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Atomic-Scale Structural Mapping of Active Sites in Monolayer PGM-Free Catalysts by Low-Voltage 4D-STEM

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Two-dimensional (2D) materials have attracted a large amount of attention in both basic and applied fields, and scanning transmission electron microscopy (STEM) is often uniquely well-suited for characterizing the atomic-scale structure of these materials [1-4]. As a result, STEM is poised to significantly impact progress on platinum group metal (PGM)-free catalysts, which are currently under intense development to enable low-cost, commercially viable hydrogen fuel cells [5]. While recent advancements have resulted in fuel cell performance comparable to Pt catalysts by some measures [6], cell durability remains a significant challenge, limiting practical applications [7]. Catalytically active sites in PGM-free materials are proposed to be FeN_4 complexes embedded in a graphene lattice (Fig. 1b) within layered or other larger materials, but this is still under debate largely due to the range of potential actives sites predicted by computational methods and lack of methods for directly validating these models [5]. Fundamental insights into the atomic structure and resulting degradation pathways of proposed active sites are therefore needed to fully understand and control cell performance and durability [6].

2D materials typically make ideal samples for STEM, but those within PGM-free catalysts present additional challenges since these materials are often defect-rich, with a high density of edges, dopant atoms, etc., which significantly increase susceptibility to beam damage at standard operating voltages. This makes analysis of potential FeN_4 active sites particularly challenging, since a large proportion of Fe exists at edge sites where beam-induced atomic displacements can prohibit high-resolution structural characterization [6]. Conventional dark-field imaging compounds this problem by producing less signal for a given dose and being less sensitive to light elements than dose-efficient phase contrast imaging techniques such as those enabled by four-dimensional (4D)-STEM [8-10] (Fig. 1a). Consequently, active site structural analysis is often left to methods such as low-resolution imaging combined with quantum chemical calculations [6], which hinders accurate determination of reaction and degradation mechanisms.

Here, we demonstrate direct atomic-scale structural mapping of FeN_4 sites by performing low-voltage 4D-STEM on a model PGM-free catalyst system with many exposed monolayer regions. To accomplish this, we pair a 30 keV aberration-corrected probe with a fast pixelated detector that has optimal performance at low beam voltages [11]. This enables us to simultaneously image light and heavy elements with high signal-to-noise by center-of-mass analysis (Fig. 1c) while minimizing beam-induced atomic displacements at sensitive sites. The monolayer nature of these materials additionally allows for experimental validation by direct comparison with multislice simulations [12] of model structures (Fig. 1d-e). This work demonstrates how low-voltage 4D-STEM will provide new insights into the atomic-scale structure and degradation mechanisms of active sites in PGM-free catalysts, facilitating the development of low-cost hydrogen fuel cells and other energy conversion technologies in the future [13].

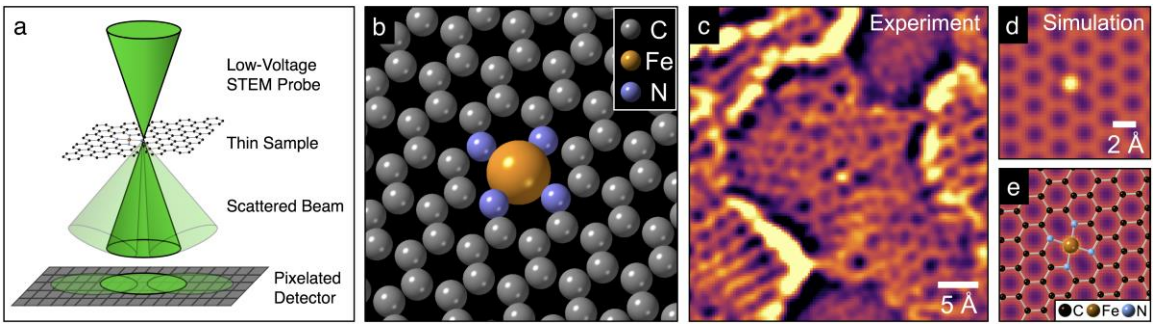

Figure 1. Figure 1. Schematics of 4D-STEM and FeN4-graphene structure, as well as example result for low-voltage atomic-scale structural mapping of an FeN4 site within a PGM-free catalyst. (a) 4D-STEM involves acquiring a diffraction pattern on a pixelated detector at each probe position. Information about the sample potential is encoded in these patterns and can be accessed by a number of methods. (b) Schematic of an FeN4 site in a perfect graphene lattice. (c) Experimental results for atomic-scale structural mapping of an FeN4 site in a defective graphene lattice from within a PGM-free catalyst by 4D-STEM with a 30 keV probe. Here, the structure is visualized through the derivative of the center of mass (dCoM) of each diffraction pattern. A ~0.5 Å gaussian filter is applied to reduce noise at frequencies significantly higher than the information limit of the instrument. (d) dCoM map generated from a multislice simulation of an FeN4 site in a perfect graphene lattice, using an aberration-free 30 keV probe. (e) Atomic structure from which the simulated data in (d) was generated, overlaid on results.

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