Study of carbon-supported bimetallic PtCu nanoparticles by ASAXS

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Abstract. Bimetallic platinum-copper nanoparticles on carbon support are studied as a perspective electrochemical catalyst by anomalous small-angle X-ray scattering near the Pt absorption L$_3$-edge. The simultaneous fitting of several diffraction patterns measured at different photon energies lead to a satisfactory agreement between experimental and model curves in the assumption of core-shell structure of the particles with Pt-rich shell and Cu-rich core. It is shown that the average size of as prepared nanoparticles is about 6 nm with distribution spread of about ±2 nm and with thickness of Pt-rich shell approximately 1.6 nm. After annealing at 350°C the average size of the particles increased by two times with additional enlargement of the Pt-rich shell thickness.

1. Introduction
Platinum-containing materials, especially nanocomposites, are widely used as a catalysts of many practically important reactions, in particular, hydrogen electro-oxidation in low-temperature fuel cells [1]. High cost of platinum catalysts severely restrains their commercial applications, so that the search of cheaper and more durable materials is very important. One of the promising ways is the synthesis of catalytic layer containing bimetallic nanoparticles of core-shell architecture, with a core of transition metal atoms and a shell of platinum atoms, in combination with new types of carbon supports [2, 3]. There were synthesized a series of bimetallic nanoparticles with platinum shell and different core metals [4], such as silver [5, 6], ruthenium, gold or copper [7, 8]. Additionally, such catalysts are expected [4] to be more stable and durable than monometal ones.

Such an increasing interest to complex multi-metallic nanosized systems requires the development and application of techniques for structural diagnostics which should be sensitive to the details of atomic structure at a scale from one to hundreds of nanometers. Particular interest is in the size distribution of nanoparticles, the composition of inner and shell regions, thickness and continuity of the near-surface area. The small-angle scattering diffraction (SASD) is proved to be a powerful tool for studying of the structure of materials at an intermediate scale range between the atomic scale, where spectroscopic methods (XAFS, XES, EELS, etc.) are applicable, and mesoscopic scales where direct observations (TEM, SEM, etc) could be performed. The small-angle scattering of X-rays (SAXS) near the absorption edge of a particular element is called anomalous SAXS or ASAXS. The dependence of scattering contrast from the energy in ASAXS experiments allows to consider the distribution of selected element in more details. This technique was successfully applied for the studies of platinum-copper alloyed particles.
in carbon [9], gold-silver core-shell particles in glass [10] and even more complex metal-oxide systems [11, 12, 13].

In the present paper the structure of platinum-copper bimetallic particles on the carbon support (PtCu/C) is studied by means of ASAXS diffraction with photon energies at Pt L₃-absorption edge. Section 2 presents the details of sample preparations and data acquiring, Section 3 describes the fitting strategy and the results of ASAXS analysis are summarized in Section 4.

2. Experimental

The considered samples were synthesized by sequential (PtCu-seq/C) chemical reduction of copper and platinum ions of corresponding salts (CuSO₄ and H₂PtCl₆) and deposition to a carbon suspension (Vulcan XC-72, Cabot) [14]. At the first step the nanostructured material Cu/C was obtained by the reduction of copper ions using NaBH₄, and at the second step aqueous solution of H₂PtCl₆ containing an excess of NH₃ and NaBH₄ was added to the solution where Cu/C were already formed. In order to boost stability of the catalyst it was annealed at 350°C for 1 hour.

The ASAXS experiments were performed near Cu K-edge (8697 eV) and near Pt L₃-edge (11558 eV) using the μSPOT beamline at the synchrotron BESSY II at Helmholtz-Zentrum Berlin (HZB) [15]. Three energy points were used for ASAXS data collection, within -10, -100 and -300 eV before each edge. The q-scale is calibrated using a silver behenate standard sample, measured at each photon energy. The integration and calibration of the detector data was done by using the software GSAS-II [16].

3. ASAXS data analysis

The scattering intensity of dilute system of dispersed particles with the number density distribution N(R) can be described as: 

\[ I(q) \propto \int_0^\infty N(R)|F(q, R)|^2 dR \]

where \( q = 4\pi \sin \theta / \lambda \) is the scattering vector, \( R \) – particle radius, \( F(q, R) = \int \Delta \eta(\vec{r}) e^{i\vec{q} \cdot \vec{r}} d\vec{r} \) is the scattering length (scattering amplitude), depended on how scattering density \( \Delta \eta(\vec{r}) = \eta(\vec{r}) - \eta_{\text{matrix}} \) is distributed in the particle. Conventionally the particle volume \( V(R) \) and averaged scattering contrast \( \Delta \eta \) are extracted from scattering length, so that remained factor \( \Phi(q, R) \) which contains only information about the shape (form-factor): 

\[ F_{\text{Sp}}(q, R) = \Delta \eta \cdot \left( \frac{4}{3} \pi R^3 \right) \cdot \left( \frac{3\sin(qR) - qR \cos(qR)}{(qR)^3} \right) = \Delta \eta \cdot V_{\text{Sp}}(R) \cdot \Phi_{\text{Sp}}(q, R), \quad (1) \]

and for core-shell object with total particle radius \( R \), core radius \( R_c = \nu R \), core contrast \( \Delta \eta_c = \xi \cdot \Delta \eta \) and shell contrast \( \Delta \eta_s \):

\[ F_{\text{CS}}(q, R) = \Delta \eta \cdot [V_{\text{Sp}}(R) \cdot \Phi_{\text{Sp}}(q, R) - (1 - \xi)V_{\text{Sp}}(\nu R) \cdot \Phi_{\text{Sp}}(q, \nu R)]. \quad (2) \]

