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Properties and Application of Nanoporous Silica Filled with Polyaniline and Iodine

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Properties of substances in a nanometric scale and combined in complex hyierarchical structures differ drastically and have become of great interest during the last decade. The most promising hyierarchical materials were obtained on the basis of MCM-41 matrix, and class of MCM41 filled with organic substances is one of them. Therefore the molecular-lattice nanoporous regular structure based on silica matrix MCM-41 fulfilled with polyaniline (PAN) and its iodine dopant was synthesised within this work, and its electrical properties were investigated for the first time to our knowledge. The hybrid structure was obtained with use of encapsulation method and radical oxidation polymerization "in-situ" technique. The impedance characteristics of as obtained porous silica matrix MCM-41 intercalated with PAN and iodine doped PAN were investigated. The effect of photoinduced negative capacity was observed for nanohybrid MCM-41<PAN>. Iodine doping of guest component results in the appearance of colossal magneto- and photo-resistive effects. The character of changes in frequency dispersion of impedance, loss tangent and permittivity with lighting and in magnetic field was determined. The thermostimulated depolarization data demonstrate the differences in impurity spectra caused by different guest content in MCM-41 matrix. Parameters, at which synthesized nanohybrids are interesting as materials for quantum accumulators of electric energy and capacitive sensing heads for magnetic carrier, were determined.

Keywords: Nanoporous matrix MCM-41, Host-guest structures, Polyaniline, Impedance spectroscopy, Dielectric permittivity, Loss tangent, Thermostimulated depolarization.

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1. INTRODUCTION

There is a rapid progress in investigation of nanohybrids prepared by method of encapsulation of guest components into molecular-lattice matrixes in a scientific world. Properties and structure of a substance in guest positions of nanoporous matrixes and out of them differ drastically. The stage of ordering of porous matrix, the occupancy degree, the particle-particle and particle-pore wall interaction play an important role for changes in material properties. The properties of nanocomposites change as well.

The features of ferroelectrics, ferromagnetics, superconductors and superionics [1-4] in nanoporous matrices have been investigated pretty well. At the same time, the scrupulous attention is payed to hosts of organic nature, especially to dye Rhodamine 6G. Such an attention is explained by the fact that biocompatible and nontoxic mesoporous silica particles with encapsulated organic dye are of great interest for fluorescent biomarkers development and for multi-functional systems of targeted drug delivery. Above listed nanohybrids are promising materials for application in systems of radiation and laser generation based on colloid photon crystals made of these nanohybrids. It was shown that the mesoporous SiO_2 matrixes with dye are photostable and their light is one order brighter than of polymer matrixes intercalated with semiconductor quantum dots relative to initial dye.

Although the heterostructured nanocomposite formation has attracted a great interest near the decade already as a method for obtaining the structures with wide variety of novel properties, goals reached in application of such structures have not been completed yet. These are just the first steps and basic experience.

Obviously, for further development of complex investigation of such nanohybrids, targeted on widening of their applications, in particular quantum accumulators, the collected knowledge must be enriched with determined parameters of polarization processes and current flow mechanism caused by current carriers and displacement current. Unfortunately, there is still a lack of knowledge in the field. The polyaniline and its dopants application as a guest component provokes a great interest as well, because of its unique physical-chemical properties, sometimes even paradoxical one. Such properties are expected to make a great advance in nanoengineering. Therefore, the goal of the present work is to fulfil some part of a gap in the field.

2. EXPERIMENTAL

The molecular-lattice nanoporous regular structure based on SiO_2 – MCM-41 (Sigma Aldrich) – was used in the experiments as a subhost matrix. It possesses a hexagonal cell structure with a wall thickness of 0.6-0.8 nm and calibrated pore size, which could be modified controllably in the 3-10 nm range. The data of electron microscopy show the pore diameter of ~ 37 Å and canal specific surface is 984 m^2/g. The pore walls of MCM-41 are amorphous but are of long range order in large scale.

Polyaniline (PAN) and its iodine dopant were chosen as guest components. The hybrid structure was

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obtained with use of encapsulation method and radical oxidation polymerization "in-situ" technique.

