Physicochemical properties of hybrid guest—host nanocomposites based on polyaniline

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The study concerns the influence of the method of preparation of hybrid guest—host nanocomposites based on polyaniline (a conducting polymer) on their structure, conductivity, electrochemical characteristics, electronic state, and redox activity.

Key words: hybrid guest—host nanocomposites, conducting polymers, polyaniline, layered transition-metal oxides.

Nanostructured materials have been the subject of intensive research in solid state chemistry and physics.[1—4] Being different from conventional materials in size of the constituent structural units, nanomaterials often possess certain properties that are significantly different from those of bulk materials and can be varied in a target fashion. This offers considerable prospects for practical applications including single-electron devices, molecular electronics, sensors, solar cells, solid-state cells, fuel cells, *etc.*

Among novel nanostructured materials, organo-inorganic hybrid materials seem to occupy a special position because in this case it is possible not only to use the advantages offered by nanomaterials themselves but also attain a synergistic effect of the properties of both components of the materials.[5] This concerns both structural materials[6] and materials possessing specific functional characteristics responsible for their use in various devices. As to organic materials, conjugated conducting polymers (CCP) have been the focus of researchers´ attention. The main reason is a unique combination of the physicochemical properties of this class of organic materials, which is a prerequisite for a variety of applications of CCP-based materials.

Design of electrode materials for lithium (lithium-ion) batteries is a field of increasing interest. It employs the intrinsic redox activity of CCP and the possibility to obtain various structures of hybrid nanocomposites, which can be divided into two main types. The first type is based on insertion of inorganic nanoparticles into a conducting polymer matrix.[7—9] A conventional procedure for fabrication of such nanocomposites involves chemical polymerization of a corresponding monomer on the surface of dispersed inorganic nanoparticles[7,8] or, *vice versa*, formation of an oxide gel in the presence of a dispersion of a preliminarily obtained conducting polymer.[9] In this type of nanocomposites, the CCP act as both the binder and the conducting matrix. The other type of nanocomposites is obtained by intercalating CCP into or by synthesizing them inside the interlayer space of inorganic nanoparticles; here we deal with the so-called guest—host compounds.[10—23] The main advantage of these types of hybrid nanocomposites is a stabilizing effect of CCP on the electrochemical operation of the electrodes made of transition-metal oxides, which can accumulate intercalated lithium without breakage of the framework.

The aim of this work was to study how methods of preparation of hybrid guest—host nanocomposites influence their structure, conductivity, electrochemical characteristics, electronic state, and redox activity taking polyaniline (**1**, a conducting conjugated polymer) as an example. Interest in polyaniline, as the organic component of this class of hybrid nanocomposites, is due to the fact that (i) nanomaterials based on this compound have the best functional characteristics[5] and (ii) it can be obtained in various forms, which allows fundamental aspects of different methods of preparation of nanocomposites to be investigated.

Experimental

Hybrid guest—host nanocomposites based on polyaniline were prepared following the known procedures.[19—23]

A Carlo Erba facility was used for C,H,N-analysis. The content of transition metals in nanocomposites was determined spectrophotometrically and the content of sulfur was determined by alloying with sodium. The content of polymers in nanocomposites was determined by dissolving the inorganic component in 2% aqueous NaOH. IR spectra of samples (KBr pellets) were recorded on a Bruker IFS 48 spectrometer. The structures of samples were studied by X-ray powder diffraction (DRON 3M) using filtered Cu-Kα-radiation. ESR spectra were recorded on a

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Varian E-9 spectrometer using isomorphically substituted Mn^{2+} ions in the crystal lattice of MgO as a reference in determining the *g*-factor and linewidth. The specific conductivity of nanocomposite pellets was measured by the four-probe technique with an accuracy of 10%. Ohmic contact with the conducting polymeric materials was achieved by electrochemically coating the probe tips with gold. When testing the operation of nanocomposites in model lithium batteries, chronopotentiometric measurements were carried out in a two-electrode cell assembled in a dry box in Ar atmosphere, in the galvanostatic mode at potentials ranging from 4.3 to 2.0 V *vs*. Li/Li^+. A mixture containing the material under study, acetylene black, and poly(tetrafluoroethylene) taken in a 80 : 15 : 5% (w/w) ratio was pressed on a stainless steel grid, dried *in vacuo* at 100 °C, and then used as a cathode in combination with a lithium anode. A 1 *M* $LiClO_4$ solution in an ethylene carbonate—diethyl carbonate (50 : 50% (v/v)) mixture was used as electrolyte. The charge-discharge curves obtained were used for the determination of the specific capacity of the cathode material and for calculating the dependence of the incremental capacity on the potential.

