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Misfit dislocations in multimetallic core-shelled nanoparticles

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Core-shelled multimetallic nanoparticles have unique catalytic properties compared to their single-element counterparts. Due to the different lattice parameters of the core and shell, the strain field is built up at the interface between the two phases. As for thin films, a formation of misfit and threading dislocations is an approach to release interface strain. However, for two-phase nanoparticles especially when their sizes are at nanometer scale, their dislocation formation in the volume remains to be investigated owing to the large surface-to-volume ratio. Here, we confirmed the existence of dislocations in the Au-FePt core-shelled nanoparticles of sizes less than 10 nm. It is suggested that the different atom sizes of the core and the shell materials are likely to be a key factor to generate and lock dislocations inside the nanoparticles. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3695332]

Many multimetallic nanomaterials show drastically improved catalytic properties compared to those of their single-element counterparts.[1,2] For example, alloying Pt with transition metals, such as Fe, Co, or Ni, can improve the activity of Pt catalysts.[3–6] Such activity enhancement can be understood from the modified electronic structures of Pt, which improved their reaction kinetics.[3,4,7,8] Further by epitaxial growth of Pt-bimetallic alloy over Au seeds, the core-shelled nanoparticles show superior durability while preserving the beneficial catalytic activity of Pt-bimetallic alloys, compared to $FePt_3$/C and Pt/C.[9] X-ray diffraction investigation showed that the {111} lattice planes of Au-$FePt_3$ nanoparticles expand in comparison to that of $FePt_3$ and Pt nanoparticles, which are in the same size range.[9]

Due to the different lattice parameters of the core and shell, the strain field is built up at the interface between the two phases. As for thin films, a formation of misfit and threading dislocations is an approach to release interface strain. However, for the two-phase nanoparticles, especially when their sizes are at nanometer scale, any dislocation formation in the volume remains to be investigated owing to the large surface-to-volume ratio. In this work, by using high-resolution transmission electron microscopy (HRTEM), we investigated the Au-FePt core-shelled structures in detail and confirmed that partial strain is released by the formation of dislocations inside the nanoparticles.

Normally, the nanoparticles of various metals take the multiply twinned structures, which have been revealed by electron diffraction and microscopy as early as in 1957.[10–14] The two well-known model structures are decahedral and icosahedral multiply twinned particles. The former is composed of five tetrahedra with sharing their common ⟨110⟩ axis, and the latter is made of 20 tetrahedra with sharing a common apex of each. However, the tetrahedra, packed in these ways, do not completely fill the space, and a solid angle deficiency remains. As a results of this deficiency, the decahedral and icosahedral nanoparticles must be strained and/or contain defects. Early works show that the smallest (<10 nm) and intermediate-sized Au particles in decahedral and icosahedral structures were free of extended defects, although considerable strain is built inside the particles. Dislocations and stacking faults were only observed in much larger particles (>50 nm).[15–17] The anisotropy strain distributions in decahedral Au nanoparticles have been mapped by applying the aberration-corrected HRTEM: there was no dislocation being observed even when the nanoparticle size was close to 30 nm.[17] In this study, 2–4 nm thick FePt shells were coated on the ∼5 nm sized Au seeds. Different forms of dislocations were identified in the core-shelled Au-FePt nanoparticles, similar to what have been noticed in the Au-Pd core-shell nanoparticles.[18] As a comparison, while coating the Au seed continuously with Au, no dislocations were observed although strains were built up in the decahedral and icosahedral structures. It is suggested that the different atom sizes of the core and the shell materials are likely to be a key factor to lock dislocations inside the nanoparticles, which may be an important factor for the durability enhancement in their catalysis for oxygen reduction reaction in $HClO_4$ solutions.[9]

The detailed sample synthesis has been reported previously.[9] The nanoparticles were transferred to carbon coated TEM grids for TEM work. A JEOL 4000EX transmission electron microscope was used to carry out the HRTEM investigation. The accelerating voltage is 380 kV with point-to-point resolution close to 0.17 nm.

