Atomic-Scale Compositional Distribution in PtRu Nanocatalysts

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Abstract: Bimetallic nanoparticles hold great promise in achieving controlled and well-defined electronic and catalytic properties highly valued in a wide variety of commercial applications. These properties are attained through a controlled interplay between particle size, atomic ordering and composition [1]. However, characterisation of the atomic structure and composition of particles smaller than 5 nm has proved extremely challenging using conventional characterisation techniques, often prohibiting the establishment of unambiguous structure-property relations. Here we use aberration-corrected high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM), electron scattering simulations and density functional theory (DFT) to probe the compositional distribution in bimetallic nanoparticles at the atomic scale. The combined theoretical and experimental characterisation allows us to establish a fundamental understanding of structure-properties relations in bimetallic nanoparticle systems.

Introduction: The detailed structure and composition of the surfaces of nanoparticles play a crucial role in their catalytic properties. Platinum-based nanoparticles have been widely used as electrocatalysts for polymer electrolyte membrane fuel cells and direct methanol fuel cells. The addition of a secondary metallic element can improve efficiency and reduce CO poisoning, according to the bifunctional mechanism and/or the electronic effect [2]. Based on these mechanisms, several parameters are of particular importance for these systems. Firstly, the spatial distribution of Pt and Ru surface sites affect the electronic structure and hence the catalytic properties. Furthermore, defect structures on the surface can also play a key role, providing e.g., more active nucleation sites for water adsorption, and potentially increase the catalyst's stability. Hence, there is an essential need to identify the precise surface structure and composition of these catalysts that, in turn, provides insight into the synthesis and structure-activity relationships in these systems.

Material Synthesis: The bimetallic PtRu systems have been developed in order to tune the efficiency of fuel cells [3]. These particles have been synthesised using a simple colloidal synthesis method and the bimetallic colloids were then deposited on carbon black supports. The particle sizes have been controlled at ~2nm, and the composition ordering has been varied to produce alloy and core-shell (Ru@Pt) nanoparticles.

Characterisation Methods: HAADF-STEM gives contrast that is proportional to atomic number (Z) with high spatial resolution. Therefore it is suitable for measuring the atomic column-by-column compositional distribution within the nanoparticles. Frozen-phonon multislice electron scattering simulations under a parallel-optimized scheme [4] allow us to make a quantitative interpretation of the HAADF intensity in terms of the compositional distribution within individual nanoparticles. Complimentary information on the averaged compositional distribution is provided by synchrotron based X-ray absorption spectroscopy (XAS) of Pt L_{III} and Ru K edges. Finally, DFT calculations on model (extended) surfaces have been conducted to understand the compositional behaviour of the surfaces.

Results: The simulated HAADF-STEM intensities for Pt and Ru atomic columns, as shown in Figure 1, establishes that the Pt and Ru intensity ratio is ≈2.35 and their intensities

increase linearly up to 7 and 10 atoms, respectively. This thickness range is within the size of the PtRu nanoparticles examined here. This linear behaviour forms the basis of the quantitative compositional analysis in this work. As an example, Figure 2a shows a typical HAADF-STEM image of a PtRu (Pt:Ru=1:1) alloy nanoparticle. The large fluctuation of the intensities of the atomic columns, shown in Figure 2b, can only be attributed to the mixed Pt and Ru atomic columns in the particle. Similar trends have been observed in the Ru@Pt core-shell nanoparticles.

In this presentation, we will demonstrate how a quantitative analysis of experimental HAADF-STEM images has been carried out to extract the quantitative composition distribution in the bimetallic nanoparticles, confirming the presence of compositional ordering. In addition, we will present DFT results confirming that the experimentally observed compositional ordering is energetically favourable.

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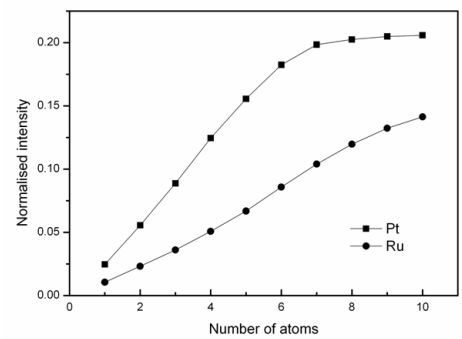

Fig 1. Simulated HAADF-STEM intensities of Pt and Ru atomic columns. Simulation parameters correspond to the experimental conditions.

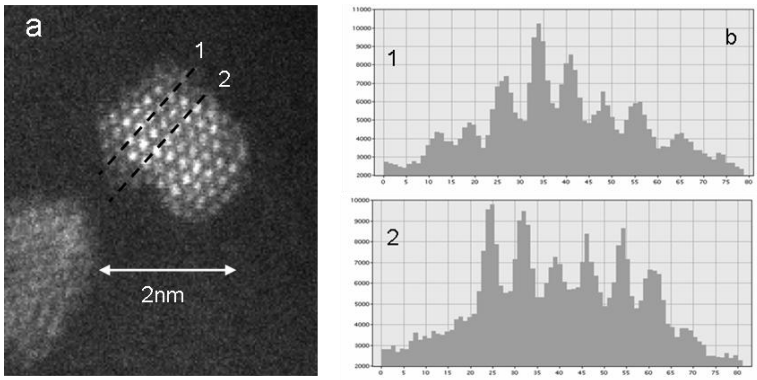

FIG. 2. (a) HAADF STEM image of a PtRu nanoparticle. (b) linescans of HAADF STEM intensities taken from the profiles shown in (a).