Results and Discussion

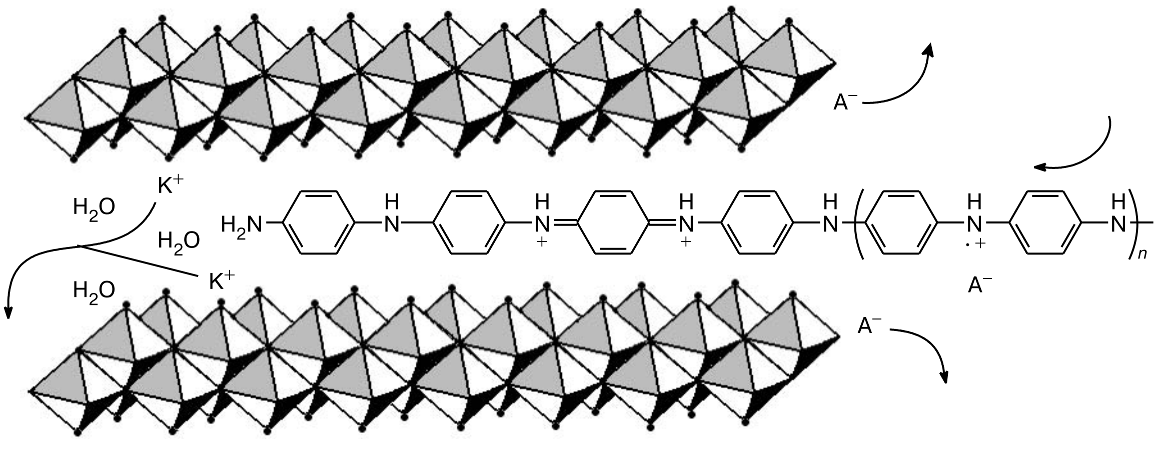
A conventional method of preparation of guest—host nanocomposites is intercalation polymerization *in situ* (method I).[24] It involves intercalation of corresponding monomers into an inorganic matrix where they undergo polymerization driven by either the oxidizing ability of the host (*e.g.*, vanadium oxide)[10—17] or an external oxidant (*e.g.*, molybdenum oxide).[25] An alternative method of preparation of guest—host nanocomposites is direct intercalation of CCP into the inorganic matrix (method II)[10,19,20—22] (Scheme 1).

It should be noted that intercalation of CCP occurs only if the inorganic host is in the form of nanoscale particles and the interlayer space of the host is expanded owing to the presence of hydrated cations. Therefore, nanocomposites are mainly prepared using aqueous metal oxide sols containing particles of size of the order of 10 nm.[10,19—23]

Intercalation polymerization of aniline, which is used for the preparation of guest—host nanocomposites by the method I, is oxidative in nature. The resulting CCP macromolecules bear a positive charge inside the host matrix, which represents a kind of dopant, which compensates the charge of polyaniline. Therefore, in this case the charge distribution over metal oxide nanoparticles, responsible for their stability in aqueous sol, is disturbed. This also holds for method II, *i.e.*, direct intercalation of polymer in the *p*-doped state. Visually, the formation of nanocomposites looks like gelation. When using method II, gelation begins virtually immediately after mixing of the aqueous metal oxide sol and the CCP solution.[22] Most probably, the process is driven by the replacement of cations located in the interlayer space of the oxide by the positively charged polymer chain.[20—22] In the case of method I, gelation is preceded by a notable induction period. When aniline is introduced into aqueous metal oxide sol, the induction period is somewhat longer than when aniline salt (*i.e.*, charged (protonated) aniline) is introduced. The induction period is likely due to another mechanism of intercalation of the organic component. Probably, in the former case aniline inserts into the oxide either initially in the form of a neutral molecule (here, the intercalation is driven by, *e.g.*, the affinity of aniline to protons located in the interlayer space, by the van-der-Waals interaction between aniline and inorganic oxide, *etc.*[9,25]) or due to ion exchange after pre-protonation in aqueous metal oxide sol. In both cases, the formation of nanocomposite must probably be accompanied by an induction period, because in the former case the driving forces of intercalation are much weaker than ion exchange and in the latter case aqueous metal oxide sol is characterized by a weakly acid pH value, which retards the protonation of aniline prior to intercalation.

