Resolving nanostructured materials down to the single-atom limit

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Determining the structural variation and the chemical inhomogeneity, ideally at atomic resolution, is critical for the understanding of nanostructured materials' functionality. However, the limited volume of parent matrix and the even smaller scale of local structural or chemical fluctuations impose great challenge onto the effective characterization, because conventional structure-analysis techniques can only provide information averaged over the whole or part of sample, overlooking the ordering spatially localized within few nanometers.[1] The maturation of aberration-corrected electron instrumentation in the past decades has enabled the extraction and quantification of weak scattering signals from individual atoms in nanostructured materials. Here we show how this powerful tool can reveal the dopant nanophases in nanoparticles and the composition-modulated dispersion behaviors of bimetallic catalysts down to the single-atom limit.

Doping has served as a popular strategy to tailor chemical and physical properties of today's materials, whose effects become increasingly important when the host dimension scales down. Rational synthesis of doped nanocrystals thus requires precise knowledge on the atomic structure and electronic configuration of each dopant-atom introduced. Using the 3at% Ce-doped Mn_3O_4 nanoparticles of <10 nm size as a model system, we demonstrated atomic-scale oxidation-state mapping and quantitative dopant-atom counting by the electron energy-loss spectroscopy in an aberration-corrected scanning transmission electron microscope (STEM-EELS).[2] In Figure 1(a), the oxidation states of Ce dopant-atoms in different coordination environments were identified, i.e. the Ce^{4+} single ions and clusters embedded inside the charge-ordered Mn_3O_4 matrix, and the partially reduced Ce^{3+x} atomic layers on certain crystal facets. Moreover, the electron-scattering simulations and refined detecting set-up allow us to distinguish the contribution of characteristic core-shell excitation from each dopant-atom quantitatively and derive a 3D dopant structure of the few-unit-cell CeO_2 nanocluster beyond a 2D projection, as shown in Figure 1(b). It's also interesting to find that EELS can pinpoint the dopant-atom position more accurately than the annual dark field (STEM-ADF) imaging. When the Ce^{4+} ions were displaced away from the substituted Mn^{3+} column, the simultaneous ADF failed to reflect the correct position while STEM-EELS worked well, which indicates that the Ce intercalation may not be so coherent as the ADF images look and that STEM-EELS owns broader displacement-depth tolerance on resolving an interstitial dopant-atom.

As for the characterization of metals supported on nanocarbon surface, however, ADF proves to be a more dose-efficient method for identifying individual atoms without concerns of channeling artefacts, as shown in Figure 2. Although the Pt-Sn catalysts have shown advantages of high thermal stability, enhanced reaction activity and selectivity over traditional Pt products for the

direct dehydrogenation of *n*-butane, how the bimetallic structure varies with the composition remains elusive.[3] We found that the addition and coordination of Sn atoms act as an effective dispersion agent to Pt species, resulting in the prominent tunability of the active-center structure and thus the catalytic performance of Pt-Sn catalysts. With increasing Sn concentration, the bimetallic nanostructure evolves gradually from Pt nanocrystals, Pt-Sn core-shell nanoparticles, fully exposed Pt-Sn single-atomic-layers, Sn-rich bimetallic nanoclusters, finally to separate Pt and Sn clusters. Figure 2(b) shows how quantitatively ADF can uncover the atomic arrangement and chemical identity of supported Pt-Sn catalysts with single-atom sensitivity.