The only energy-dependent term is the scattering contrast (\( \Delta \eta \) and \( \xi \) for core-shell), which is calculated with account for anomalous contribution to atomic factor as it implemented in GSAS-II:

\[ \eta \propto \rho \sum c_a(Z_a + f_a'(E)) / \sum c_a M_a , \quad (3) \]

where \( \rho \) is the density, \( c_a \) is the number of atoms with charge \( Z_a \) and mass \( M_a \) in the unit cell, \( f_a'(E) \) is a real part of anomalous correction (tabulated). Figure 1 compares the energy dependence of experimental SASD curves at arbitrary chosen value of \( q = 0.1 \AA^{-1} \) of two samples and calculated behavior of squared scattering contrast \( |\Delta \eta|^2 \) of pure platinum or copper with respect to carbon matrix. It can be seen, that experimental and theoretical curves are in
good agreement near Pt L$_3$-edge, but near Cu K-edge anomalous copper corrections are not visible. The exact reasons of non-anomalous Cu K-edge behavior is not clear, so that current consideration was limited by Pt L$_3$-edge.

**Figure 1.** The energy dependence of: a) experimental scattering intensity of as prepared (●) and annealed (○) samples at $q = 0.1$ Å$^{-1}$ and b) theoretical contrast of pure copper (△) and platinum (▼) with respect to carbon matrix.

**Figure 2.** The comparison of experimental data measured at energies within 10 (●), 100 (△) and 300 (▽) eV before Pt L$_3$-edge and calculated curves (lines) of: a) as prepared and b) annealed samples. The insets c) and d) shows obtained size distributions.

According to EXAFS study of bimetallic catalysts [8, 6], prepared by the same technique of sequential deposition, the structure of averaged particle is expected to be close to core-shell architecture with platinum shell and copper core. This allows to use form-factor of core-shell particle (2) with pure platinum shell and copper core for the calculation of scattering intensity. The radii $R$ of the particles were distributed according to log-normal law [10], with two free parameters controlling average value ($\mu$) and dispersion ($\sigma$). The common scale parameter and the fraction of core radius $\nu = R/R_{\text{core}}$ were varied. The background contributions are clearly distinguished and were fixed to observed values. The contrast of the core and shell with respect to the matrix was not varied and was set to calculated by eq.(3) values for platinum and copper at different photon energies.

Table 1 presents the results of simultaneous fitting of the samples together with goodness of fit parameter (R-factor) and Figure 2 illustrates the fitting quality. For clarity the curves at Figure 2ab are shifted along vertical axis. The extension of the fitting model by inclusion of free dispersed platinum particles to the core-shell particles produced very small volume fraction of pure particles (< 10 %), with approximately the same parameters of core-shell particles. The average size ($D_{\text{av.}} \approx 2\mu$) of core-shell particles is reasonably [17] increased from 6 nm to 12 nm as a result of annealing procedure. The observed distribution spread is increasing too,
Table 1. Results of simultaneous fitting of the ASAXS curves near Pt L$_3$-edge.

| Sample   | $R_w$-factor, % | $\mu$, nm | $\sigma$ | $\nu = R/R_{core}$ |
|----------|-----------------|------------|---------|-------------------|
| as prepared | 19              | 3.0        | 0.6     | 0.5               |
| annealed  | 22              | 6.4        | 0.9     | 0.3               |

as it illustrated on the insets of Fig. 2. The average shell thickness of Pt-rich shell region is estimated as $\mu(1 - \nu) = 1.6$ nm before and 4.7 nm after annealing. However, the estimations of the number of platinum and copper atoms corresponding to the core and shell volumes does not agree with total composition of the materials estimated by EDX, so that more detailed analysis of the chemical compositions of core and shell regions is required.

4. Conclusions
Pt L$_3$-edge ASAXS data of as prepared and annealed PtCu/C can be satisfactorily explained by a model of log-normally distributed core-shell particles with Cu-rich core and Pt-rich shell. The performed study showed that annealing at $350^\circ$ resulted in i) the increase of the particle size from $\sim 6$ nm to $\sim 12$ nm; ii) the increase of the distribution spread from $\sigma \approx 0.6$ to $\sigma \approx 0.9$ and iii) enlarging of the average Pt-rich shell thickness from $\sim 1.6$ nm to $\sim 4.7$ nm.

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