The formation of a guest—host structure is verified by an increase in the interlayer spacing of the inorganic matrix. Both methods of preparation of guest—host nano-

Scheme 1



composites lead to similar results. For instance, in the case of V_2O_5 the interlayer spacing increases from the value characteristic of xerogel (11.6 Å) to 14.0—14.4 Å, so that the height of the galleries (5.2—5.6 Å with allowance for replacement of polymer monolayer by water molecules of height 2.8 Å) corresponds to the conformation of polyaniline macromolecules in which most phenyl rings are located perpendicular to the host layers.[24] However, another types of arrangement of the polymer macromolecules are also possible, namely, (1) with the polyaniline phenyl ring plane parallel to the host layers (interlayer spacing is 4.2 Å [20]) and (2) with the polymer chain in a helical conformation (interlayer spacing is 6.8 Å [25,26]).

Based on values of the interlayer spacing in the metal oxide nanoparticles given above, one can draw an important conclusion about the structure of nanocomposites prepared by different methods. Indeed, even if we deal with a direct intercalation (method II) of polyaniline doped with the Keggin-type heteropolyacids[22] whose bulky anions have a size of the order of 1 nm, the interlayer spacing of the order of 0.5 nm implies no dopant insertion along with the polymer chains into the structure of the inorganic host. If nanocomposites are prepared by method II, the average CPP chain length much exceeds the size of inorganic nanoparticles.[19,20] Therefore, polymer chains can be present both inside the interlayer space of inorganic particles, thus forming a structurally uniform phase (X-ray diffraction patterns exhibit reflections corresponding to only one interlayer spacing value), and outside it. Taken altogether, these data allow the composition of nanocomposites based on polyaniline doped with camphorsulfonic acid (**2**) and vanadium or molybdenum oxides (based on elemental analysis data[19,20]) to be represented as follows:

$$(\mathbf{1}\cdot\mathbf{2}_{0.25})_{0.67}\mathrm{V_2O_5} = \mathbf{1}_{0.30}\cdot\mathrm{V_2O_5}/(\mathbf{1}\cdot\mathbf{2}_{0.45})_{0.37}, \qquad (1)$$

$$(\mathbf{1}\cdot\mathbf{2}_{0.124})_{1.06}\mathrm{MoO_3} = \mathbf{1}_{0.33}\cdot\mathrm{MoO_3}/(\mathbf{1}\cdot\mathbf{2}_{0.18})_{0.73}. \qquad (2)$$

The right sides of Eqns (1) and (2) show in explicit form that part of the polymer, which is located in the interlayer space of transition-metal oxides without dopant anions and the remaining part of the polymer, which is located outside the inorganic nanoparticles and is doped with corresponding dopant anions. It is important that the degree of doping of this part of the polymer in the V_2O_5-based nanocomposite is much higher than in the nanocomposite based on MoO_3. We believe this provides an explanation for both high absolute value of the conductivity of the V_2O_5-based nanocomposite (~10 S cm^{-1} [20]) and a much lower conductivity of the MoO_3-based nanocomposite ($6\cdot10^{-1}$ S cm^{-1}).[19]

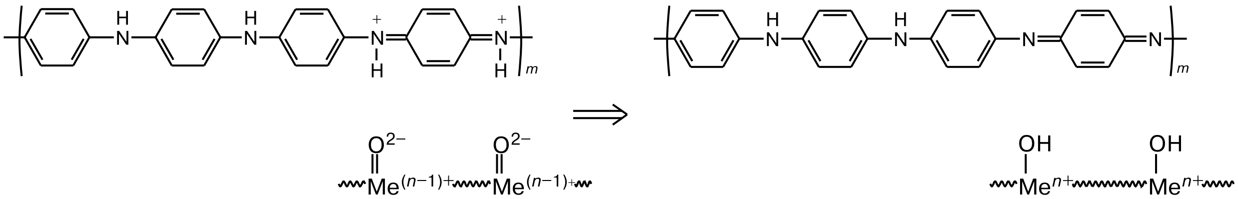
The doping degree of polyaniline inside the inorganic matrix affects the electrochemical activity of the nanocomposite when it is used as the active component of cathode in a lithium battery. If guest—host nanocomposites are prepared following method I, the polyaniline macromolecules are in the doped state and the negatively charged inorganic matrix acts as a dopant. This is confirmed by the ESR and IR spectroscopic data. The ESR spectra of nanocomposites exhibit only one intense singlet with the *g*-factor corresponding to paramagnetic ions V^{4+} or Mo^{5+}. These ions appear in the oxides in the sol formation step. In the case of vanadium oxide the content of ions increases after intercalation polymerization, namely, if the ESR spectrum of xerogel exhibits eight lines due to hyperfine coupling between the unpaired electron and ^{51}V nuclei ($I = 7/2$) of isolated V^{4+} ions, the ESR spectrum of nanocomposite exhibits an intense singlet with $g = 1.97$, which can be due to an increase in the content of V^{4+} ions above the 16% level.[27,28] The absence of the signal of delocalized organic radical cations of doped polyaniline in the ESR spectrum of nanocomposite is likely due to fast antiferromagnetic exchange of their spins with the spins of localized paramagnetic centers of the inorganic matrix.[29] The IR spectra of nanocomposites prepared by method I exhibit a band near 1140 cm^{-1} [20,24,25] characteristic of the conducting (doped) state of polyaniline.[30]