In summary, the single-atom-resolved capabilities provided by the modern aberration-corrected electron microscopy and spectroscopy are widely applicable to other nanostructured materials, such as the twisted bilayers of transition metal dichalcogenide, which exhibit reconstructed moiré domains regulated by the marginal twist angles. These techniques may also extend to facilitate the *in-situ* study of materials' functionality under realistic conditions.[4]
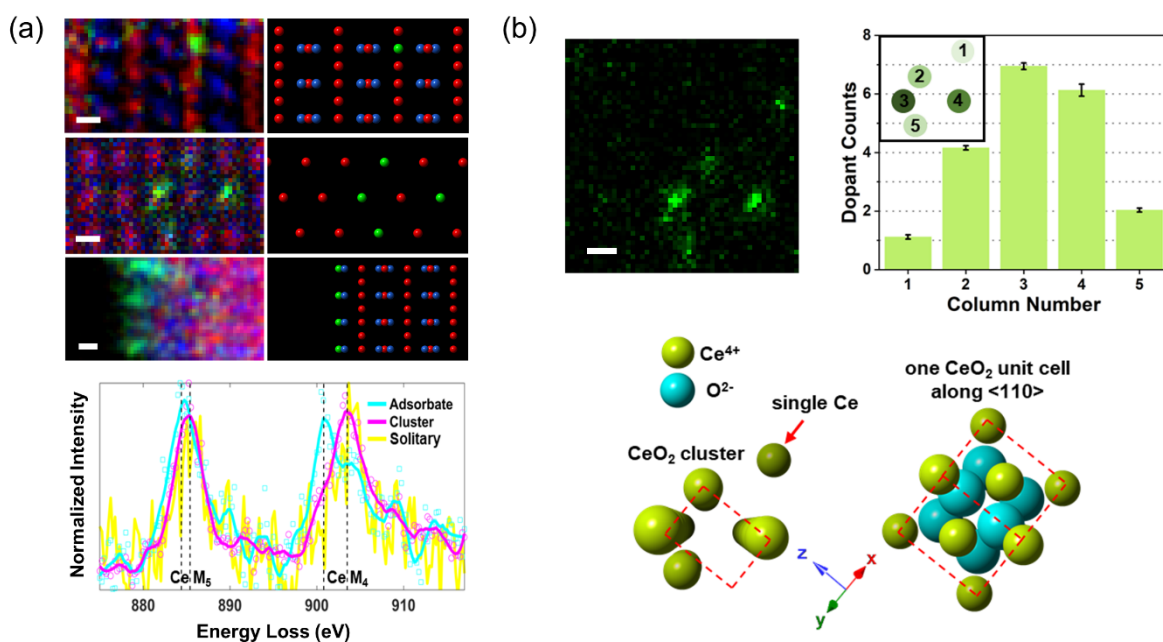

Figure 1: (a) STEM-EELS mapping of various dopant nanophases, including the Ce^{4+} single ions and clusters inside Mn_3O_4 nanoparticles and the Ce^{3+x} atomic layers on the Mn_3O_4 {101} facets. Red, blue and green colors represent Mn^{3+}, Mn^{2+} and $Ce^{4/3+}$, respectively. (b) Quantitative dopant-atom counting revealing a CeO_2 nanocluster. The scale bars are 2 Å. Reprinted and adapted with permission from reference [2]. Copyright (2019) American Chemical Society.
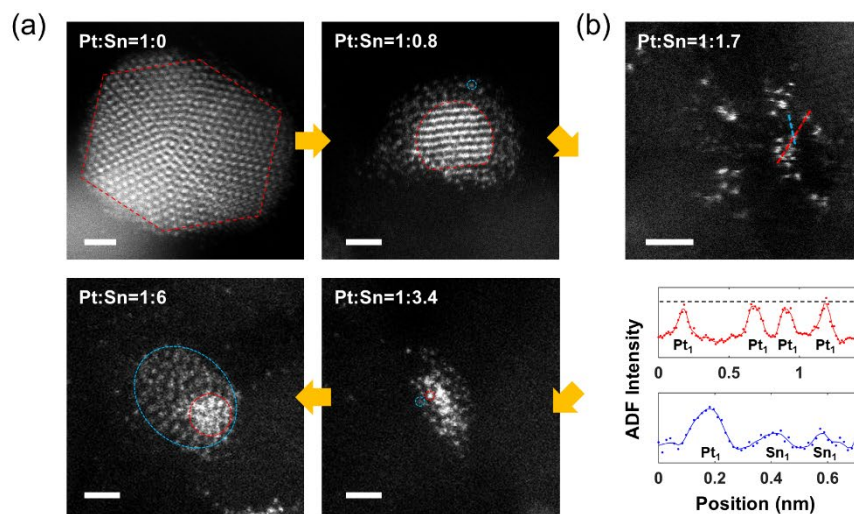
Figure 2: (a) Structural evolution of the catalytically active centers in Pt-Sn catalysts modulated by the Sn coordination. (b) Fully exposed Pt-Sn single-atomic-layers with line profiles showing the single-atom sensitivity of ADF. The scale bars are 1 nm.

References:
[1] S. Billinge and I. Levin, Science **316**, 561-565 (2007).
[2] X. Cai *et al.*, Chemistry of Materials **31**, 5769-5777 (2019).
[3] J. Zhang *et al.*, ACS Catalysis **9**, 5998-6005 (2019).
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