Highly porous carbon materials filled with gold and manganese oxide nanoparticles for electrochemical use

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ABSTRACT

The reduction of aqueous solutions of precursors ($HAuCl_4$ and $KMnO_4$) by the carbon matrix was used to synthesize nanostructured composites based on highly porous carbon materials that are filled with Au or Mn_xO_y nanoparticles. The resulting composites were characterized using a complex of complementary physicochemical methods (XRD, SAXS, low-temperature nitrogen sorptometry, and CV). It was shown that at low concentrations of Au or Mn_xO_y the surface of matrix pores is decorated with the filler nanoparticles, which block mesopores; the role of such blocking increases with the filler content. The optimal concentration of fillers in the composites was found. A maximum capacitance of composite electrodes, which exceeds the capacitance of electrodes based on the initial matrices by a factor of 2–2.5, was observed at a gold content of 1 wt.%. Nanocomposite Au/C electrodes based on highly porous carbon material Kemerit2, which were obtained in the study, showed the highest capacitance (up to 1000 F/g). For the composite systems filled with manganese oxides, a 700 F/g capacitance of composite electrodes (at a 10 mV/s scanning rate of potential) was reached at a 2 wt.% content of manganese in the composites.

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1. Introduction

A synergetic combination of component properties in nanostructured composites (NC) based on highly porous carbon materials (HPCM) that are filled with nanoparticles of metals or their oxides makes such systems quite promising for the use as supercapacitor electrodes, catalysts, particularly in electrocatalysis, and various sensors [1–5]. Special attention is paid to the development of gold-containing composites, because gold can form ultrafine conductive films that are stable to oxidation on the surface of various substrates [6–9]. Nanocomposites filled with Mn_xO_y are promising as a pseudocapacitance electrode material for supercapacitors [10–12] because manganese has a great number of oxidation states, which allows a substantial enhancement of capacitance due to occurrence of various electrochemical reac-

tions. Therewith, the phase composition, structure, morphology and dimensions of the filler particle phases can be varied in a wide range depending on the synthesis method, which opens a way for targeted control of the general properties of composites.

The main problem is the development of chemically pure and spatially regular NC with high specific surface area (S_{sp}) and porosity, which are decorated with ultrafine layers of the filler. Another challenges are related to simplifying the synthesis process and reducing the product cost; controllable formation and modification of the size, shape and phase composition of filler nanoparticles; increasing the accessibility of the active surface of filler nanoparticles to solutions of electrolytes or reacting components. Solution of the indicated problems will provide high functional characteristics, in particular the catalytic activity and electrochemical capacitance.

The goal of this work was to devise methods for the synthesis of nanostructured composites based on highly porous carbon materials that are filled with nanoparticles of gold or manganese oxides, and to investigate their properties for developing the highly efficient supercapacitor electrodes and acquiring the information (the NC morphology, shape and size characteristics of the filler particles, electrode properties of NC and features of electrochemi-
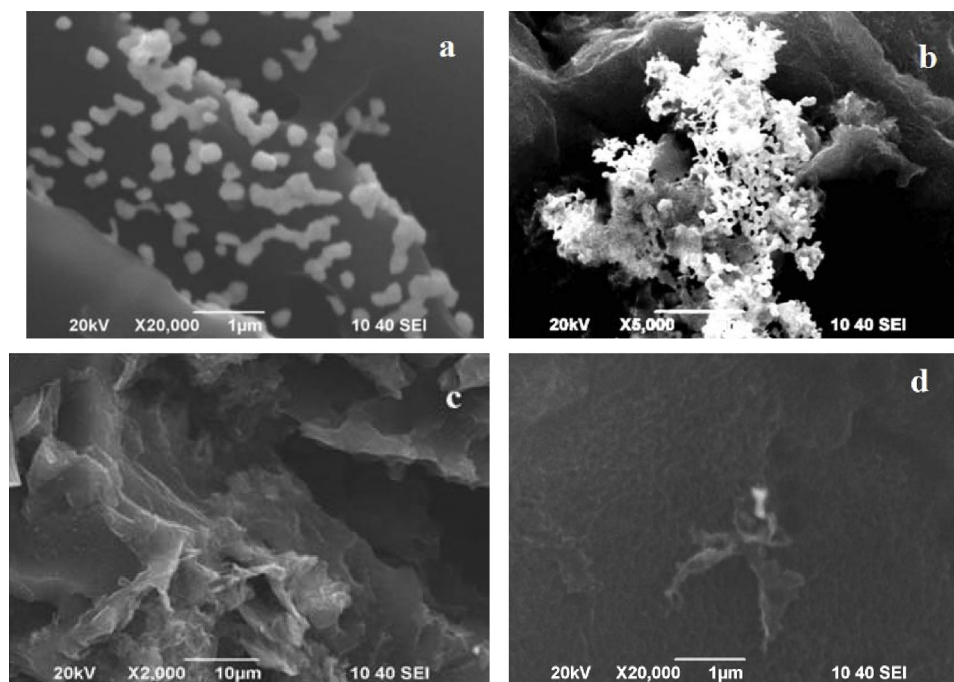
Fig. 1. SEM images of nanocomposites synthesized by the reduction of $HAuCl_4$ with hydrazine (a, b) and Carbonizate carbon matrix (c, d).