In the guest—host nanocomposites prepared by method II, polyaniline is likely located in the interlayer space in the form of emeraldine base, *i.e.*, in the dedoped state. Indeed, the IR spectra of nanocomposites[19—20] exhibit a considerable contribution of the band near 1160 cm^{-1} characteristic of this state of the polymer.[30] Besides, attempts at detecting the signal of reduced Mo^{5+} ions in the ESR spectra of a MoO_3-based nanocomposite failed[19] and only traces of the hyperfine structure due to the V^{4+} ions were detected[20] for the nanocomposites based on V_2O_5. Taken altogether, these data suggest that intercalation causes a transition of polyaniline from the doped state (emeraldine salt) to the dedoped state (emeraldine base), as shown in Scheme 2. Probably, this is due to the specific nature of polyaniline, which differs this compound from other CCP, namely, the equilibrium between the conducting (doped) and insulating (dedoped) states of polyaniline is acid-base in nature.[31,32]

From the standpoint of achievement of optimum functional characteristics for this type of hybrid nanocomposites (see below) it is important to establish the possibility of influencing the state of this acid-base equilibrium. Taking vanadium oxide as an example, it was shown[21,23] that this can be done if the interlayer space simultaneously contains polyaniline macromolecules and an ion-conducting polymer poly(ethylene oxide) (**3**),[21] which can interact with cations, or a redox active polymer poly(2,5-dimercaptothiophene),[23] which has a high proton affinity in the reduction and can form a concertedly operating couple with polyaniline.[33]

It should be noted that nanocomposites, in which the organic component consists of two polymers of different

Scheme 2



nature, obey regularities identical to those described above for the nanocomposites containing polyaniline only. For instance, from the data of elemental analysis for the ternary nanocomposites $\mathbf{1}_{0.29}\cdot\mathbf{3}_{0.86}\cdot V_2O_5$, (**1**+**3**)—$V_2O_5$, and $(\mathbf{1}\cdot\mathbf{2}_{0.12})_{0.62}\cdot\mathbf{3}_{0.85}\cdot V_2O_5$, (**1**•**2**+**3**)—$V_2O_5$ prepared by methods I and II, respectively,[20] it follows that at virtually identical content of poly(ethylene oxide) the second nanocomposite contains a much larger amount of polyaniline than the first one. This can be explained by the fact that a fraction of polyaniline macromolecules is not intercalated into the interlayer space of V_2O_5 and a part of the polymer remains outside the oxide particles, thus forming a corresponding supramolecular structure (see above). In the formation of ternary nanocomposites only a small fraction of the macromolecules of polymer **3** goes out from V_2O_5 (and is then removed during purification of the material) and polyaniline undergoes an insertion into the interlayer space mainly in addition to compound **3**. Besides, the content of **1** in the nanocomposite (**1**•**2**+**3**)—V_2O_5 and in its analog **1**•**2**—V_2O_5 also differs insignificantly;[21] *i.e.*, the presence of poly(ethylene oxide) inside V_2O_5 presents no obstacles to the intercalation of charged polyaniline macromolecules into vanadium oxide. This is consistent with the assumption that direct intercalation of *p*-doped polymer into the layered oxide is driven by replacement of cations (in the case of V_2O_5, these are protons) located inside the inorganic nanoparticles by the positively charged polymer chains.[20,24] At the same time the content of polyaniline in the nanocomposite (**1**+**3**)—V_2O_5 is somewhat lower than in its analog, **1**—V_2O_5; this implies a limiting effect of intercalated poly(ethylene oxide) if the nanocomposite was obtained using method I.

