JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **12** No 3, 03032(5pp) (2020)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **12** № 3, 03032(5cc) (2020)

Electroconductive and Polarization Properties of Inorganic-organic MCM-41 <PTHQ> Encapsulant

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(Received 07 March 2020; revised manuscript received 15 June 2020; published online 25 June 2020)

The paper presents findings on the formation of inorganic-organic hybrid material MCM-41 <PTHQ>. The selection of a guest material proved to meet the condition of geometric complementarity of guest positions of a starting host matrix as to a guest cavitand component. The guest material appeared to be sensitive so that one could obtain the functional hybridity of the clathrate structure MCM-41<PTHQ>. The synthesis resulted in the formation of a structure with a large area of hetero-nano networks.

The research of permittivity was conducted through the method of impedance spectroscopy. An introduction of the guest component led to the splitting of the impurity energy spectrum followed by the occurrence of quantum wells. This, in turn, gave rise to oscillations that manifested in a middle-energy region of dependences ReZ(ω). The superimposition of a constant magnetic field significantly affects the behavior of ReZ(ω) in the middle-frequency region – the dependency mirroring takes place. This may suggest a certain shift in the energy spectrum in relation to the Fermi level by the constant magnetic field, as a result of which the sign of asymmetry of the density of states changes above and below the Fermi level. An assumption has been made that the asymmetry of the density of states occurs precisely due to the guest component as clearly demonstrated by thermally stimulated discharge spectra (a miniband character of a spectrum with deep quantum wells). The two-curve Nyquist diagram and given equivalent circuit with an inductive link visualize a barrier that is observed at the phase boundary. Such an increase coupled with a low value of tgδ makes it possible to accumulate electric charge under the action of a magnetic field at a quantum level. Also, the paper demonstrates conditions under which synthesized nanohybrids could be attractive when used as quantum storage batteries.

Keywords: SiO_2-MCM-41, PTHQ, Intercalation, Cavitand, Impedance spectroscopy, Quantum battery.

DOI: 10.21272/jnep.12(3).03032 PACS number: 81.05.Rm

1. INTRODUCTION

Advancement in stand-alone energy generation is increasingly associated with the creation of nanosystems that would not electrochemically convert and accumulate electrical energy. This refers to transition to a new quantum level of energy conversion, accumulation, and storage. One of the promising areas of research in this regard is the synthesis of heterostructured nanocomposite materials that would feature a large interfacial interface and ensure anisotropy of permittivity depending on the direction. Such structures were required to achieve high values of permittivity in combination with an electric loss tangent of less than 1, particularly for frequencies less than 10^{-2} Hz. In the above circumstances, it has been theoretically speculated [1, 2] that injected electrons can be accumulated at the nano-hetero-phase interfaces and the corresponding heterostructures can be represented as a quantum battery.

The development of ferroelectric nanostructures brought a fundamental question of size effects in ferroelectric polarization to the foreground [4] (existence of a critical size of ferroelectric domains, the Curie temperature change). The use of porous matrices, the typical size of pores of which is in the nanometer range, has proved to provide the best possible experimental evidence (see [5-8] and references therein). An advantage of such structures lies in the capability to control the size and relative position of embedded ferroelectric phases by using a varied geometry of a porous network. The research has shown that significant changes occur in parameters of phase transitions for nanostructured substances under conditions of nano-limited geometry. Additionally, quantities and nature of these changes depend on the type of porous matrix and guest component. Thus, a temperature shift of a ferroelectric phase transition to the low-temperature region is observed by 18 K for $NaNO_2$ nanoparticles, unlike the bulk material, and a sharp increase in the permittivity from 10^2 to 10^5 whereas the permittivity of nanocomposite SBA-15 <$NaNO_2$> with a pore size of 52 Å was equivalent to 10^3. The same is true for ammonium sulfate in pores of a molecular lattice matrix MCM-41 with a pore size of 40 Å. In this case, permittivity is considerably lower (for macrostructures, 235 versus 27). In a mixed ferroelectric guest material $NaNO_2 \oplus KNO_3$, however, pores of MCM-41 exhibit a shift in the temperature of the ferroelectric phase transition to a high-temperature region with the permittivity of MCM-41 <$NaNO_2$ KNO_3> nanocomposite, simultaneously increasing up to 10^4. Moreover, an order parameter $\eta(T)$ for $NaNO_2$ in porous glass with a diameter of pores of 3200 Å and 200 Å, respectively, almost coincides with the dependence of bulk material. For $NaNO_2$ in opal, this dependence largely differs

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from both the dependence observed in bulk material and that of $NaNO_2$ in porous glasses with diameters of 30 Å and 70 Å.

