

Quantitative HAADF Study of Twin Boundaries in Cu₃Pt Nanoparticles

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The properties of Pt-based intermetallic nanoparticles, used as a cathode catalyst for oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFC) strongly depend on their size, shape and the crystal structure [1]. Imperfections of the crystal structure, such as partial ordering, formation of core-shell and Pt rich skin improve the electrocatalytic activity [2]. Controlling the lattice strain was found to be an efficient way of tuning the Pt-based catalyst activity because lattice strain can have an impact on surface reactivity, even if the source of strain is more than a few atomic layers away [3]. Strasser et al. reported an enhanced ORR activity of CuPt core-shell nanostructures, owing to the compressive strain that was induced on the Pt shell by the PtCu core [4]. In the case of twinned structure, the induced lattice strain caused by planar defects significantly influences the interatomic distances and consequently the energy levels of bonding electrons, which determines the catalytic, electrical and optical properties [5].

Using a novel, modified sol-gel method we prepared partially ordered (Pm3-m) intermetallic Cu₃Pt nanoparticles for catalytic ORR application. Varying specific synthesis parameters the degree of ordering, presence of Pt rich layer (skin) at the surface and the amount of particles with lamellar (111) twins could be tailored. The material obtained exhibits up to 5-fold improvement of mass activity and a 9-fold improvement of specific activity compared to the Pt/C benchmark [6].

In this work we studied the local structure and chemistry near lamellar (111) twin boundaries at the atomic level using HAADF-STEM (Jeol ARM 200 CF) in conjunction with image simulations. Coordinates of atomic column intensity maxima were determined using 2D Gaussian fit. Experimental Cu-Pt column intensities were measured using modified approach by LeBeau and Stemmer [7] where average intensity of the background and HAADF STEM detector signal were measured from the image of HAADF detector at non-saturating settings of brightness and contrast. The detector background intensity was subtracted from the intensity of each pixel in experimental images. The resulting intensities in experimental images were divided by background-corrected average intensity signal of the detector. This normalized intensity corresponds to the relative scattering of each atom column. Experimental intensities were compared to the intensities from simulated images where chemical composition and thickness of individual Cu-Pt columns were varied.

In Fig. 1a a HAADF micrograph of (111) twin boundary in 20 nm sized Cu₃Pt nanoparticle is displayed. From HAADF images the intensity ratios were extracted and correlated to the average chemical composition of individual columns. Fig. 1b is the distribution of normalized intensities around the twin boundary where a significant decrease in the intensity near the twin boundary is observed. Using a geometrical phase analysis (GPA) it was found that there are alternating compressive and tensile stresses near the twin boundary (Fig. 2a). Using models such as that presented in Fig. 2b the HAADF images were simulated using a multislice method with frozen phonon approximation (Fig. 2c). To extract the chemical composition information the ratio of Cu and Pt atoms were varied in the model and experimental and simulated images were compared. Similar structure models were used for DFT calculations where energies and lattice relaxations were calculated as a function of local chemical

composition. Taking into account the local strain and chemical composition variation the influence of twin boundaries on electrocatalytic properties will be discussed in details. [8]

