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Spectroscopic study of nickel(II) hydroxide surface modifications induced by a small iron(III) addition

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Abstract Comparative Auger electron spectroscopic data on the surface composition and depth profiling for β-$Ni(OH)_2$ and $Ni(OH)_2$ coprecipitated with iron(III) (3 at.%) are given showing a non-uniform distribution of the latter. They are considered together with their structural characteristics obtained using Fourier-transform infrared spectroscopy (both samples) and Mössbauer spectroscopy (Fe-containing sample). The results obtained provide an explanation for the specific behaviour of the Fe(III)-doped nickel(II) hydroxide in heterogeneous processes (adsorption, electrocatalysis).

The structure and physicochemical properties of nickel hydroxides have previously been shown [1–4] to be essentially influenced by ferric species. The resulting composite Ni–Fe hydroxide systems have found diverse practical applications in heterogeneous processes comprising adsorption, catalysis and electrocatalysis, electrode processes and energy conversion, etc. [4–8], for which the surface structure, chemical state and elemental composition are of primary importance.

Recently we have found [7] that the surface layers of binary Ni(II)–Fe(III) hydroxide electrocatalysts (9:1 and 4:1 atomic ratios) are essentially enriched with Fe as compared to the bulk composition. As for small Fe additions, the similarity of the adsorption properties of pure $Ni(OH)_2$ and that with 3 at.% Fe added by coprecipitation led the authors of Ref. [4] to the conclusion that the small Fe addition is uniformly distributed over the bulk of the crystallites. In order to elucidate this obvious discrepancy, we compare the results of Auger electron spectroscopic (AES) studies of the surface composition and depth profiling for β-$Ni(OH)_2$ and a binary coprecipitated system with 3 at.% Fe(III), as well as their structural characteristics obtained using Fourier-transform infrared (FTIR, for both samples) and Mössbauer spectroscopy (for the Fe-containing one). All experimental details of sample preparation, AES and depth profiling, FTIR and Mössbauer measurements and data treatment may be found elsewhere [2, 3, 7].

The same phase composition for both samples corresponding to the β-$Ni(OH)_2$-type structure [9] can be seen from their FTIR spectra (Fig. 1). Comparing the absorption at ca. 3440 cm^{-1} and the δ_{H-O-H} bands at 1636 cm^{-1}, one may conclude that the Ni + Fe sample (see Fig. 1, curve 2) is more hydrated than β-$Ni(OH)_2$, in agreement with [10], while a number of bands at 1500–1000 cm^{-1} reveal the presence of anion impurities, viz. NO_3^- and CO_3^{2-} [11] included during synthesis (cf. also the AES data presented below).

Mössbauer measurements for the binary system showed two clearly resolved quadrupole-split doublets corresponding to two Fe(III)-containing forms. For the more intensive doublet I the parameters (Table 1) are close to those for cathodically [6] and chemically [7] coprecipitated Ni(II)–Fe(III) hydroxides, while doublet II comprising ca. one fifth of the spectral intensity is featured by a significantly increased quadrupole splitting (QS) exceeding the values known for hydroxide phases with hydroxo- or oxo-bridged ferric ions [12]. The latter effect, observed and discussed in more detail previously [2, 3, 7, 13], may be attributed to lowering of the coordination symmetry of ferric ions in the crystallites surface layers. As was noted earlier [7], some redistribution of the components within the surface layers, as compared to the gross averaged composition, may also contribute to the above effect.

The data of AES layer-by-layer analyses for both samples are presented in Tables 2 and 3 (depth profiling

