated STO surfaces. A better wetting between Pd and the TiO_2–STO surface can be observed.