The purpose of this paper is to develop a theoretical basis for the formation of intercalated hetero-phase structures with various nano-limited geometry, composition, and level of hierarchical architecture to convert and accumulate electrical energy at the quantum level and maximize the capabilities of electromagnetic field sensors. Physical properties of the resulting nanohybrid and its behavior in a constant magnetic field will be also examined.

2. EXPERIMENTAL AND METHODS

SiO_2 – MCM-41 [9] of Sigma Aldrich trademark was selected as a host matrix to construct an inorganic-organic hybrid material. This silica matrix has a hexagonal structure likened to a honeycomb with a wall thickness of 0.6-0.8 nm and a calibrated pore size that can be altered within the 3-10 nm range. As shown by electron microscopy data, pores are ~ 37 Å in diameter. Accordingly, the specific surface of channels is 984^2/g. Pore walls of MCM-41 are amorphous but, on a large scale, molecular lattices exhibit a long-range order.

The selection of the guest material was done on the basis of the geometric complementarity of guest positions of the starting host matrix in the guest cavitand content and the ability of formation of hetero-nano boundaries of high area. Moreover, the guest material is required to be sensitive to external physical fields. Polythiocyanatohydroquinone (PTHQ) fully fits these requirements [10]. This organic compound is a polymer that can be represented in the form of an amorphous mixture of linear polymer chains of various lengths. The real structure can be interpreted as a dendrimer-like branched composite. The experimental absorption spectrum consists of a single absorption band with a maximum at 315 nm and a wide structureless absorption band in the right-side region.

A guest component was formed through encapsulation as reported in [11] and in situ radical oxidation polymerization. As a result, a powdery material was obtained and pressed into a tablet, and then contacts were applied. Hence, a tablet-shaped encapsulant with a diameter of 5 mm, thickness of 0.85 mm, and applied contacts was obtained.

Impedance measurements were made using AUTOLAB measuring system (ECO CHEMIE, Netherlands) equipped with FRA-2 and GPES software in the frequency range of 10^{-3}-10^{6} Hz under normal conditions and constant magnetic field intensity of 2.75 kOe. Uncertain points were filtered out with the Dirichlet-enhanced filter [12, 13]. Frequency dependences of complex-valued impedance Z were analyzed through the graph-analytical method using ZView 2.3 software (Scribner Associates). The approximation errors did not exceed 4 %. The adequacy of constructed impedance models of an experimental data set was confirmed by the completely random nature of frequency dependences of first-order residual differences [12, 13]. The thermally stimulated discharge spectra were recorded in the mode of short-circuited contacts when linearly heated at a rate of 5 °C/min.

3. RESULTS AND DISCUSSION

A nanostructured hybrid structure MCM-41 <PTHQ> is obtained as a result of accomplished operations. The next step presupposed examination of electrical conductivity through impedance spectroscopy. Fig. 1 shows the frequency dependences of the real component of the specific impedance of ceramic samples from the desorbed matrix MCM-41 under investigation intercalated with PTHQ polymer. The studied starting matrix appears to be a good dielectric (Fig. 1, curve 1). In the frequency range of 10^{-4}-0.3 Hz, mostly free intrinsic or injected carriers contribute to conductivity. The superimposition of a constant magnetic field during measurements did not lead to changes in Re$Z(\omega)$ of the starting molecular lattice structure MCM-41.

