Chemical Mapping of Peptide-mediated Bimetallic Nanoparticles

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Inspired by nature, the utilization of biological molecules for the genetic control of nanomaterials synthesis is an emerging field at the frontier of the “green chemistry” revolution [1]. At the heart of this scientific concept lays the challenge of faithful and detailed characterization of the resulting novel nanostructured biohybrid materials - a system potentially less resilient than its purely inorganic counterpart. Among various structural characterization tools, scanning transmission electron microscopy (STEM) offers unique incoherent imaging directly interpretable at unparalleled resolution, as well as a host of analytical techniques including electron energy-loss spectroscopy (EELS) and energy dispersive x-ray (EDX). In this work, we demonstrate a protocol for monitoring and controlling e-beam induced artifacts that permits dose-rate-controlled STEM-EDX mapping and reveals unambiguously the native chemical distribution of peptide-mediated palladium-platinum (PdPt) bimetallic nanoparticles.

First introduced in 2010 [2, 3], 2D high-resolution elemental EDX mapping is capable of accessing higher core-loss energies atomic resolution. Recent development in silicon drift detector (SSD) has significantly boosted the collection statistics, allowing a one-to-one correlation between the detected small feature and the spectral signal under a relatively fast acquisition, mitigating concerns of stability during acquisition [4]. Here, we employed a probe-aberration corrected JEOL ARM200F microscope, equipped with a SSD with a large solid angle of 0.98 sr (conventional ~0.13 sr) for EDX signal acquired within the high-resolution pole piece. In the synthesis of PdPt bimetallic nanoparticles, the conjugated Flg-A3 peptide was used to provide a biomimetic template for the controlled growth of the metallic nanoparticles [5].

To establish a safe electron dose (rate) for the biomolecule-mediated nanoparticles during the EDX chemical analysis (essentially a high dose technique), we conducted electron dose testing in STEM imaging mode. By varying the e-beam illumination intensity and duration, we found (Fig. 1) it is high electron dose rate rather than accumulated dose that induces visible structural alterations to the sample. With an increased dose rate (Fig.1(b)), artifacts are observed at the surface of the nanoparticle shell where probably contains residual peptides as well as at smaller less stable nanoclusters after only 30 s imaging; however, no obvious damage was observed at a lower dose rate even after 2 minutes (Fig.1(a)). Based on this, electron dose rates in the order of 10⁵ e/A²s were adopted for STEM-EDX mapping (in contrast to, for example 2 × 10³ e/A²s used for other metallic nanoparticle systems [6]). One representative result of such dose-rate-controlled EDX elemental mapping is shown in Fig. 2 (f-j). Comparing with the non-controlled acquisition (Fig. 2 (a-e)), the low dose rate at each pixel allows a much longer integration and thus maintains good EDX signal statistics while preserving the sample
integrity (corresponding STEM images were examined after every frame acquisition). In sum, we showcased that with proper control of electron dose rate, the state-of-the-art large solid angle STEM-EDX elemental mapping is capable of faithful and unambiguous chemical nanocharacterization for biomolecule mediated materials [7].

References:
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Figure 1. Time sequence STEM images of the peptide-mediated PdPt nanoparticles under (a, b) a relatively low dose rate and (c, d) an approximately 10 times higher dose rate.

Figure 2. A comparison of STEM EDS mapping of the peptide-mediated PdPt nanoparticles under (a-e) a high dose rate of 6.70x10^3 e/Å^2 s integrated over 4 frames when detectable damages emerged (total dose 1.32x10^5 e/Å^2), and under (f-j) a controlled dose rate of 3.30x10^2 e/Å^2 s integrated over 20 frames (total dose 6.50x10^5 e/Å^2).