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TEM Study of Heavily Twinned Cu_3Pt Nanoparticles

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The efficiency of proton exchange membrane fuel cells (PEM-FC) is mainly limited by the activity of the cathode catalyst for oxygen reducing reaction (ORR). Various materials based on Pt – transition metal alloys are used for such application [1, 2] where it was found that electrocatalytic activity can be substantially increased through the formation of ordered intermetallic compound (like Cu_3Pt) and the formation of core-shell structure [3].
The physicochemical properties of metal nanoparticles strongly depend on their size, shape and the internal crystal structure. Nanocrystals with twinned structures can exhibit different properties comparing to single-crystal counterparts, due to a large defect-to-volume ratio. The lattice strain caused by twin defects could have a significant impact on the electronic structure of metal nanocrystals influencing the interatomic distances and thus the energy levels of bonding electrons, which in turn determines the catalytic, electrical and optical properties [4]. It was reported, that in the case of the parallel twined structure of platinum nanoparticles, the conductivity is increased significantly, up to 6 times compared to pure (defect free) Pt. [5] Some particles could exist as single twin (just one twin defect) or as multiple twin particles. Two types of multiple (repeated) twinning are known in metal nanoparticles: lamellar and cyclic. Lamellar twinning is characterized by parallel contact twins repeating continuously one after another while cyclic twinning requires nonparallel coplanar composition planes forming decahedron and icosahedron morphologies.

Using a novel, modified sol-gel method the ordered (Pm3-m) intermetallic Cu_3Pt nanoparticles for catalytic oxygen reduction reaction applications were prepared. Varying specific parameters like chemical composition, temperature profile and atmosphere of synthesis the degree of ordering, presence of Pt rich layer (skin) at the surface and the amount of particles with lamellar 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.

In this work we report the structure and properties of Cu_3Pt nanoparticles with high amount of lamellar twins, investigated with a Cs probe-corrected JEOL ARM 200 CF microscope. In Fig. 1 LAADF (low-angle annular dark-field) and HAADF (high-angle annular dark field) micrographs of nanoparticles with (111) twin boundaries are displayed. With LAADF technique the local strain field can be detected through its distortion of adjacent atomic sites and subsequent dechanneling of the electron beam from the atomic columns [6]. We can see that at the twin boundaries the contrast is much higher indicating large local strain field. From XRD measurement it was found that beside ordered (Pm-3m) Cu_3Pt and disordered $Cu_{3-x}Pt$ (Fm-3m) phases also some other phase in small amount is present. In Fig. 2 the XRD diffractogram splitting of (011) peak is visible. Using selected area electron diffraction we found that spots with identical d-values (2,55 Å and 2,72 Å) are always present in pair on the same reciprocal vector ***g***, indicating they are in close crystallographic relationship. Fig. 2b, c represents SAED patterns where two pairs of spots and bright and dark-field images of the twined particles are displayed. Those findings could be explained with rhombohedral distortion of the Cu_3Pt structure near the (111) twin boundary. The influence of twin boundaries on electrocatalytic properties will be discussed in details.

