Supplementary material

Experimental data

MWCNTs were synthesized by means of the pyrolysis of the propane-butane mixture in the presence of catalysts in G. K. Boreskov Institute of Catalysis of SB RAS (Novosibirsk, Russia). To remove the catalyst admixture, MWCNTs were treated with a mixture of hydrochloric and nitric acids. The specific surface area of MWCNTs was 250 m^2/g, the outer diameter of the nanotubes was 10 – 20 nm, and the inner diameter was 2 –10 nm. To functionalize the surface, carbon nanotubes were treated with ozone (MWCNT-f).

Synthesis of Mn_xO_y/MWCNT nanostructured composites

Nanocomposites were obtained by the reduction of $KMnO_4$ solutions, by active electron-donor centres on the surface of the multi-wall carbon nanotubes (MWCNTs) without introducing additional reducing agents. The synthesis was carried out at a temperature of 25, 60 and 80°C. Nanocomposite materials were prepared as follows: a necessary amount (≈25 ml) of a 0.005 M $KMnO_4$ solution was poured into a flask 50 mL in volume, then a weighted portion (200 mg) of carbon nanotubes was added. The samples 5%Mn_xO_y/MWCNT_25°C were made at a temperature of 25°C for 48 h. The samples 5%Mn_xO_y/MWCNT_60°C were obtained at a temperature of 60°C for 60 min. The samples 5%Mn_xO_y/MWCNT_80°C were sinthesized at a temperature of 80°C for 30 min. The time of rhe reaction completion was determined from the solution decolouration. Then the samples were washed with distilled water, separated by filtering and kept for 2 h at a temperature of 105 –110°C to the constant mass.

Synthesis of Au/MWCNT nanostructured composites

The preparation of composites was carried out by means of the reduction of precursor solutions (10–4 M $HAuCl_4$) directly by the matrix (MWCNT) itself, without additional reducing agents. The carbon matrix was placed in bottles and impregnated with the precursor solution. Then the resulting reaction mixture was heated at a temperature 60°C for 2 hours. Then the samples of Au/MWCNT nanocomposites were washed with distilled water, separated by filtering and kept for 2 h at a temperature of 105 –110°C to the constant mass.

The control over the process completion of the precursors reduction was carried out spectrophotometrically, by the absence of MnO_4^- or $AuCl_4^-$ ions in the filtrate.

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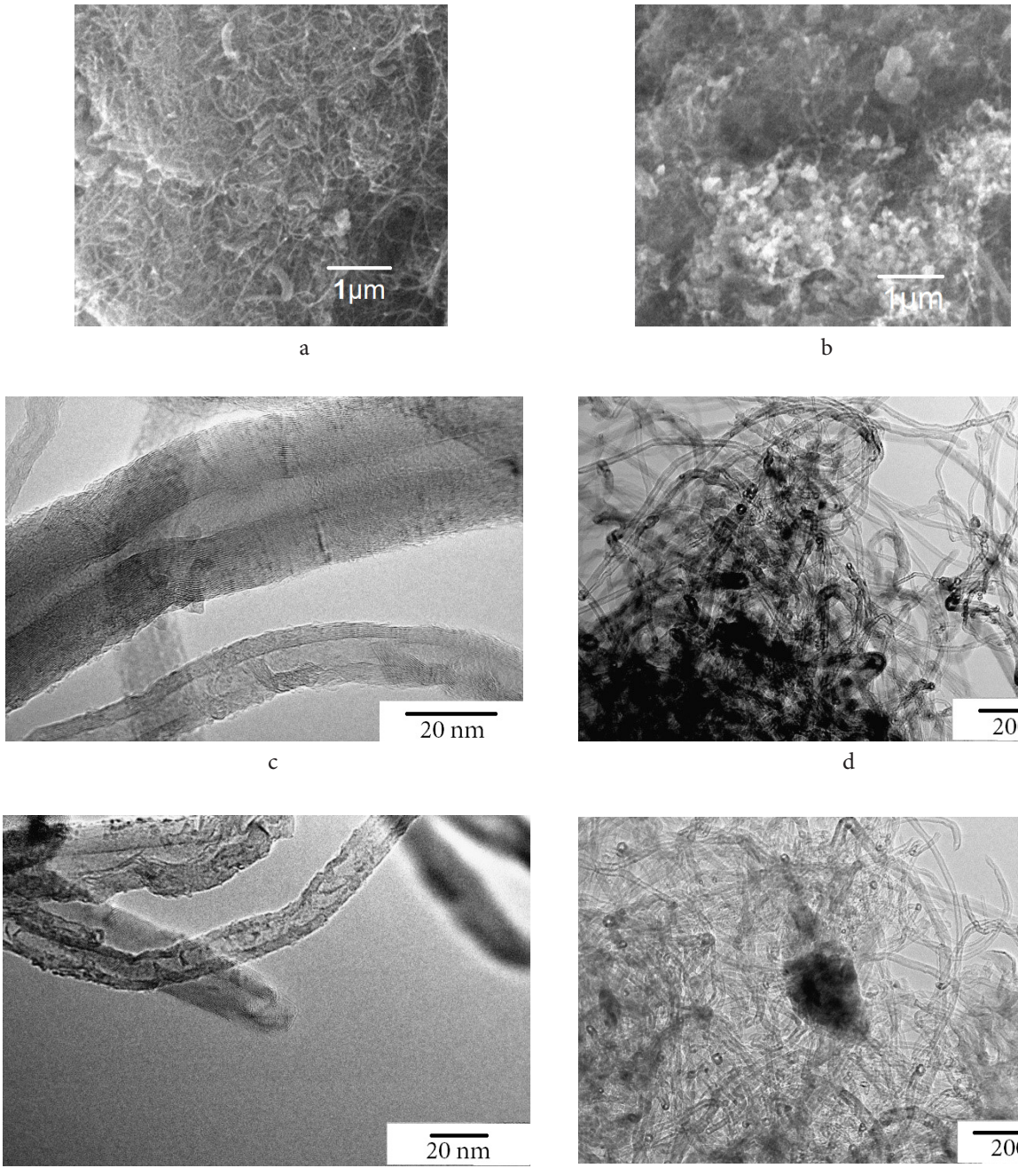