Impedance measurements were executed in $10^{-3} \div 10^{6}$ Hz frequency range at $-30 \div 60$ °C temperature with and without lighting and application of magnetic field strength of 2.75 kOe using the spectrometer "AUTOLAB" (ECO CHEMIE company, the Netherlands), equipped with FRA-2, and GPES software. The questionable points were processed with Dirichlet filter technique [5, 6]. The frequency dependence of complex impedance Z was analyzed by graph-analytic method in the environment of software package ZView 2.3 (Scribner Associates). An approximation inaccuracy did not exceed 4 %. Impedance models adequacy to experimental data was confirmed by completely random nature of frequency dependencies for the 1st order residual differences [5, 6].

Spectra of thermostimulated depolarization were recorded using short-circuit mode of contacts at linear heating 5 °C/min.

3. RESULTS AND DISCUSSION

Fig. 1 shows the frequency dependence of the real component of the complex impedance ReZ for MCM-41 with inserted PAN measured without lighting (curve 1), under lighting (curve 3) and in magnetic field of 2.75 kOe (curve 2) strength.

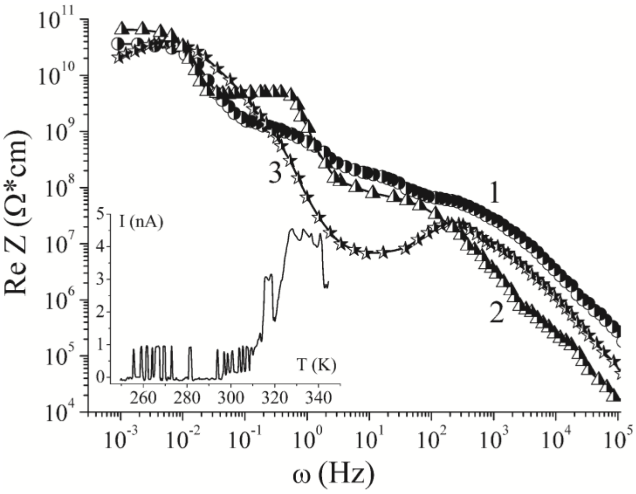

Fig. 1 – Frequency dependence of the real component of the complex impedance ReZ for MCM-41<PAN> measured without lighting (1), in magnetic field (2) and with lighting (3). Insert: spectrum of thermostimulated depolarisation current

As seen from Fig. 1, the giant magneto- and photoresistive effects for nanohybrid MCM-41<PAN> in the frequency range were not observed in contrast to cavitate β-cyclodextrin <$FeSO_4$> [7].

The Nyquist diagram for nanohybrid MCM-41<PAN> measured without lighting demonstrates two-arc behavior (Fig. 2-4). Each arc cannot be presented as a superposition of few semicircles with centres located below the real axis of the complex impedance. In the last case, as for the regular heterophase structure with limited conductivity of each phase with its own time constants, it is possible to determine the exact relaxation time. But, in the case of nanohybrid MCM-41<PAN>, an interesting configuration is realized. The matrix nanolayers with conductivity characterized by time constant and guest component with complex conductivity characterized by phase constant are alternating. Therefore, the impedance model structure should consist of alternating serial and parallel units, in other words, should be presented by a ladder structure modified with units, which reflect necessary distribution of structure elements.

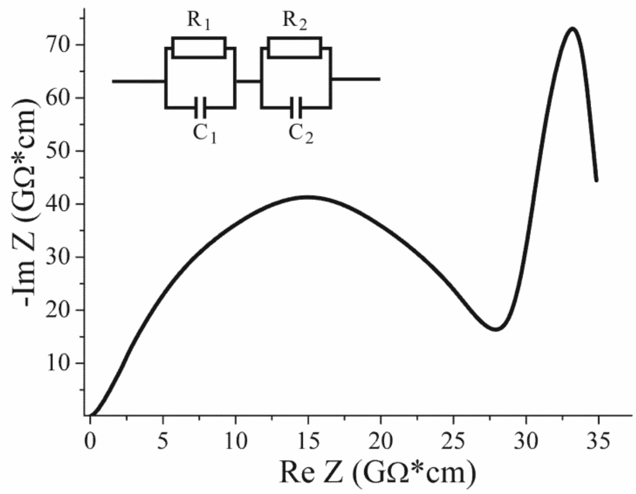

Fig. 2 – The Nyquist diagram for nanohybrid MCM-41<PAN> measured without lighting and magnetic field

