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Atomic-scale Imaging of PGM-free Catalyst Active Sites by 30 keV 4D-STEM

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Platinum group metal (PGM)-free catalysts have attracted a large amount of attention due to their potential for enabling low-cost, commercially viable hydrogen fuel cells and electrolyzers [1]. Degradation of cell performance remains a significant challenge, however, currently limiting implementation of devices that utilize PGM-free materials [2]. A detailed understanding of the atomic structure of active sites, which are generally thought to be FeN_4 structures within a graphitic carbon lattice, is needed to control degradation in these materials since this would enable accurate prediction of associated degradation pathways. The exact structural arrangement of active sites is still debated, however, since a range of structures have been computationally predicted and methods to directly validate these models are still needed [1,3-5].

While scanning transmission electron microscopy (STEM) has provided initial glimpses into the nature of the proposed active sites, detailed evaluation of active site structure is challenging since it involves characterization of defects such as vacancies, edges, and dopants in the graphitic lattice, which are susceptible to beam damage at standard operating voltages [6,7]. Conventional STEM imaging and spectroscopy methods exacerbate this problem with dose-inefficiency or non-ideal contrast characteristics for imaging light and heavy elements simultaneously. A method that minimizes damage while generating dose-efficient, easily-interpretable contrast for both light and heavy elements is therefore needed to facilitate imaging of sensitive active site atomic structure.

Here, we demonstrate direct atomic-scale imaging of PGM-free catalyst active sites by low-voltage four-dimensional (4D)-STEM, as shown in Figure 1. To accomplish this, we pair a 30 keV aberration-corrected probe, which minimizes knock-on damage, with a fast pixelated detector that has optimal performance at low beam energies [8]. This setup enables us to use relatively simple center-of-mass (CoM) techniques [9,10] to produce images with an increased signal-to-noise ratio (SNR) and light-element contrast over conventional imaging modes, allowing the entire active site structure to be imaged at the atomic scale. Moreover, we show that electron ptychography [11,12] enables images with further improved characteristics to be obtained, for example by minimizing residual aberrations, which provides a more accurate structural representation. The increased understanding that these low-voltage 4D-STEM techniques will provide about the atomic structure of PGM-free active sites and their associated degradation pathways will facilitate rational design of next-generation materials, promoting development of low-cost hydrogen fuel cells, electrolyzers, and other energy conversion devices [13].

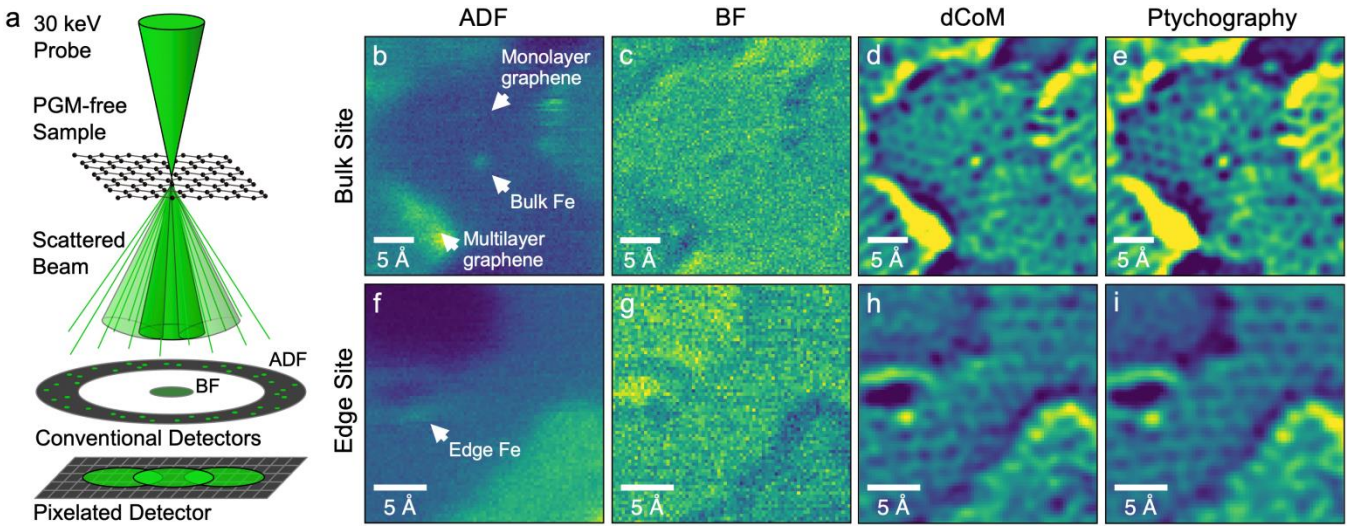

Figure 1. Schematic of conventional and 4D-STEM imaging, as well as 30 keV atomic-scale imaging of PGM-free active sites. (a) Low-voltage STEM experimental setup, including a 30 keV probe, conventional detectors such as bright-field (BF) and annular dark-field (ADF), and a pixelated detector for 4D-STEM. (b-e) Imaging of a PGM-free active site embedded in a defective graphene lattice by ADF and BF (reconstructed from 4D data), as well as 4D-STEM divergence of center-of-mass (dCoM) and residual aberration-corrected Wigner distribution deconvolution ptychography. While ADF and BF show the active site Fe atom, they do not have the right combination of light-element sensitivity, in-focus contrast transfer function, and signal-to-noise ratio to resolve the carbon lattice. dCoM reveals the carbon lattice after application of a <0.5 Å gaussian filter to reduce noise at frequencies significantly higher than the information transfer limit of the instrument. Ptychography further reduces noise (without applying a filter) and minimizes residual aberrations, improving contrast and more accurately reproducing the structure of the material. (f-i) Imaging of an edge site using the same methods as (b-e), demonstrating that a 30 keV probe enables atomic-scale imaging of these sensitive sites as well.

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