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# Characterization of Core/Shell Bi-Metallic Cube-Shaped Nanoparticles with Scanning Transmission Electron Microscopy

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Bi-metallic nanoparticles (NPs) demonstrate superior catalytic performance as compared to their single metal counterparts because of “synergistic” effects. One of the most interesting bi-metallic NP systems is gold-palladium (Au-Pd) due to their wide-range of catalytic and energy applications [1]. Depending upon the synthesis conditions, the elemental distribution of these metals leads to different shape alloy NPs namely the core/shell, segregated, uniform mixing, and multi-shell [2]. In this report, we present a scanning transmission electron microscopy (STEM) analysis of core/shell cube-shaped Au-Pd NPs. These NPs are supposed to have the Pd metal in their cores which are then surrounded by Au and Pd metal shells.

A TEM-instrument of model Titan $G^2$ 80-300CT S/TEM from FEI Company was employed and was used by setting the electron beam energy of 300 keV to accomplish the underlined analysis. At first, conventional high-angle annular dark-field STEM (HAADF-STEM) analysis was performed to identify the distribution of Au and Pd metals in these NPs. Second, electron tomography (ET) analysis, also in HAADF-STEM mode, was applied to determine structures of their cores and shells. Third, the spectrum imaging (SI) line profiles were acquired by combining the STEM with X-ray energy dispersive spectroscopy (EDS) techniques to confirm the presence of outer Pd shell on NPs since its thickness was of merely a couple of nanometers (nm). STEM and SI datasets were acquired in Digital Micrograph Software Package from Gatan, Inc. While the ET datastes were acquired in Xplore3D and were reconstructed in Inspect3D Packages both from FEI Company.

The results from STEM and ET analyses of above mentioned Au-Pd NPs are shown in Fig. 1 (A-D). It can be noticed from the HAADF-STEM micrograph (Fig. 1A) that the NPs have cube shape morphology. Such HAADF-STEM micrographs were acquired at a relatively low camera length of 58 mm so that the Z-contrast dominates in acquired micrographs [3]. Hence, owing to this imaging condition, it is safe to state that the dark-color core region of about 50 nm in length is containing the Pd metal and this region is surrounded by bright-color 15 nm thick Au metal shell. A couple of more observations can also be made from the micrograph shown in Fig. 1 A. First, the presence of thin layer (~ 2 nm in length around the NPs “1” and “2”) surrounding the Au shell and, second, the morphology of the Au shell seems to be of irregular shape. However, it cannot be exerted with full confidence that the 2 nm layer of Pd-metal is indeed present as it may be just due to the misalignments of NPs with respect to the electron beam. This is why these both questions were attempted with the single-axis ET analysis and the results (slices from the tomograms) are shown in Fig. 1B-D. ET analysis revealed that the Au-shells around Pd-cores are indeed of irregular shapes (Fig. 1D). Furthermore the Au-shells can be of either concave or convex morphology as seen in the middle slices of NP “2” and NPs “1” & “3” in Fig. 1C, respectively. However, the presence of the thin Pd-shells around the Au-shells could not been verified with the ET analysis. This can be due to the "missing-cone" artifact in the single-axis tomography datasets [3]. On the other hand the SI analysis of these NPs, whose results are shown below in Fig. 2 (enclosed by a "red" box), revealed the presence of Pd-shell around Au-shell. It should be noted that the SI datasets were acquired with 1 nm pixel size and 10 s of dwell time at each pixel to acquire the EDS spectra. Then the EDS-signals from both Au and Pd metal were plotted and superimposed on the same NP.

In conclusion, STEM is an excellent technique for characterizing the structure and morphology of core/shell NPs. Single-axis ET analysis of NPs has limitations in verifying the presence of less than a couple of nanometer thick layers around them. Although, it can be improved further by a factor of at least 10% with the acquisition of dual-axis ET datasets [3]. Nevertheless the best way possible for this type of characterization of core/shell NPs can be achieved by combining the ET and SI analyses in the form of 4-dimensional (4D) analysis in an S/TEM instrument.

References:

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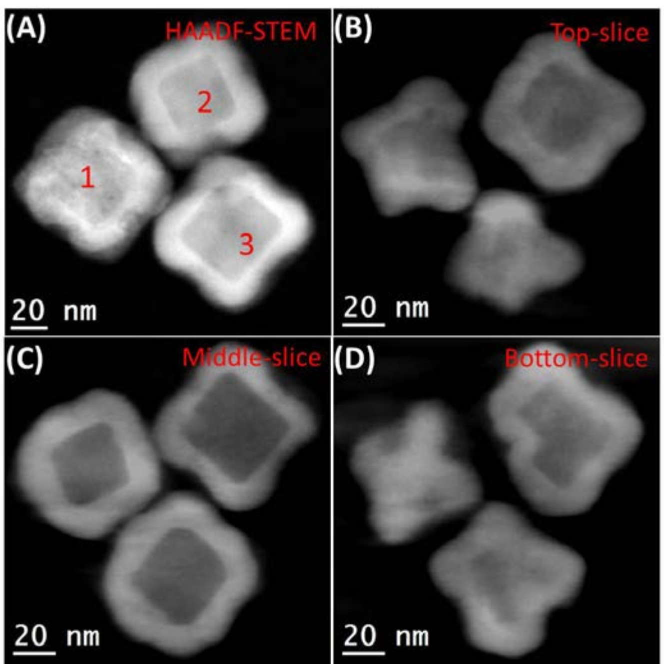


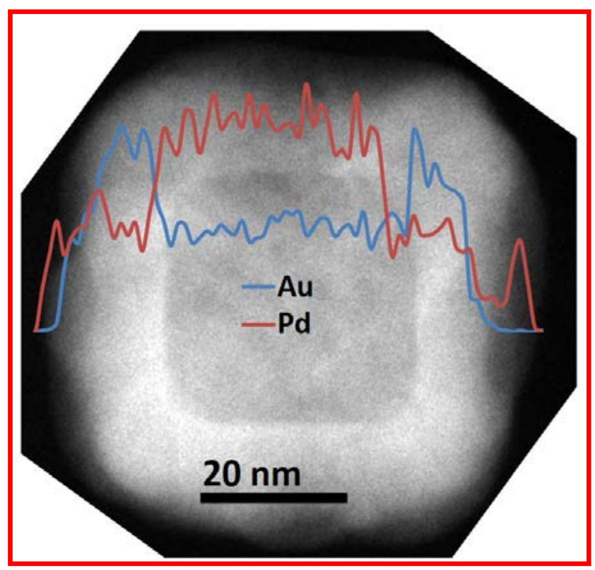


**Fig. 2**

**Fig. 1:** STEM and ET analyses of core/shell Au-P NPs. (**A**): HAADF-STEM micrograph showing cube shape core/shell NPs. (**B**): Top-region of the tomogram, reconstructed with SIRIT routine, of the region in Fig. 1 (A) by tilting the specimen from -74° to +74° with an angle-increment of 1°. (**C**): Middle-region of the tomogram. (**D**): Bottom-region of the tomogram.

**Fig. 2:** SI line-profile analysis of an Au-Pd NP acquired with STEM-EDS technique. HAADF-STEM micrograph of a NP is shown along with its corresponding Pd and Au line-profiles. Pd and Au EDS-signals are superimposed on the NP to elucidate the three core/shell structure of these cube shape NPs.