The introduction of PTHQ leads to a minor change in terms of magnitude, but important from the perspective of behavior of Re$Z(\omega)$, which is manifested as the deformation of the low-frequency spectrum (10^{-3}-1 Hz), exhibiting a non-monotonic character (Fig. 1, curve 2). A middle-frequency region that becomes oscillatory in nature undergoes significant changes. The main cause for such an effect is the splitting of an energy spectrum and occurrence of quantum wells that are formed upon the introduction of an organic polymer; and able to capture and hold current carriers over the time associated with the half-period of a sinusoidal signal when measuring the frequency spectra [14-16]. One can see that superimposing a constant magnetic field when making measurements does not alter the magnitude and behavior of Re$Z(\omega)$ in the low-frequency region, however, affects to a great extent the behavior in the middle-frequency range. If under normal conditions a maximum of MCM-41 <PTHQ> is observed at a frequency of 12 Hz and a minimum – at 60 Hz, then both minimum and maximum appear when measurements are made at a constant magnetic field. This could be indicative of a certain shift in the energy spectrum as to the Fermi level caused by a constant magnetic field that resulted in doing the change sign of asymmetry of the density of states above and below the Fermi level. If the starting matrix is insensitive to the magnetic field, then it can be assumed that the asymmetry of the density of states occurs precisely due to the guest component.

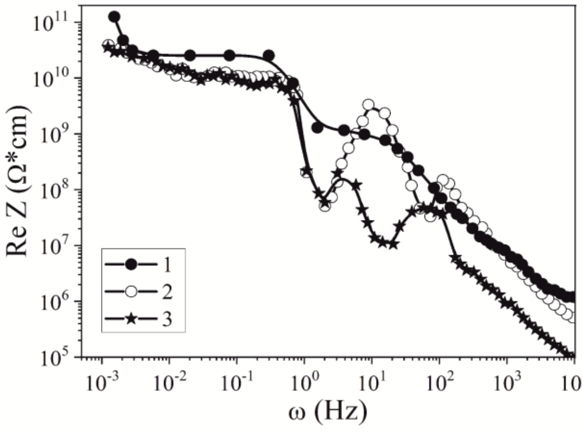

Fig. 1 – Frequency dependences of the real component of specific impedance of MCM-41 (1) and MCM-41 <PTHQ> as measured in the dark (2) and at the action of a magnetic field (3)

This statement is explicitly confirmed by thermally stimulated discharge spectra shown in Fig. 2. Thermally stimulated discharge currents were not found for the starting molecular lattice structure MCM-41. Instead, with the introduction of PTHQ, a miniband character becomes typical of the spectrum with deep quantum wells.

In addition, this is confirmed by displaying Nyquist diagrams (Fig. 3) whose branches enter the fourth inductive quadrant of the plane of complex-valued impedance. This indicates the phenomenon of 'negative capacitance' [17, 18], the mechanism of which has been described above.

For a silica matrix, there is the situation: Nyquist diagrams are expected to be of two-arc form on the basis of the texture of a ceramic sample and can be represented in practice by an equivalent electric circuit (insert 1, Fig. 3) containing two links $R \,||\, C$ connected in series. In case of PTHQ intercalation, this circuit is supplemented by a third inductive link (insert 2, Fig. 3), visualizing a barrier that occurs at the phase boundary.

The above-mentioned features of mechanisms of current passage in external physical fields might emerge in a certain way in polarization properties at least due to the Maxwell-Wagner and additional polarization. The latter occurs when charge carriers jump over localized states near the Fermi level. To substantiate this, an analysis of polarization characteristics was carried out, considering the values of electric loss tangent (tgδ) since from a practical point of view, it is necessary for the tangent to be less than 1. Fig. 4 shows the values of electric loss tangent versus frequency.

One can see that the introduction of PTHQ leads to a rapid increase in tgδ in the low- and middle-frequency regions of the spectrum represented by two peaks. In the low-frequency region, the values of tgδ for MSM-41 <PTHQ> are less than 1 in a narrow neighborhood of 10^{-3} and 10^{-2} Hz. The action of the magnetic field is observed in the low-, middle-, and high-frequency regions. At low frequency values, the magnetic field reduces the value of tgδ, combining the said points into a continuous interval where tg$\delta < 1$. In the high-frequency region, the value of tgδ decreases significantly under the magnetic field action.

For practical application, it is required that the values of permittivity be as high as possible in the specified intervals. For this reason, Fig. 5 shows that low/middle-frequency spectra will be of particular interest where the permittivity has high values.