cal processes on the filler particles) required for the planned study of electrocatalytic activity of the systems in Red-Ox reactions.

2. Experimental

2.1. Synthesis of nanocomposites

The study was carried out with $HAuCl_4 \cdot nH_2O$ ($n = 3 \div 4$, 48.5% Au, Krastsvetmet, Krasnoyarsk, Russia) and $KMnO_4$ (chemically pure, 99.3%, Russia) as the precursors, and acetone (superpure, 99.7%, EKOS-1, Moscow, Russia). Solutions of the precursors were prepared with distilled water.

HPCM were represented by Carbonizate and Kemerit2, which have been created at the Institute of Coal Chemistry and Materials Science SB RAS [13,14] and possess a high S_{sp} and a developed meso- and micropore structure with the sizes favorable for the access of reactants to the pore space (see Section 3.3).

2.1.1. Reduction of $HAuCl_4$ with carbon materials

HPCM samples were impregnated with a $HAuCl_4$ solution at room temperature for 30 min using the dropwise incipient wetness impregnation. Concentration of the solution was chosen so as to obtain a required gold content in the composite, and volume corresponded to the revealed parameters of the HPCM pore structure. The samples were then held at 50–60 °C for 20–25 min, cooled to room temperature, washed with water and acetone, filtered and dried on a filter under vacuum.

2.1.2. Reduction of potassium permanganate with the carbon matrix

A HPCM sample was supplemented with 5 ml of an aqueous solution of potassium permanganate. The concentration of permanganate was varied with respect to the matrix sample and a required manganese content in the composites. The reaction was terminated after decoloration of the solution. Depending on the concentration of potassium permanganate and type of the matrix, the reaction time varied from several seconds to 24 h. After the reaction, the composites were washed with a large amount of water and acetone, and dried under vacuum.

2.2. Methods for investigation of nanocomposites

The phase composition of NC was determined by X-ray diffraction using a DIFRAY 401 X-ray diffractometer with a filtered iron radiation. The average sizes of the coherent scattering cross-sections (crystallites) were found from the broadening of diffraction profiles by approximation [15]. The instrument-error correction was estimated using the standard crystalline sample of zinc oxide. To provide a more accurate estimation of the broadening, the diffraction patterns (in the region of corresponding peaks) were recorded with a 10-fold accumulation. Size distribution functions of inhomogeneities (SDFI) were calculated from experimental small-angle X-ray scattering (SAXS) spectra in approximation of homogeneous spherical particles [16] using a KRM-1 instrument. The difference size distribution functions of inhomogeneities were found by subtraction of SDFI for matrices from SDFI for nanocomposites. The pore structure parameters of the initial HPCM and their nanocomposites were determined from the isotherms of low-temperature (77 K) nitrogen adsorption–desorption using the software for an ASAP 2020 Micromeritics analyzer.

Capacitance of the composites was measured with a two-electrode test cell using cyclic voltammetry at a potential window of −1 to +1 V and a scanning rate of potential equal to 10–80 mV/s, on an IPU-1 measuring feeding device. 30% KOH solution (aqueous) was used as electrolyte. Capacitance of supercapacitor cells was calculated by the formula [17]:

$$C_{cell} = (mv\Delta U)^{-1} \cdot \int I(U)dU \qquad (1)$$

where C_{cell} is the capacitance of an electrode cell; m is the mass of a composite electrode (0.01 g); v is the scanning rate (V/s); ΔU is the potential window (2 V); and $\int I(U)dU$ is the area under the CV curve, ($A \times B$).