Figure 1(a) gives a typical HRTEM image of an Au seed, in which the incident electron beam is along the [110] direction. The five-fold twinned structure indicates that the particle belongs to the decahedral structure.[13] Simulation indicates that the dark dots correspond to the Au atoms. In each tetrahedron, the structural periodicity is well preserved, and no dislocation was observed. Figure 1(b) gives an HRTEM image of a core-shelled Au-FePt nanoparticle, which belongs to the decahedral structure as well. Due to the close scattering power of Au and Pt, the core-shell interface cannot be seen clearly in Fig. 1(b). In the bottom tetrahedron,

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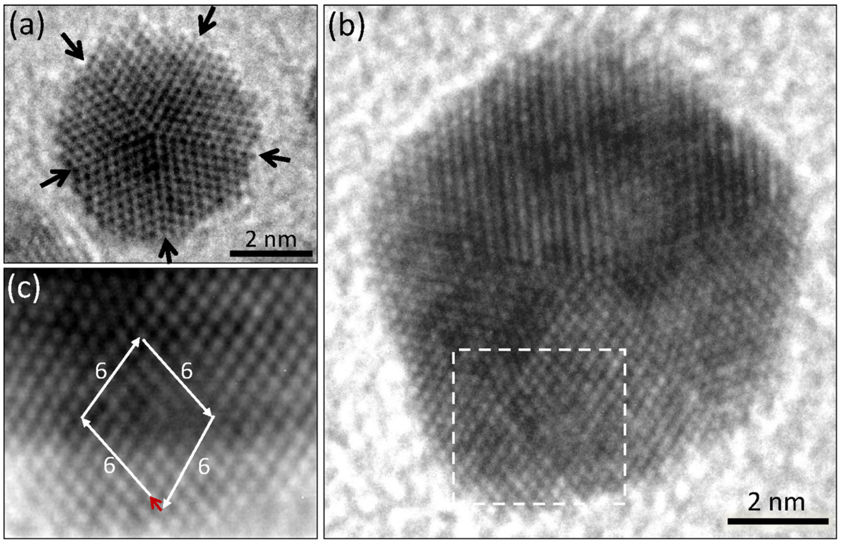

FIG. 1. (Color online) (a) HRTEM image of a $\sim$5 nm Au decahedral nanoparticle, (b) HRTEM image of an Au-FePt core-shelled nanopartilce in decahedral shape, (c) magnified image from the rectangle-enclosed area in (b), and the white arrowheads represents the Burgers circuit.

the dashed-rectangle enclosed area shows blurred contrast. After data processing of fast Fourier transformation followed by applying mask and inverse Fourier transformation to reduce the noise, the contrast-enhanced image is displayed in Fig. 1(c), in which the Burgers circuit around the blur area is drawn. The chain of base vectors made exactly in a perfect reference lattice is not close. A special vector marked by red arrowhead is needed to close the circuit. Such a special vector $a/4\ [1\bar{1}2]$ is the projection of the Burger vector $a/2\ [1\bar{1}0]$ in the image plane. The dislocation in the center of the dashed-rectangle is a perfect one: no dissociation has been observed. Considering that the formation of misfit dislocations can release the interface mismatch, we assume that the core of the dislocations is at the Au-FePt interface. Then, the measured shell thickness is $\sim$2 nm, which is similar to the results of the elemental mapping reported early.[9] For a comparison, we coated the Au seeds continuously with Au atoms: no dislocations were observed. It is consistent with the experimental results reported in literatures.[17]