a b c d e f

Fig. S1. Scanning (a, b) and transmission (c – f) electron microscopy images of the MWCNTs (a, c, d) and Mn_xO_y nanocomposites(b, e, f).

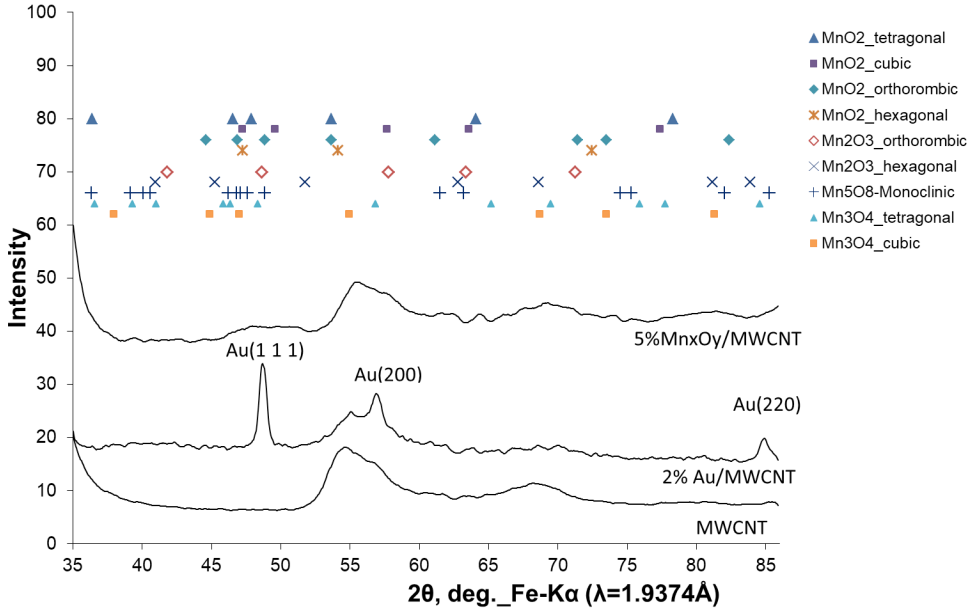

Fig S2. (Color online) XRD patterns of the MWCNTs and nanostructured composites.