References

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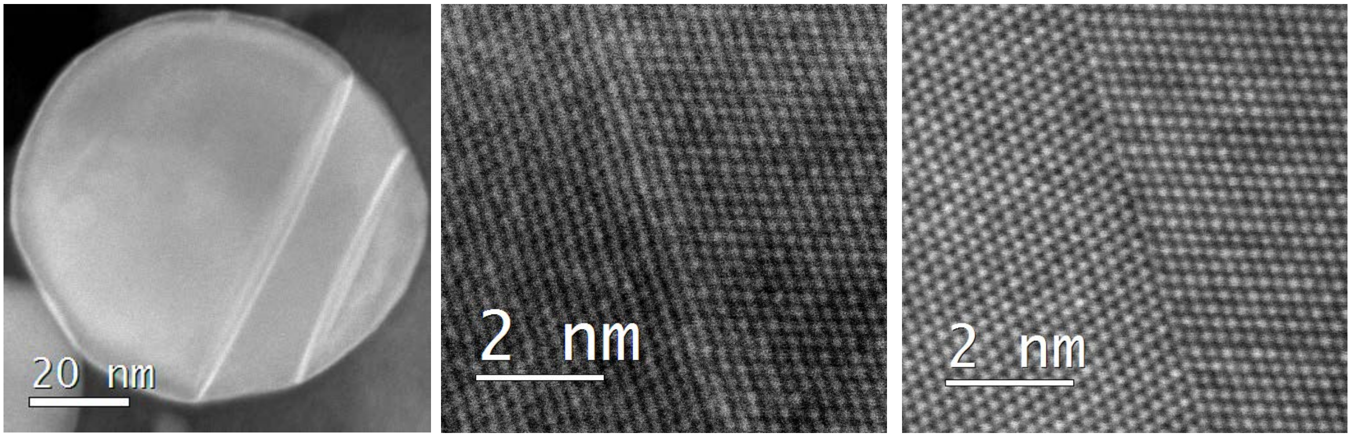
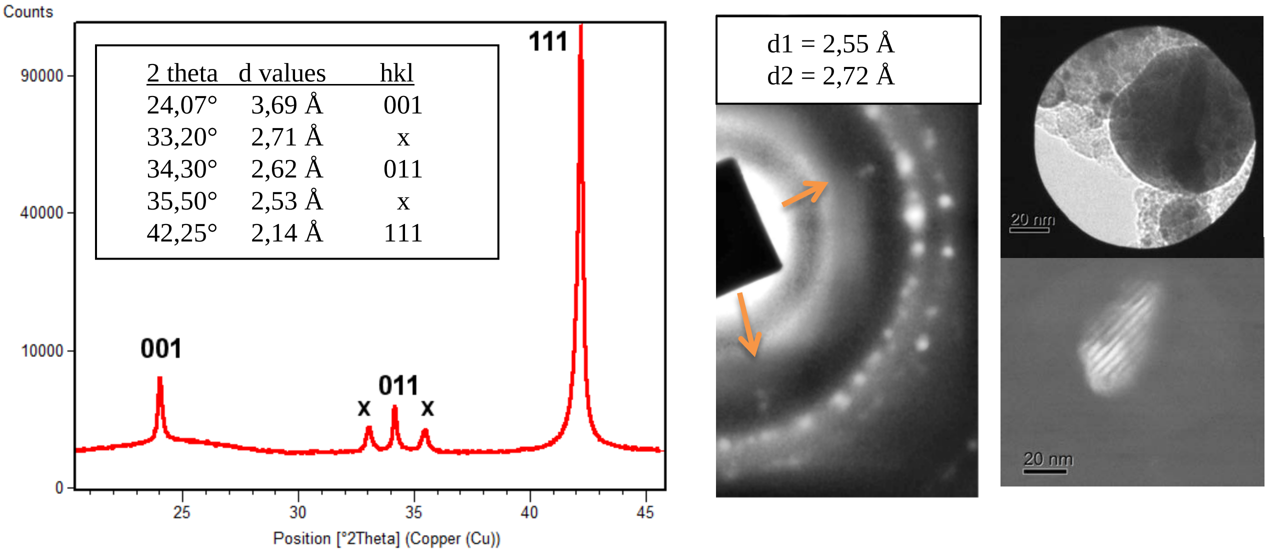


a. b. c.

Figure 1. a. – LAADF micrograph of Cu3Pt nanoparticle, b. – LAADF micrograph of the (111) twin boundary and c. – HAADF micrograph of the same twin boundary



2 theta	d values	hkl
24,07°	3,69 Å	001
33,20°	2,71 Å	x
34,30°	2,62 Å	011
35,50°	2,53 Å	x
42,25°	2,14 Å	111

d1 = 2,55 Å
d2 = 2,72 Å

a. b. c.

Figure 2. a. XRD pattern and listing of d-values (inset) of heavily twined sample, b. selected area electron diffraction pattern of Cu_3Pt heavily twined particles, c. – dark-field, bright-field micrograph of twined particle using lower pair of the labeled diffraction spots in b.