The main field of application of the hybrid guest—host nanocomposites under consideration can be lithium batteries. Consider the capacity characteristics of the nanocomposites taking V_2O_5-based materials as examples. The results obtained in this work show that the nanocomposites prepared by method I have much better characteristics (150—200 mA h g^{-1}) compared to the nanocomposites prepared by method II (20 mA h g^{-1}).

We believe there is a number of reasons that can be responsible for this ratio of the characteristics of the materials under consideration. First of all, mention may be made of the fact that the guest—host nanocomposites prepared by method II contain a considerable proportion of polyaniline macromolecules in the dedoped state, especially that part of the polymer component which is inside the interlayer space of the host and that emeraldine base is not electrochemically active in aprotic electrolytes.[34,35] Therefore, the intercalated polyaniline macromolecules can serve only as a "pillaring agent" for inorganic matrix layers, making almost no contribution to the specific charge capacity of the material. A part of polyaniline located outside the inorganic matrix also has a low specific capacity (because of partial dedoping (Eq. (1)) and a low, compared to V_2O_5, specific capacity of even fully doped polyaniline), which leads to apparent decrease in the specific characteristics of the bulk material. It should be mentioned that the nanocomposites obtained by method II contain a large amount of polyaniline solvent used in the course of synthesis, which can also deactivate the surface of electrodes.[36]

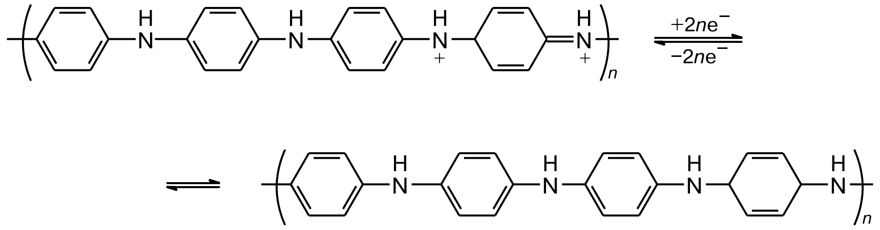
In contrast to this, in the nanocomposites prepared by method I polyaniline is located only inside the interlayer space[9,25,26] in the doped state, so the discharge of this type of nanocomposites is described as follows

$$[\mathbf{1}^+]_x\cdot V_2O_5{}^{x-} + (x+y)Li^+ + (x+y)e^- \xrightarrow{i} Li^+{}_{x+y}\cdot[\mathbf{1}]_x\cdot V_2O_5{}^{(x+y)-}. \quad (3)$$

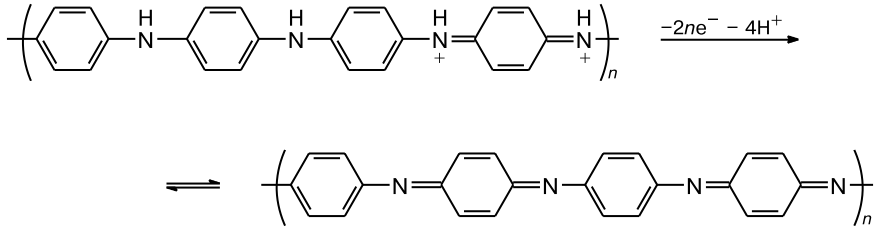
i. Reduction.

Therefore, the polymer can contribute to the specific charge capacity of the material.

It should be emphasized that high initial specific capacity of V_2O_5 xerogel rapidly decreases on cycling (Fig. 1). Cycling stability of the specific capacity of an electro-active material is one of the most important characteristics of electrodes made of it.[36] In this respect, the nanocomposite **1**—V_2O_5 exhibits much better characteristics compared to individual V_2O_5 xerogel.[37] This is likely due to the effect of strengthening of the layered structure of vanadium oxide because of pillaring of the host layers by guest macromolecules and to a reduction of the undesired effects[38] as a result of replacement of hydrated protons by positively charged polyaniline chains. It is essential that the redox transitions occurring in polyaniline in the course of charge-discharge cycling in accordance with Eqn. (3) not be associated with the loss of protons (Eq. (4)), *i.e.*, polyaniline must not be oxidized to the



(4)



(5)

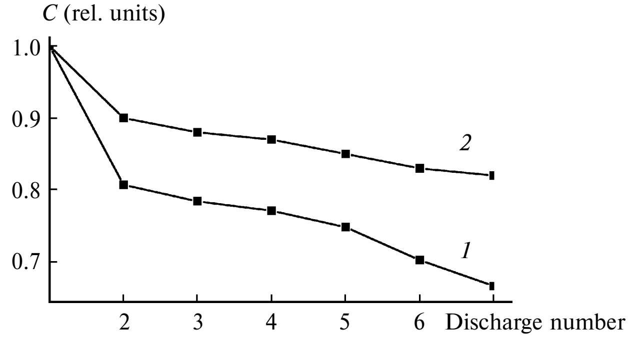


Fig. 1. Specific capacity *C* (relative to the capacity for the first discharge) of V_2O_5 xerogel (*1*) and **1**—V_2O_5 nanocomposite (*2*) plotted *vs.* discharge number.