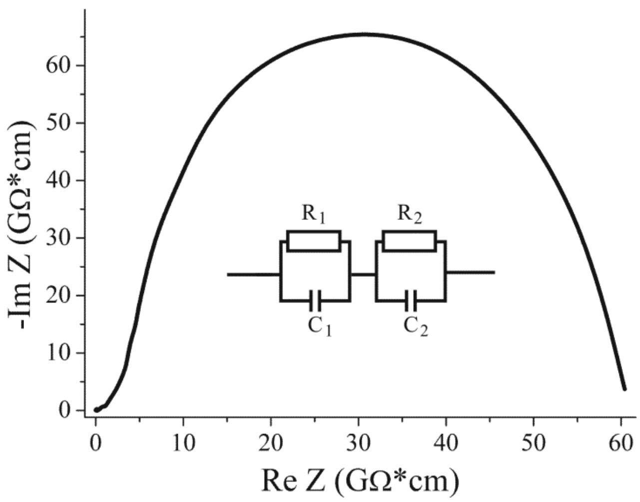

Fig. 3 – The Nyquist diagram for nanohybrid MCM-41<PAN> measured in magnetic field

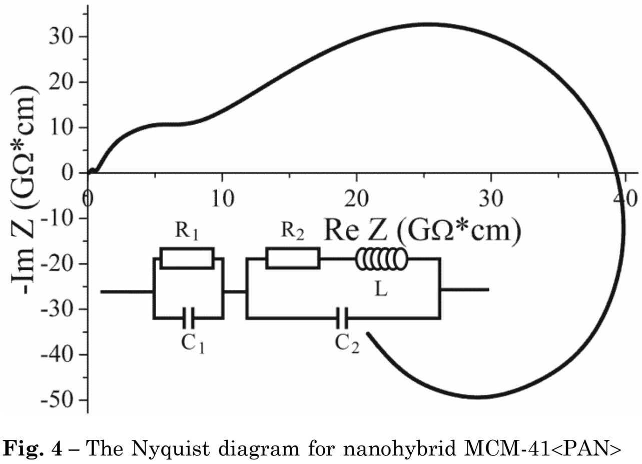

Fig. 4 – The Nyquist diagram for nanohybrid MCM-41<PAN> measured with lighting

On this basis and considering the fact that the investigated nonhomogeneous nanohybrid demonstrates the finite resistance at $\omega \to 0$, the model scheme has the structure presented in the insert in Fig. 2. In this scheme, capacitor C_1 reflects the distribution of resistive element R_1 due to the capacity of delocalized states in matrix layers. The unit $C_2||R_2$-L represents the current flow limited by the guest component, which initiates the induction in synthesized nanohybrid caused by trapping and confinement of injected carriers during some time on the attachment centres and forms a phase angle. As it was confirmed by computer parametric identification, the ratio of noninductive relaxation times is a condition for two-arc visualization and is provided by capacity-capacity relation:

$$R_1C_1 < R_2C_2.$$

It is proved well by the character of the frequency dependence of the complex resistance (Fig. 3) where two arcs flow into one at magnetic field with no noticeable magnetoresistive effect. It is supposed that Zeeman splitting modifies energetic topology of impurity levels and reduces the density of states in a short interval just under the Fermi level. Peculiar character of the frequency dependence of the impedance at lighting (Fig. 4) appears in the formation of low frequency arc in IV-th inductive quadrant of a complex plane as a “negative capacity”. This phenomenon is known in literature [8-10], but the difference is in its appearance at lighting. In the last case, the condition for visualizing the “negative capacity” effect is a combination of:

$$L/R_2^2 > C_2,$$
$$R_1C_1 < R_2C_2,$$

where the second inequality is defined by R_1. Indeed, R_1 decreases at lighting in the low frequency region of inductive quarter, what serves as a reason to assume that the first inequality is caused by the photoinductive formation of trapping centres with relaxation time larger than half period of measured sinusoidal signal for injected electrons.

It is well known that PAN could be successfully activated by iodine doping [11]. Modified by this method PAN became a good conductor because of increase in free charge carriers. Therefore, the nanohybrid MCM-41<PAN + I_2> with intercalated guest component was synthesized. Its formation is accompanied by the spectral transformation for thermostimulated depolarization currents (see inserts in Fig 1 and Fig. 5) from intermittent to quasicontinuous what indicates the formation of quasicontinuous spectra for localized states near the Fermi level. As it is seen from Fig. 5, the conductivity of MCM-41<PAN + I_2> with no lighting is of 6 order higher than conductivity of MCM-41<PAN> what is an evidence of charge transfer from guest to host component. In this case, the centre of semicircle, which is a representation of delocalized carrier impact, should be shifted to high frequency (phonon) region. The character of the frequency dependence of impedance (Fig. 6) confirms the previously mentioned assumption.

