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 microscopy instrumentation in the past decades has enabled the extraction and quantification of weak scattering signals from individual atoms in nanostructured materials. Here we present 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 the refined detecting set-up allow us to quantify the dopant-atom number in each atomic column 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 surprising to find that STEM-EELS can pinpoint the dopant-atom position more accurately than the annual dark field (ADF) imaging. When the Ce^{4+} ions were displaced away from the substituted Mn^{3+} column, the simultaneous ADF failed to reflect the correct dopant position while STEM-EELS worked well, which indicates that the Ce intercalation may not be so coherent as ADF images look. Corroborated by simulations, STEM-EELS is proved to be more sensitive to small displacement of dopant-atoms and suffers less from channeling artefacts than the ADF imaging. The Pt-Sn catalysts supported on nanocarbons have shown advantages of high thermal stability, enormously enhanced reaction activity and selectivity over traditional Pt products for the direct dehydrogenation of *n*-butane, but how the bimetallic structure varies with the composition remains elusive.[3] In Figure 2, we demonstrated that the addition and coordination of Sn atoms act as an effective dispersion agent to Pt species, resulting in the prominent tunability of the dispersed metal sizes, the active-center structure and thus the catalytic performance of Pt-Sn catalysts. With increasing Sn concentration, the bimetallic nanostructure evolves gradually from Pt crystals (~5 nm), Pt-Sn core-shell nanoparticles (~3 nm), fully exposed Pt-Sn single atomic layers (~1 nm), Sn-rich bimetallic nanoclusters (~1.5 nm), finally to segregated Sn and Pt clusters (~2 nm). 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 dichalcogenides, which exhibit reconstructed moiré domains regulated by the marginal twist angles. These quantitative techniques may also be extended to facilitate the *in-situ* study of materials' functionality under realistic conditions.[4]
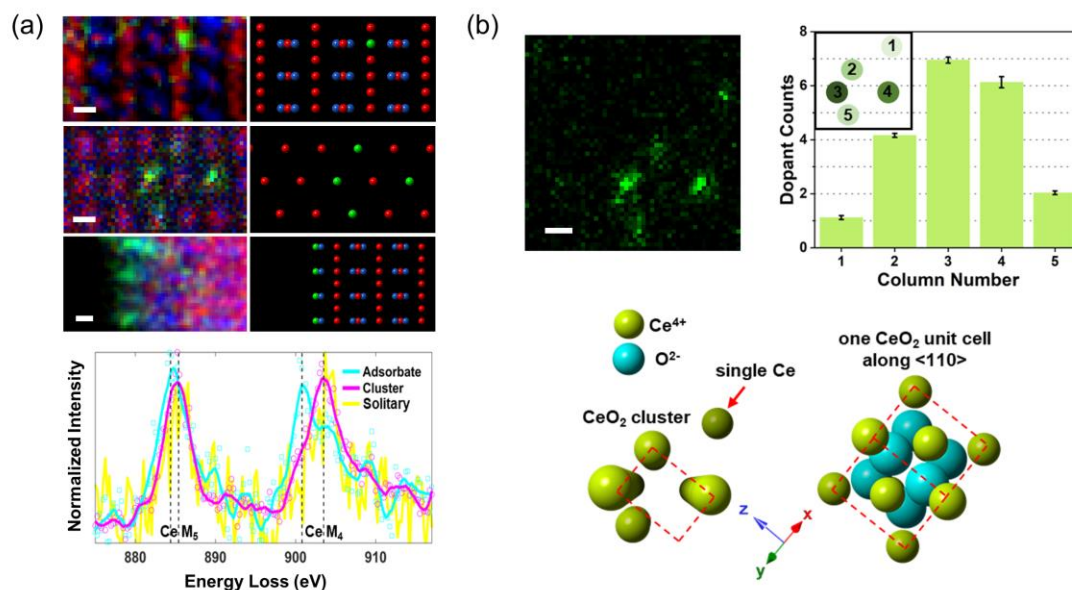

Figure 1. (a) STEM-EELS mapping of various dopant nanophases, including the Ce4+ single ions and clusters inside Mn3O4 nanoparticles and the Ce3+x atomic layers on the Mn3O4 {101} facets. Red, blue and green colors represent Mn3+, Mn2+ and Ce4/3+, respectively. (b) Quantitative dopant-atom counting revealing a CeO2 nanocluster. The scale bars are 2 Å. Reprinted and adapted with permission from reference [2]. Copyright (2019) American Chemical Society.
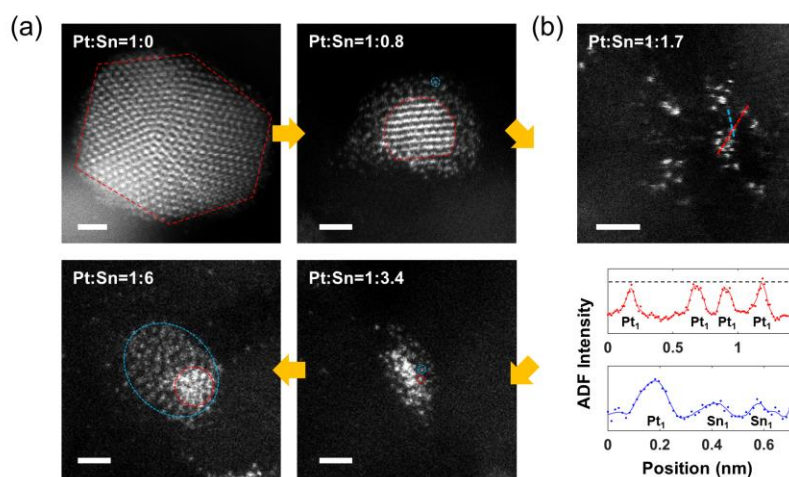

Figure 2. (a) Structural evolution of the catalytically active centers in Pt-Sn catalysts, which is modulated by the Sn concentration. (b) Fully exposed Pt-Sn single atomic layers with line profiles showing the single-atom sensitivity of ADF. The scale bars are 1 nm.

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