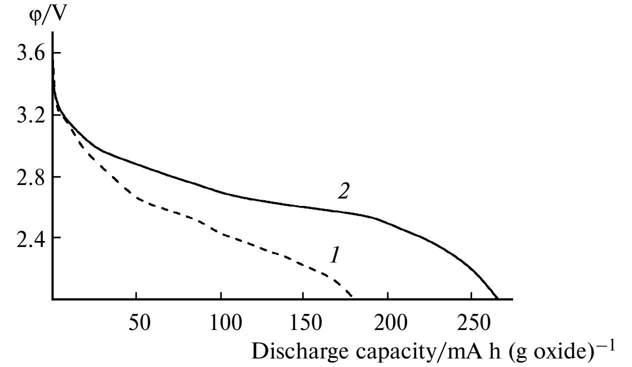


Fig. 2. Discharge curves of nanocomposites: **1**—V_2O_5 (*1*) and (**1**+**3**)—V_2O_5 (*2*); φ is the potential *vs.* Li/Li^+.

nigraniline or even pernigraniline state (Eq. (5) in the charge step).

Cycling stability on charge-discharge of the hybrid nanocomposite cathodes can be significantly improved if the interlayer space of the guest—host nanocomposites based on V_2O_5 simultaneously contains polyaniline and macromolecules of ion-conducting polymer poly(ethylene oxide)[21] or redox active polymer poly(2,5-dimarcaptothiophene) (**4**).[23] Indeed, even with non-optimized composition, nanocomposite (**1**+**3**)—V_2O_5 possesses a charge capacity of 150 mA h g^{-1} after five charge-discharge cycles. This is nearly 1.2 times higher than the charge capacity of analogous nanocomposite **1**—V_2O_5 and about 1.5 times higher than that of the initial xerogel V_2O_5.[21] besides, the charge capacity of nanocomposite (**4**+**1**)—V_2O_5 (~175 mA h g^{-1} at a current density of 15 mA g^{-1}) remains virtually unchanged after twenty charge-discharge cycles.[23] It should also be noted that discharge of ternary nanocomposites occurs at high potentials (Fig. 2), *i.e.*, this type of nanocomposites provides with a higher specific energy stored in the electrode made of this material.

Thus, based on layered transition-metal oxides and polyaniline, one can obtain hybrid guest—host nanocomposites with different structures. When using method I, the polymer macromolecules are located only inside the interlayer space of the host, whereas in the case of method II the polymer chains are both inside and outside the inorganic matrix. In both cases, the materials have a uniform layered structure, as shown by X-ray diffraction data.

Structural differences are responsible for different physicochemical characteristics of nanocomposites. Method II allows preparation of hybrid materials with high conductivity. They can find applications in electrocatalysis[22] and, probably, in metal protection from corrosion.[39] Prospects for application in lithium batteries are still questionable, although is it known that hybrid nanocomposites, in which nanoparticles of different transition-metal oxides are incorporated into CCP matrices, can have stable and higher capacity characteristics.[7,8]

The conductivities of the guest—host nanocomposites obtained by method I are lower than those of materials prepared using method II but much higher than those of individual transition-metal oxides. Taken altogether with the electrochemical activity of both inorganic host and organic guest, this predetermines prospects for the use of such hybrids as active components of electrode materials for lithium batteries. The key advantage of the nanocomposites described above is an enhanced cycling stability compared to individual oxides. At the same time mention may be made that at present experimental investigations in this field do not move beyond the use of conventional methods of fabrication of electrode materials.[10—21,23] Therefore, we believe that the electrochemical characteristics of the materials under study are probably far from the maximum achievable values. Morphology control provides a way for further improvement of nanostructured materials.[40] Some examples of this approach to fabrication of inorganic electrode materials are available.[41,42] Application of this strategy to hybrid nanocomposites seems to be appropriate for further improvement of their functional characteristics.

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