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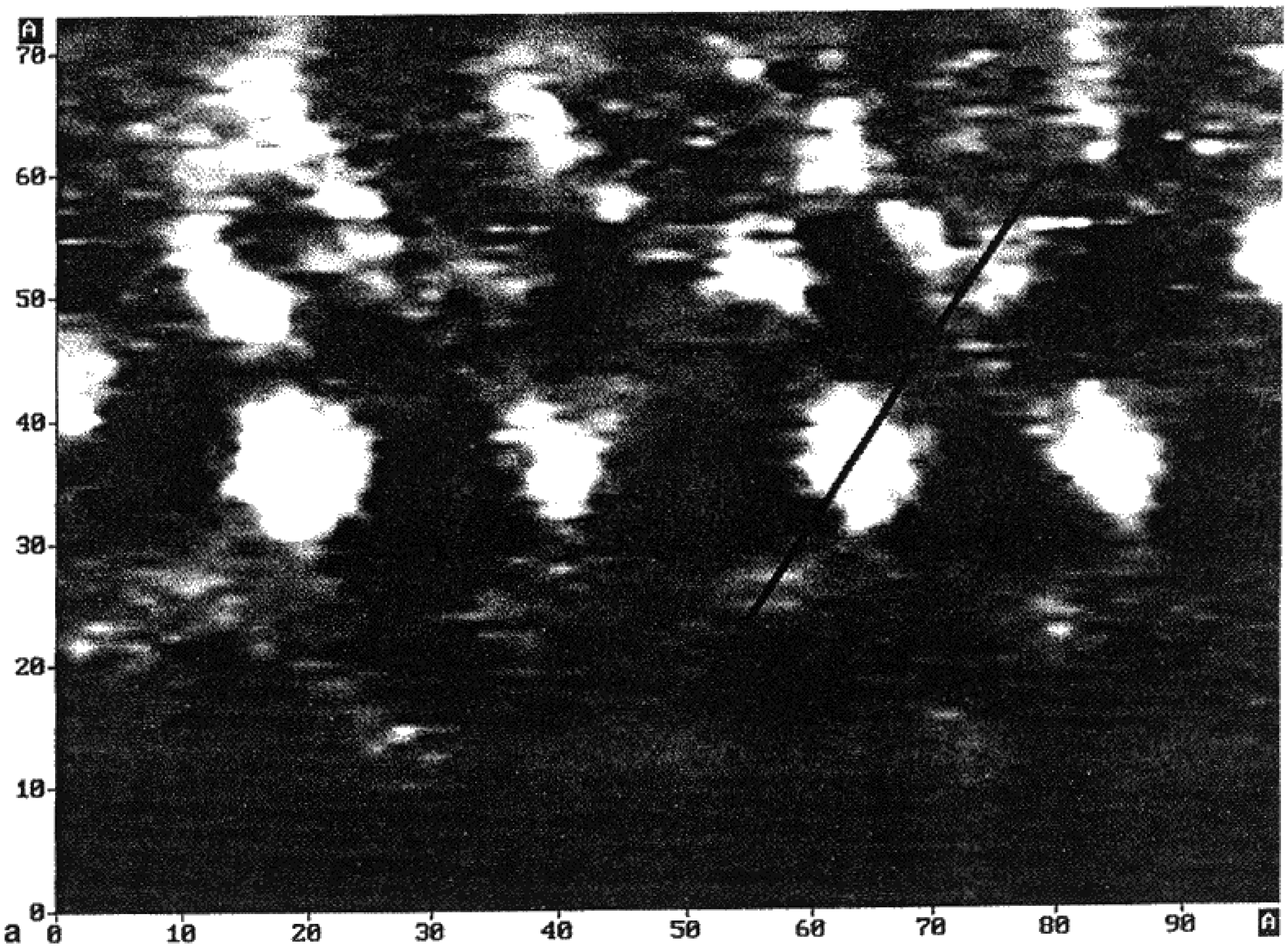
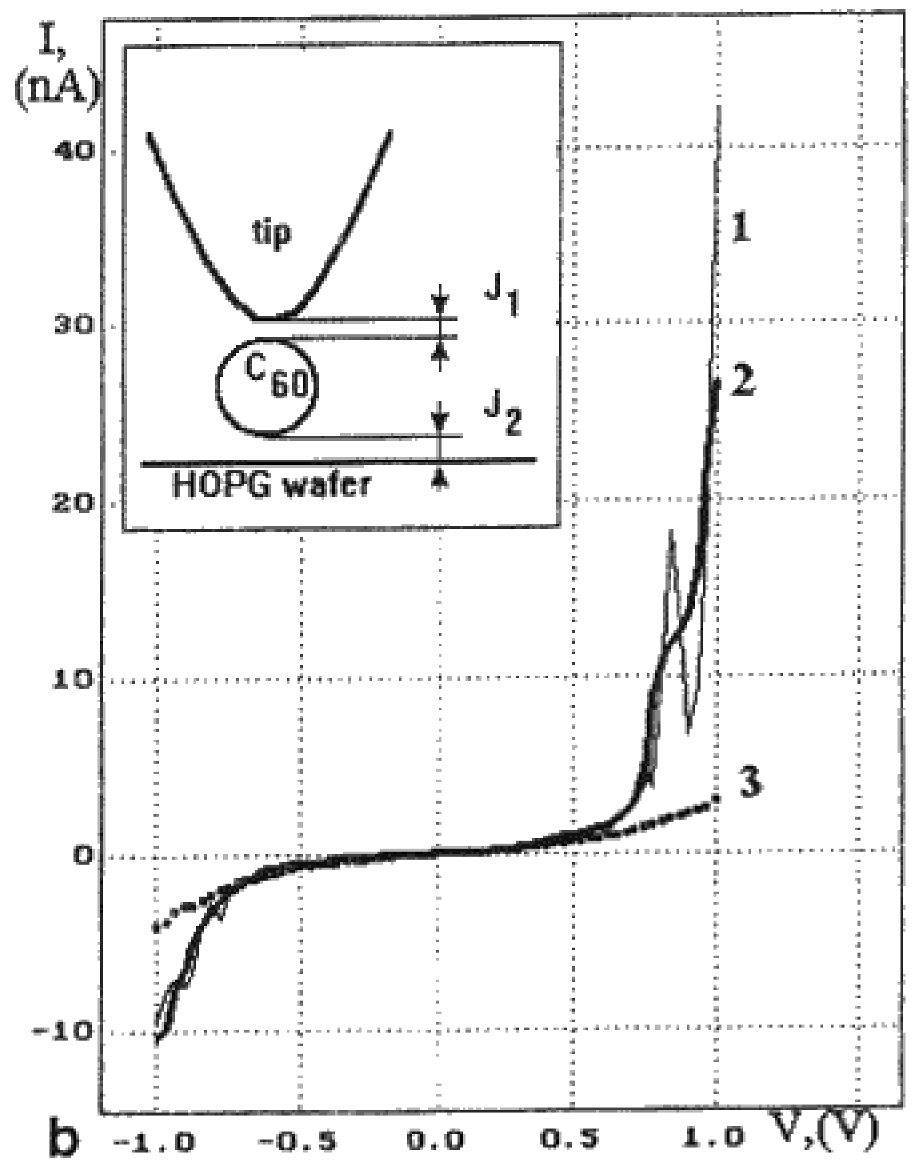
Fig. 3 **a** $dI/dz)_{I=\mathrm{const}}$ image of fullerene-in-surfactant monolayer. **b** $I(V)$ spectra from different points of the structure presented at **a**