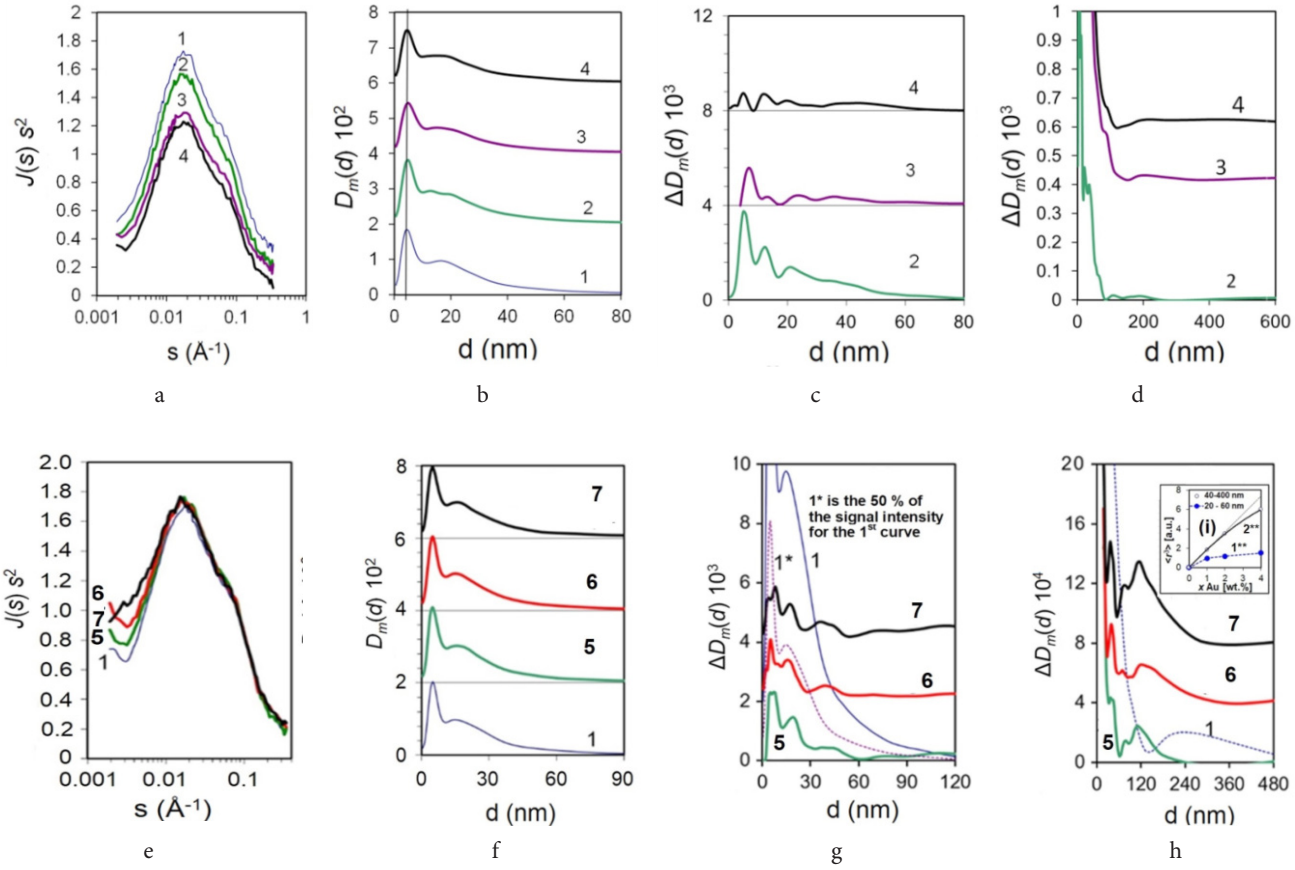

Fig. S3. (Color online) Experimental SAXS spectra (a, e). SDFI (b, f). Difference SDFI obtained by subtracting SDFI in MWCNTs from SDFI in the composites (c, d, g, h). Curves 1 — MWCNTs; 2 – 4 — Mn_xO_y/C NSCs, obtained at temperatures: 20°C (curve 2); 60°C (curve 3); 80°C (curve 4); 5 – 7 — Au/C composites with different Au content: 1% (curve 5), 2% (curve 6); 4% Au (curve 7). Integral intensity dependence of the difference SDFI maxima on gold content in the NSC (i): 1** — in the region of 20 – 60 nm; 2** — 40 – 400 nm, where $<r^3>$ — the area under the peaks at the logarithmically normal approximation.