It is worth to mention, the first fragment of semicircle (Fig. 6) visualizes as incomplete arc because it was not possible to measure impedance at frequencies out of the limits (higher than 10^6 Hz) for spectrometer used

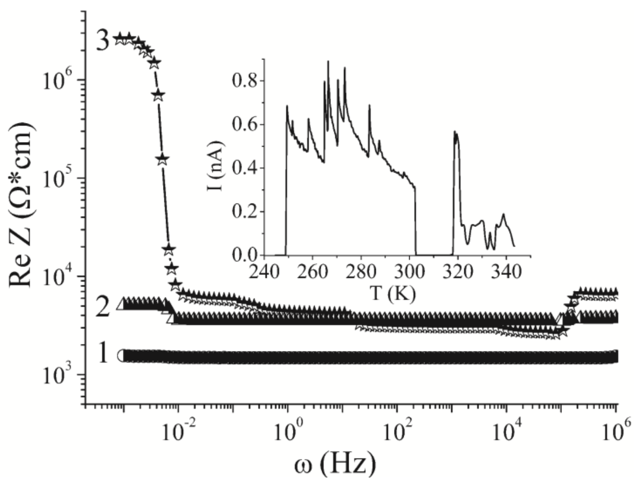

Fig. 5 – Insert: spectrum of thermostimulated depolarisation current

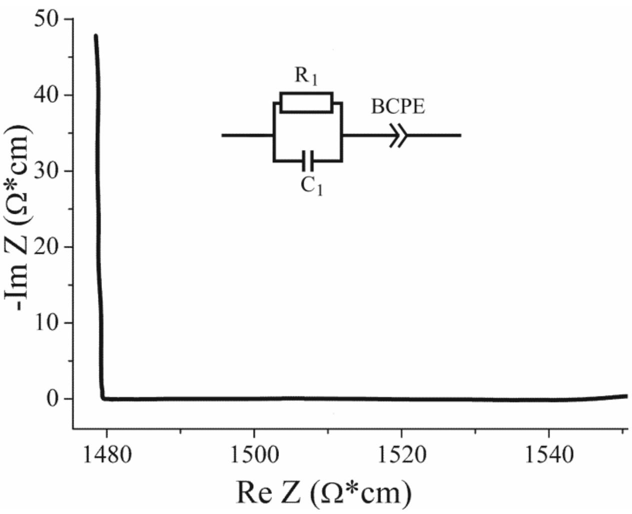

Fig. 6 – The Nyquist diagram for nanohybrid MCM-41 <PAN + I_2> measured without lighting and magnetic field

in experiments. At the same time, the second unit of the electric equivalent scheme for MCM-41<PAN + I_2> should be transformed into resistive element because of high conductivity of PAN doped with I_2. It is confirmed by the character of the Nyquist diagram (Fig. 6) with the boundary constant phase element (BCPE) for the corresponding part of the impedance at the fractional exponent $0 < n \leq 1$ [6], which characterizes a unit volume with complex conductivity.

The fractional exponent becomes negative $-1 \leq n < 0$ in the applied magnetic field demonstrating the “deformed” inductance in a nanolimited region (Fig. 7). The conjugation of “deformed” inductance appearance with noticeable positive magnetoresistive effect (Fig. 5) provides a reason to relate the nature of this inductance to Zeeman localization of injected charge carriers on trapping centres with life times higher than half-period of measured sinusoidal signal. At lighting with integral light, the giant photoresistive effect appears (Fig. 5) which is negative and is represented by an increase in the real component of the complex impedance at lighting by three orders of magnitude (Fig. 8). This phenomenon is supposedly provoked by the photoinducted formation of deep trapping centres [12] with

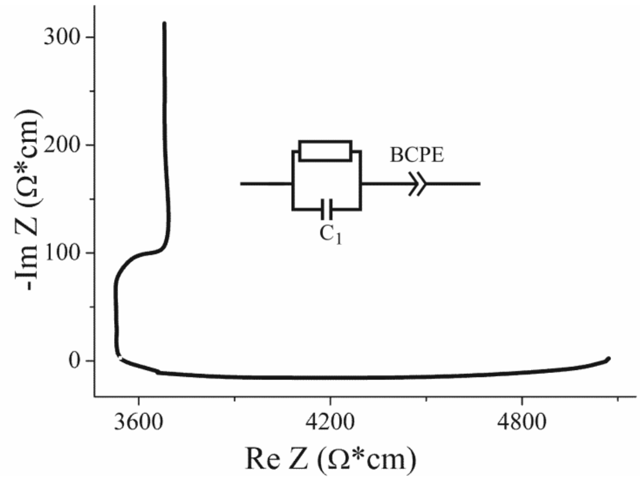

Fig. 7 – Nyquist diagram for nanohybrid MCM-41<PAN + I_2> measured in magnetic field