The HRTEM image in Fig. 2(a) is recorded from a large pure Au nanoparticles; with reference to the published literatures, the two-fold symmetry of the particle indicates that it takes the icosahedral shape.[19,20] The white lines have been used to highlight the two twin planes. The lattice periodicity is well kept in each domain, which is the same as the results reported by other groups.[19,20] However, in the core-shelled Au-FePt nanoparticles, the misaligned atomic planes can be identified, as shown in both Figs. 2(b) and 2(c). The dashed lines have been used to show such misalignment in the top-left corner of the particle in Fig. 2(b). It indicates that a stacking fault is formed inside the nanoparticles. As we know, a stacking fault cannot terminate inside the crystal unless a partial dislocation is formed at the end. Such a partial dislocation can be seen much clear in Fig. 2(d), which is a magnified image from the rectangle enclosed area in Fig. 2(c). The stacking fault and the partial dislocation at one end of the stacking fault are marked by "⊥" and "—," respectively. The displacement of the dislocation indicates that it is a Shockley partial dislocation. The distance measured from the stacking fault to the surface is close to 2 nm, which is consistent to the thickness of the FePt shell. Therefore, the formation of the stacking faults with Shockley partial dislocations is another way to release the interface mismatch strain.

Figure 3 gives another HRTEM image of the Au-FePt nanoparticle in icosahedral shape. In the top-right corner of the particle, we observed a new twin plane instead of stacking fault. This twin plane is terminated inside the crystal. Therefore, there has a partial dislocation located at its end as indicated in the magnified image in Fig. 3(b). Same as the stacking fault case, the twin plane linked partial dislocation is another way to release the interface strain as well.

We observed the dislocations in single crystalline Au-FePt nanoparticles as well. The line fringes inside the nanoparticle in Fig. 4(a) indicate the existence of dislocation in

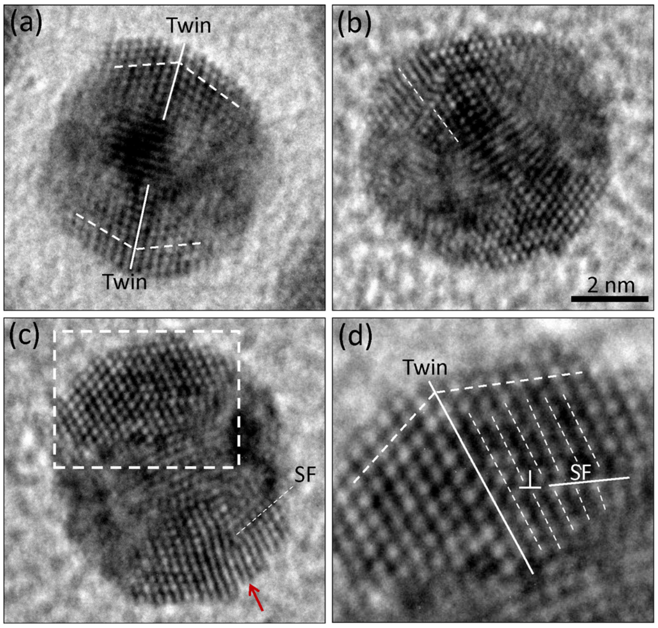

FIG. 2. (Color online) Dislocations in icosahedral nanoparticles: (a) pure Au particle with no dislocation, (b) and (c) stacking faults linked partial dislocations in Au-FePt core-shelled nanoparticles, and (d) magnified image from the rectangle enclosed area in (c).

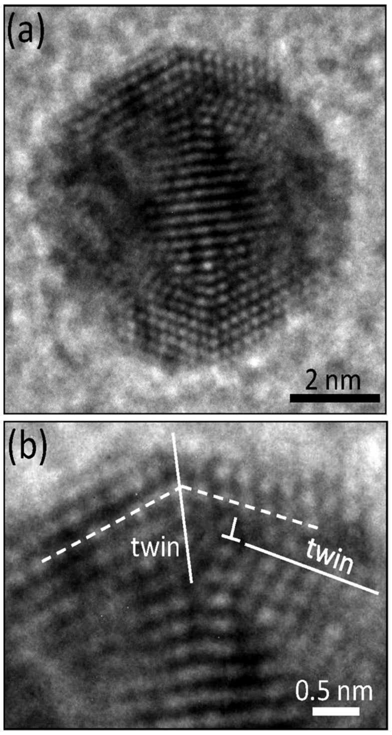

FIG. 3. (a) A HRTEM image from an Au-FePt icosahedral nanoparticles showing twin plane linked partial dislocation, which can be seen much clear in the magnified image in (b).