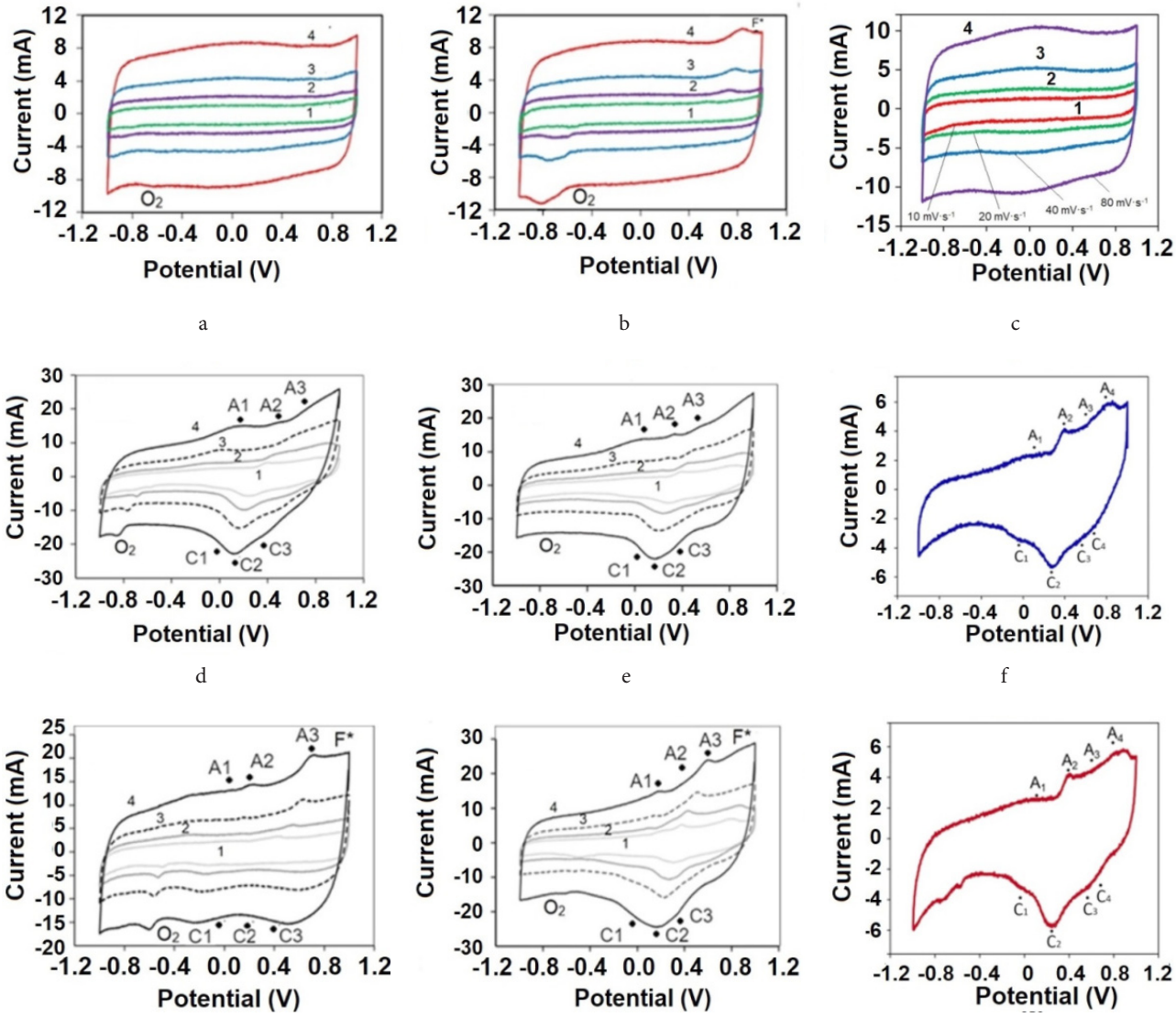

Fig. 4. (Color online) CV for symmetric cells with MWCNT (a) and MWCNT-f electrodes (b). CVs for asymmetric cells with NSC working electrodes and counter electrodes from the corresponding matrices; NSC are 4% Au/C (c); Mn_xO_y/C obtained at 60°C (d) and 80°C (e); Mn_xO_y/C-f obtained at 60°C (g) and 80°C (h). Potential scanning rate: 1 — 10 mV·s^{-1}, 2 — 20 mV·s^{-1}, 3 — 40 mV·s^{-1}, 4 — 80 mV·s^{-1}. (CVs for an asymmetric cell with NSC working electrodes at a scanning rate of 10 mV·s^{-1}: Mn_xO_y/C NSC (f), Mn_xO_y/C-f NSC (i) obtained at temperature 60 °C.