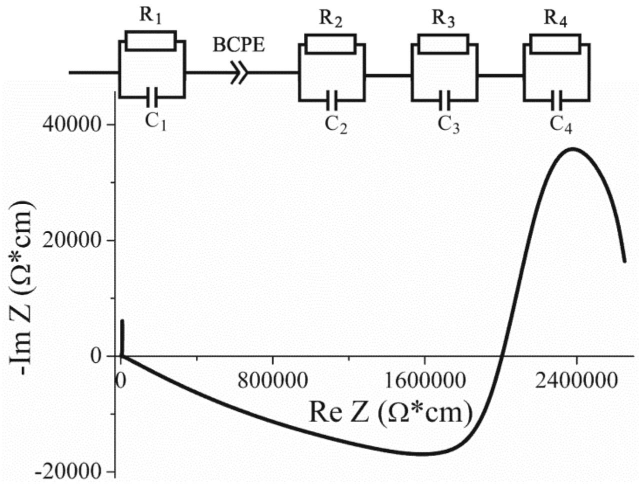

Fig. 8 – Nyquist diagram for nanohybrid MCM-41<PAN + I_2> measured with lighting

main charge carriers localized on them, what is the reason of the decrease in delocalized charge carrier number, in other words, the reason of observed negative photoconductance. If to explain the phenomena from the point of view of energy relief, than the negative photoconductance indicates the formation of additional barriers, with its own relaxation time for each barrier for current flow. The result of the additional barrier formation is clearly represented by low frequency arc in the I-st quadrant of the complex plane. This process is modelled well with three serial $R||C$ units (insert in Fig. 8). At the same time, it is difficult to find a reasonable explanation of abrupt increase in the real component of the specific complex impedance at frequencies above 10^5 Hz.

It is supposed that the cointercalated nanohybrid MCM-41<PAN + I_2> demonstrates a relatively high value of conductivity and loss tangent above 1 because of low ohm resistance. The interval with loss tangent less than unit in the frequency region $10^{-3} \div 10^6$Hz is not observed as opposed to MCM-41<PAN> where tgδ is a decreasing function of frequency. But the fact that the loss tangent of MCM-41<PAN> is less than unit even in an ultra-low frequency region, where the permittivity reaches high values (Fig. 9), is an important point for the development of quantum accumulators and high-power ultra-low frequency generators. The nanohybrid MCM-41<PAN + I_2> is also an interesting material for the development of electric energy nanogenerators and not with capacitive but faradaic current forming mechanism. It is confirmed by hysteresis character of the current-voltage plot for nanohybrid MCM-41<PAN + I_2> measured in magnetic field and with lighting (Fig. 10).

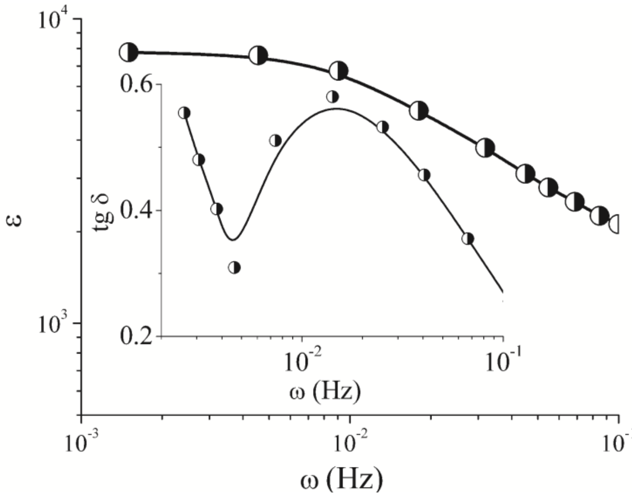

Fig. 9 – Ultra-low frequency dependence of permittivity for MCM-41<PAN> measured without lighting. Insert: loss tangent tgδ