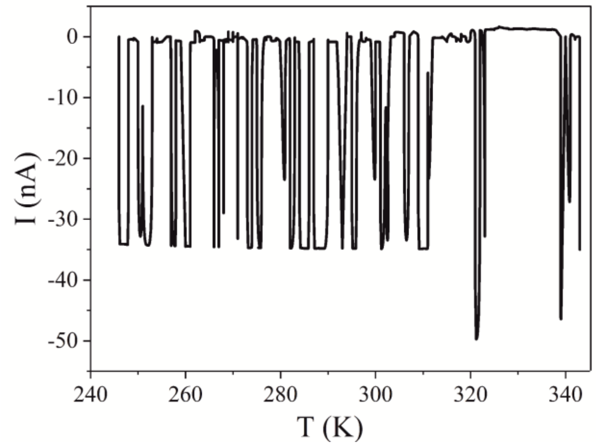

Fig. 2 – Thermally stimulated discharge currents of MCM-41 <PTHQ>

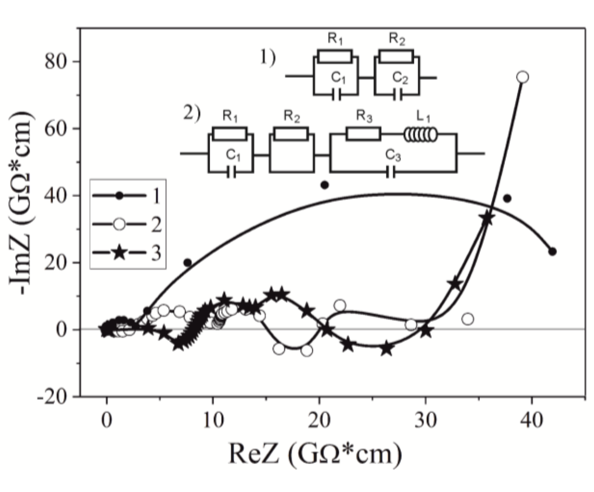

Fig. 3 – Nyquist diagrams of MCM-41 (1) and MCM-41 <PTHQ> as measured in the dark (2) and at the action of a magnetic field (3)

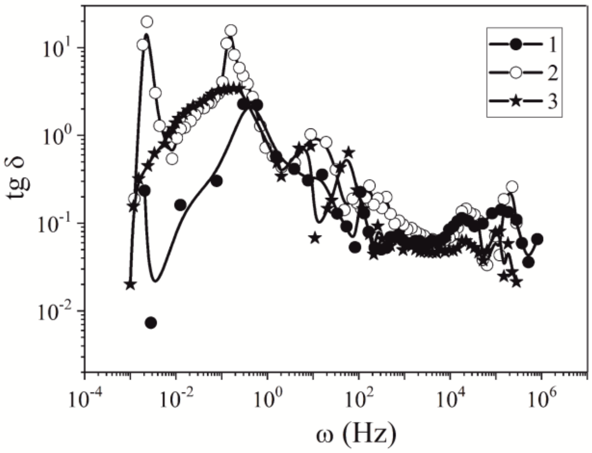

Fig. 4 – Frequency dependences of dielectric loss tangent of MCM-41 (1) and MCM-41 <PTHQ> as measured in the dark (2) and at the action of a magnetic field (3)

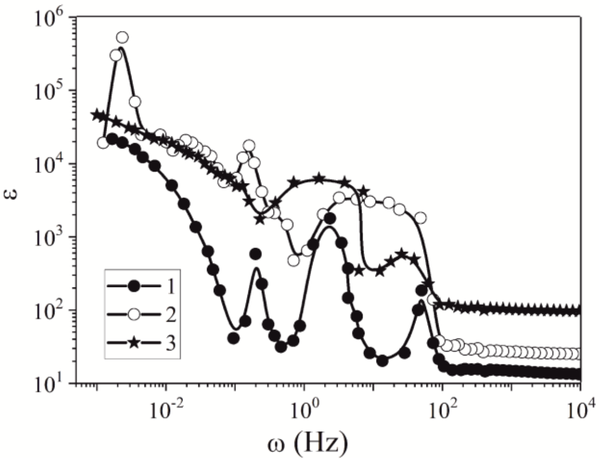

Fig. 5 – Frequency dependences of permittivity of MCM-41 (1) and MCM-41 <PTHQ> as measured in the dark (2) and at the action of magnetic field (3)