References

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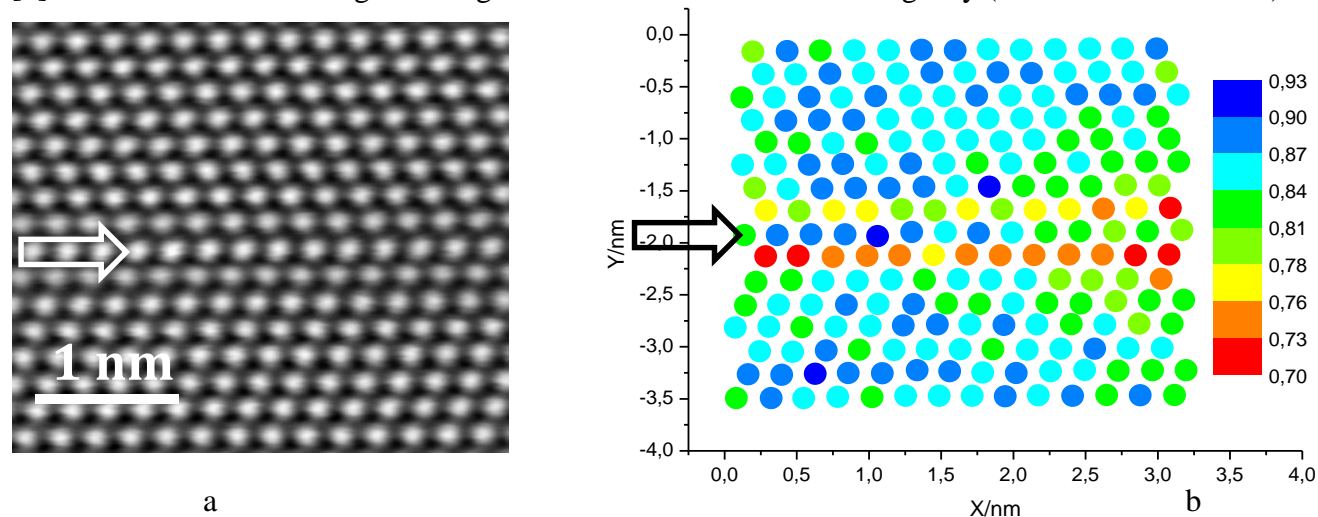


Figure 1 a – HAADF micrograph of (111) twin in Cu_3Pt nanoparticle in [110] zone, b – normalized intensity distribution of Cu-Pt columns measured from Fig 1a used for chemical composition estimation

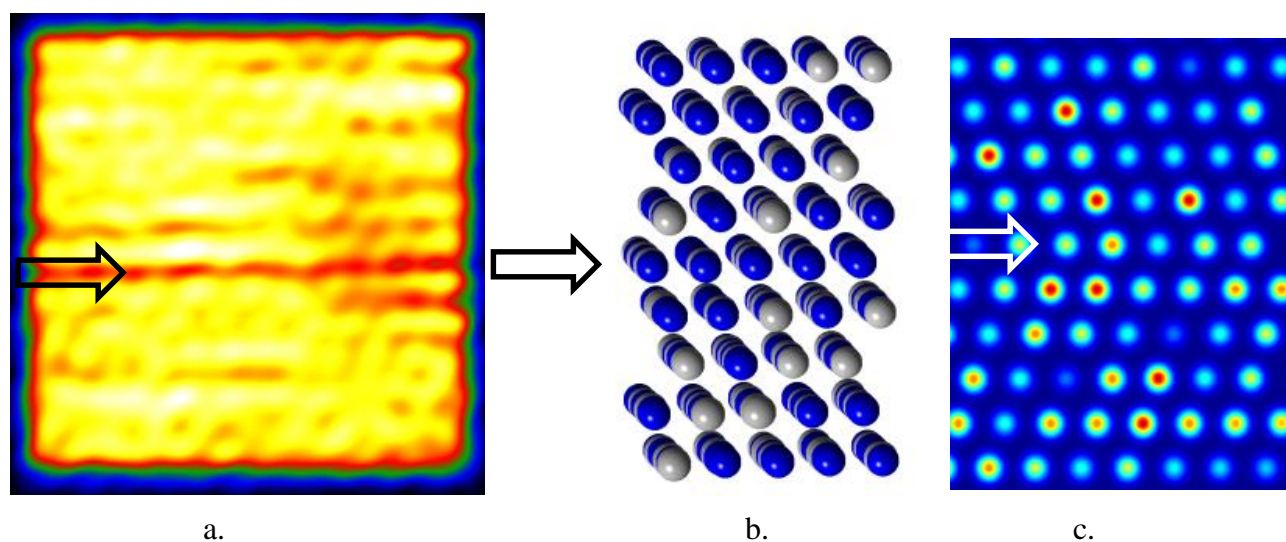


Figure 2 GPA (Geometrical phase analysis) showing tensile stress at the twin boundary (a). Example of a structural model (b) (Cu – blue spheres, Pt – gray spheres) used for HAADF images simulations (c), chemical composition estimation and DFT calculations