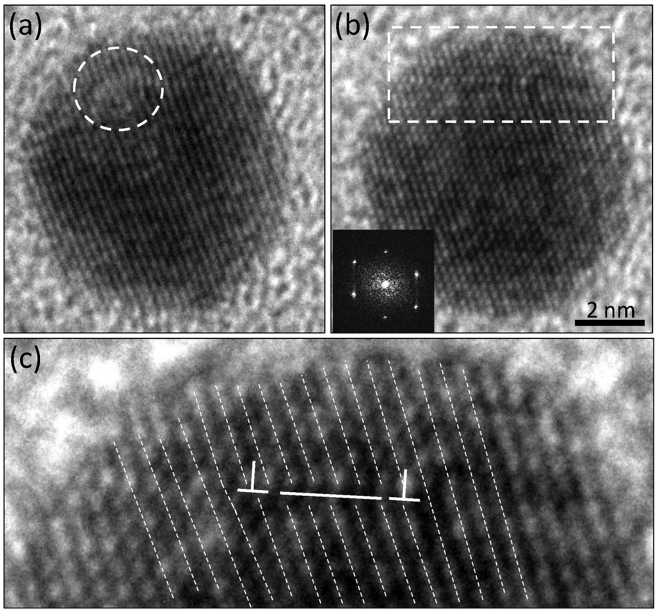

FIG. 4. (a) and (b) dislocations in single-crystal Au-FePt core-shelled nanoparticles, and the magnified image in (c) indicates that the dislocation is dissociated into partial dislocations and a stacking fault.

the dashed-circle enclosed area. The clear lattice image in Fig. 4(b) is recorded from the same particle, as shown in Fig. 4(a). The magnified image in Fig. 4(c) from the defect area reveals that the dislocation is dissociated into two Shockley partial dislocations and a stacking fault. It is understandable from the energy point of view that the dissociation of the perfect dislocation into partial ones is energetically favorable.

The reason why the dislocations can be formed in the core-shelled nanoparticles with sizes smaller than 10 nm could be understood from the different atom sizes of the core and shell materials. Fe and Pt atoms have comparably smaller size than that of Au atoms. Therefore, at the Au seed surface, more Fe or Pt atoms can be packed at the same area. These extra atoms correspond to the formation of misfit dislocation lines. Although the dislocations are so close to the surface, the different atom sizes at the interface may lock the dislocations and prevent them from migrating to the surface. Possibly, if the large-sized Au atoms can diffuse from the core into shell area, the interface mismatch may be much released by the formation of an alloy phase. Then, the defects were observed to move to the new interface. This is the case we observed in the Au-Pd core-shelled nanoparticles. The partial dislocations linked stacking faults moved out from the original interface due to the formation of AuPd alloy phase.[18,21]

By using the high-resolution transmission electron microscopy, we investigated the dislocations in the Au-FePt core-shelled multimetallic nanoparticles in detail. Perfect dislocations have been identified in the core-shelled decahedral nanoparticles. While in icosahedral nanoparticles, the partial dislocations are linked with stacking faults or twin planes. Even in single-crystalline core-shelled nanoparticles, we confirmed the existence of dislocations, which are normally dissociated into Shockley partial dislocations and stacking faults. The formation of dislocations in the core-shelled nanoparticles can release at least partial strain built at the interface. The different atom sizes of the core and shell metals are considered as the key factor to generate and stabilize the dislocation inside the nanoparticle, even when the size of nanoparticles is smaller than 10 nm.

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