is used as a kind of matrix and a fullerence Langmuir-Blodgett (LB) monolayer can be deposited. A constant tunnelling current mode of operation with a current value as small as 10^{-10} A is used. One can see a regular surface structure with a rhombic two dimensional lattice. The lattice period ~ 0.9 nm is in the order of the diameter of a C_{60} molecule ~ 0.8–1.0 nm [3]. One may imagine that fullerene molecules are embedded in the cells of the surfactant which form a regular surface structure.

The results of the tunnelling electron spectroscopic measurements of the monolayer are presented in Fig. 3 a, b. Figure 3a presents the work function image $dI/dz(x,y)$. The $I(V)$ curve under the condition z = const resembles in main features the curves 1,2 of Fig. 3b. A typical small current ($I < 0.1$ nA) section of the curve of about $\Delta V \approx 1.5$–2.5 V width is followed by a sharp increase of the current with both polarity voltages increasing. The results may be interpreted in terms of single electron tunnelling through the two junctions of different transmittance [4] which appear between the tip electrode and a fullerene molecule as well as between the molecule and the HOPG wafer (see inset in Fig. 3b). The characteristic mutual capacitance C may be estimated from the Coulomb blockade voltage ΔV

$$C = C_1 + C_2 = e/\Delta V \approx 6 \cdot 10^{-20}\ \mathrm{F},$$

C_1 and C_2 are respectively the capacitances of the tip - C_{60} molecule (J_1) and the C_{60} molecule - HOPG (J_2) tunnel junctions (e - being the electron charge). This correlates well with the C_{60} molecule size. The resonant tunnelling occurs when the bias voltage exceeds the Coulomb blockade resulting in the observed sharp increase of the current (see Fig. 1b, 3b,$/\Delta V/ > 1V$). The nature of the small peak at the ascending section of the $I(V)$ curve is yet not clearly understood.

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