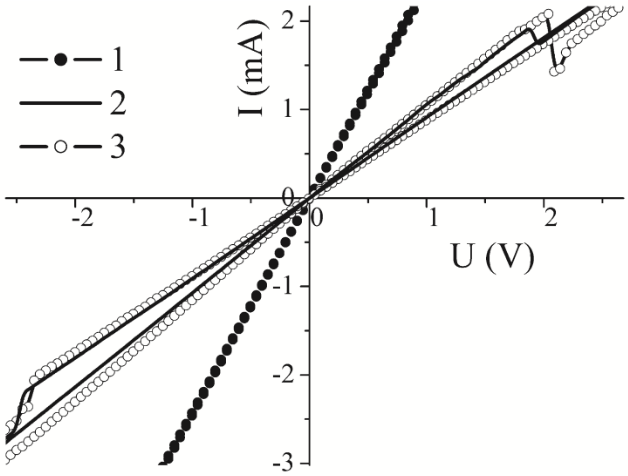

Fig. 10 – Current-voltage characteristics for nanohybrid MCM-41<PAN + I_2> measured without lighting (1), in magnetic field (2) and with lighting (3)

4. CONCLUSIONS

1. Nyquist diagrams for nanohybrid materials without lighting are two-arc in nature. Each arc cannot be represented by a superposition of semicircles with centres under the real axes of the complex impedance diagram and therefore cannot be related to exact relaxation times.

2. The effect of photoinduced negative capacity was observed for nanohybrid MCM-41<PAN>. It was determined that the effect is conjugated with anomalous

low frequency behavior of Re$Z(\omega)$ with lighting, which increases with frequency.

3. The MCM-41<PAN + I_2> formation is accompanied by spectral transformation for currents of thermostimulated depolarization from intermittent to quasicontinuous character. It gives the reason to consider the guest subsystem as an ensemble of quantum dots, the nature of which covers the coordination defects with structure other than structure of host matrix.

4. Iodine doping of the guest component results in the appearance of giant magneto- and photoresistive effects. The last effect is negative what exhibits the increase in the real component of the specific complex impedance with lighting more than by three orders of magnitude.

5. The loss tangent for MCM-41<PAN + I_2> is less than unit in ultra-low frequency region, where the permittivity reaches ~ 10^4. It makes the nanohybrid an attractive material for application in quantum accumulator and high-power generator of ultra-low frequency. In contrast to MCM-41<PAN>, the iodine doped nanohybrid is attractive for the development of nanogenerators of electric energy with faradaic, not capacitive, mechanism of current formation, because of the hysteresis character of current-voltage plot measured in magnetic field and with lighting.

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Властивості та застосування нанопористого оксиду кремнія, наповненого поліаніліном та йодом

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Властивості речовин в нанометровому масштабі та поєднаних в складні ієрархічні структури значно відрізняються між собою і завдяки цьому стали предметом зацікавленості науковців протягом останнього десятиліття. Найбільш перспективні матеріали було отримано на основі MCM-41 матриць, і клас MCM-41, виповнений органічними сполуками, є одним із таких. Тому в роботі було синтезовано молекулярно-граткову нанопористу регулярну структуру на основі силікатної матриці MCM-41, виповненої поліаніліном (PAN) та поліаніліном легованим йодом. Вперше було досліджено електричні властивості синтезованих сполук. Гібридну структуру одержано з використанням методу інкапсулювання та методики радикально-окислювальної "in-situ" полімеризації. Імпедансні характеристики одержаних пористих силікатних матриць виповнених PAN та PAN, легованим йодом, було досліджено в рамках цієї роботи. В результаті проведених досліджень було виявлено явище фотоіндукованої негативної ємності в наногібриді MCM-41<PAN>. Легування йодом гостьового компоненту призводить до появи гігантського магнето- та фоторезистивного ефектів. Характер змін частотної дисперсії імпедансу, тенгенса кута втрат та діелектричної проникливості за умов освітлення та в магнітному полі було встановлено. Дані дослідження термостимульованої деполяризації показують зміни в домішковому спектрі, спричинені різним вмістом гостьового компоненту в матриці MCM-41. Встановлено параметри, при яких синтезовані наногібриди стають перспективними для застосування в квантових акумуляторах електричної енергії та ємнісно чутливих головок для зчитування інофрмації з магнітних носіїв.

Ключові слова: Нанопориста матриця MCM-41, Структура гість-господар, Поліанілін, Імпедансна спектроскопія, Діелектрична проникливість, Тангенс кута втрат, Термостимульована деполяризація.