A positive result can be obviously reported for the encapsulant MCM-41 <PTHQ> in the frequency range 1-10^2 Hz. Here, ε is equal to $3.5\cdot10^3$, which, in contrast to the starting silica matrix, represents a considerable increase and is observed in a much wider frequency range. The action of the magnetic field is of particular interest as it leads to an increase in the permittivity in the low-frequency region with the maximum value of $4.6\cdot10^4$, which coupled with a low value (< 1) of tgδ, makes it possible to accumulate electric charge under the action of the magnetic field at the quantum level.

4. CONCLUSIONS

A nanostructured hybrid structure MCM-41 <PTHQ> is fabricated. The new guest component was formed through encapsulation and in situ radical oxidation polymerization.

The introduction of the organic compound PTHQ leads to considerable changes in the middle-frequency area of the frequency dependence of the real component of the specific impedance and becomes oscillatory in character. The main cause for such an effect is the splitting of an energy spectrum and occurrence of quantum wells that are formed upon the introduction of an organic polymer.

Given that the starting matrix is insensitive to the magnetic field, it could be assumed that the asymmetry of the density of states occurs precisely due to the guest component. Upon introduction of PTHQ, a miniband character becomes typical of the spectrum of thermally stimulated discharge with deep quantum wells, and this is confirmed by Nyquist diagrams (the effect of 'negative capacitance').

The action of the magnetic field was proved to lead to an increase in the permittivity in the low-frequency region with the maximum value of $4.6\cdot10^4$, which coupled with a low value (< 1) of tgδ, makes it possible to accumulate electric charge when exposed to the magnetic field at the quantum level.

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Електропровідні та поляризаційні властивості неорганічно-органічного інкапсулянта MCM-41<PTHQ>

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В роботі представлено результати досліджень формування неорганічно-органічного гібриду MCM-41 <PTHQ>. Вибір матеріалу-«гостя» задовольняв умові геометричній комплементарності гостьових позицій вихідної матриці-«господаря» по відношенню до гостьового кавітандного компоненту. З метою отримання функціональної гібридності клатратної структури MCM-41 <PTHQ> матеріал-«гість» підбирався чутливим до зовнішніх фізичних полів. В результаті синтезу було створено структуру із великою площею наногетеромеж.

Дослідження електропровідності проведено методом імпедансної спектроскопії. Впровадження гостьового компоненту приводить до розщепленням домішкового енергетичного спектру, що супроводжується виникненням квантових ям. Це в свою чергу приводить до появи осциляції в середньочастотному діапазоні залежності Re$Z(\omega)$. Накладання постійного магнітного поля значним чином впливає на поведінку Re$Z(\omega)$ в середньочастотному діапазоні (відбувається дзеркальне відображення залежності). Це може свідчити про певний зсув енергетичного спектра відносно рівня Фермі постійним магнітним полем в результаті якого міняється знак асиметрії густини станів над і під рівнем Фермі. Зроблено припущення, що асиметрія густини станів відбувається саме за рахунок гостьового компоненту, і це підтверджує вигляд спектрів термостимульованого розряду (мінізонний характер з глибокими квантовими ямами). Двохдуговий вигляд діаграм Найквіста та представлена еквівалентна схема з індуктивною ланкою відображають бар'єр, який виникає на межі розділу фаз. Дія магнітного поля призводить до зростання діелектричної проникності в низькочастотному діапазоні, що в поєднанні з низьким значенням tgδ дозволяє накопичувати електричний заряд під дією магнітного поля на квантовому рівні. Знайдено умови, при яких синтезовані наногібриди можуть виявитися цікавими в якості квантових акумуляторів електричної енергії.

Ключові слова: SiO_2-MCM-41, PTHQ, Інтеркаляція, Кавітанд, Імпедансна спектроскопія, Квантовий акумулятор.