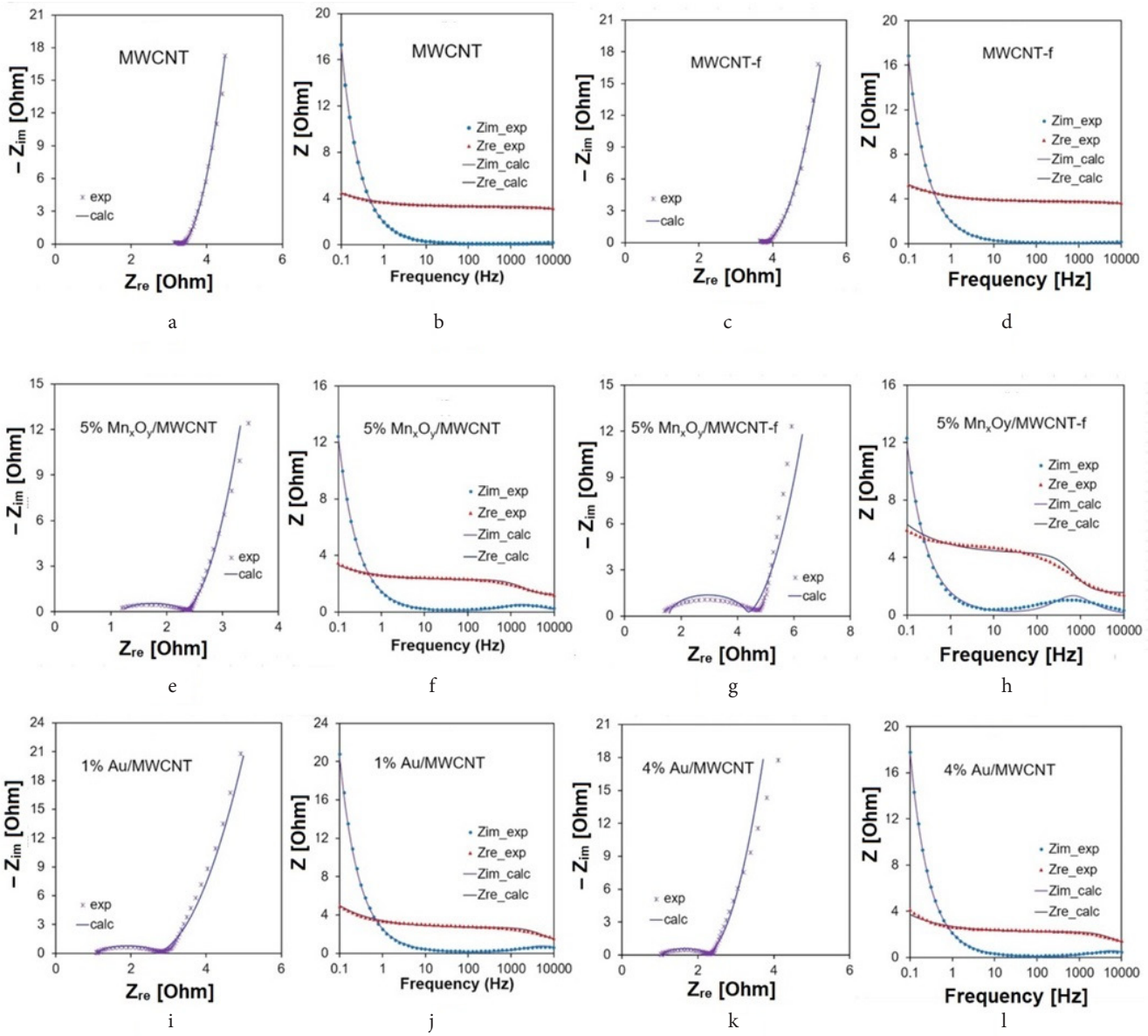

Fig. S5. (Color online) Comparison of the experimental Nyquist (a, c, e, g, i, k) and Bode (b, d, f, h, j, l) dependences with the results of simulation in accordance with Scheme (Fig. 3 d) for the electrochemical cells based on MWCNT (a, b), MWCNT-f (c, d) and NSCs (e – l) on their basis with various fillers.