

Nanoparticles Transport Using Polymeric Nano- and Microgranules: Novel Approach for Advanced Material Design and Medical Applications

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(Received 27 November 2017; published online 29 April 2018)

The results of practical implementation of new technology of nanoparticles transport for advanced material design and medical applications are presented. As model objects, porous piezoceramics, and ceramic matrix piezocomposites were chosen. Different types of polymeric microgranules filled and/or coated by metal-containing nanoparticles were used for pilot samples fabrication. Polymeric nano- and microgranules were examined using transmission and scanning electron microscopy as well as by EXAFS and X-ray emission spectroscopy. Polymeric nano- and microgranules, coated or filled with different chemicals, were introduced in raw ceramics powders with successive porous ceramics or composite fabrication processes. A pilot samples of nano- and microporous ceramics and composites based on different piezoceramics compositions (PZT, lead-potassium niobate and lead titanate) were fabricated and tested. Resulting ceramic matrix piezocomposites were composed by super lattices of closed or open pores filled or coated by nanoparticles of metals, oxides, ferromagnetics etc. embedded in piezoceramic matrix. Dielectric and piezoelectric parameters of a pilot samples were measured using piezoelectric resonance analysis method. New family of nano- and microporous piezoceramics and ceramic matrix piezocomposites are characterized by a unique spectrum of the electrophysical properties unachievable for standard PZT ceramic compositions and fabrication methods. The developed technology of nanoparticles fabrication and transport can be used also for advanced medical applications such as gene and drug delivery, cancer and neurodegenerative disease therapy etc.

Keywords: Nanoparticles transport, Polymeric microgranules, Porous ceramics, Ceramic matrix composites, Scanning electron microscopy, X-ray spectroscopy, Drugs delivery.

DOI: [10.21272/jnep.10\(2\).02005](https://doi.org/10.21272/jnep.10(2).02005)

PACS number: 62.23.Pq

1. INTRODUCTION

In recent years, multiphase ceramic composites (nanocomposites, porous ceramics, composites ceramics/ceramics, and ceramics/crystals) are widely used for industrial and ultrasonic transducers applications [1-3]. Numerous technologies based on incorporating of nanoquantities of functional ceramics into structural ones and vice-versa has been developed and the novel design idea has been applied in the field of functional ferroelectric ceramics [2]. Nanoparticles are perfect building blocks offering a wide variety of compositions, structures and properties, ideally suited to designing functional nanomaterials and nanodevices. Nanoparticles can be embedded in various matrixes. A major technological problem is spontaneous aggregation of nanoparticles which, as a result, lose their unique properties. One possible solution to this problem is to use supports interacting with nanoparticles. Many organic polymers have been used in various nanoparticle surface engineering approaches [4].

Recently polymeric nano and microgranules filled with nanoparticles (magnetic, metal, oxides etc.) start widely used as a delivery means of nanosubstances in medical, biotechnology and chemical applications [5]. Very recently, there was a tendency to fix (immobilize) 2-10 nm particles on the surface of spherical polymeric microgranules (typically 0.1-20 μm in size) [6, 7]. Such composite micro-nano systems offer a number of significant advantages. When fixed to a surface or embedded in microgranules, nanoparticles loose their

tendency to readily aggregate but retain their reactivity and, for the most part, their physical properties. Besides, microgranules are easier to manipulate than nanoparticles. Microgranules, coated or filled with nanoparticles can be used to produce "homogeneous" disperse systems, such as sols and aerosols, and fabricate films, coatings or bulk materials. The preparation and properties of microgranules for different applications as well as the properties of particular types of nanoparticles were described elsewhere [6-9].

Intensive research and technological works as well as improvements of fabrication methods have allowed large-scale manufacture of porous piezoelectric ceramics with reproducible and controllable porosity and properties [5, 10, 11]. Closed cell porous ceramics are usually formed by adding porosifiers to ceramics powders (burnable plastic spheres) [5]. An universal manufacturing method suitable for mass production of a wide class of nano and microporous piezoceramics and ceramic matrix piezocomposites (CMPC) were described in [5, 12, 13].

In this paper we propose an universal approach of nanoparticles transport useful for advanced material design and medical applications. The technology is based on nanoparticles transport in target objects using polymeric nano- and microgranules coated or filled by nanoparticles of various chemicals. To demonstrate the advantages and capabilities of the new technology, solid-phase ceramics matrices were used as model samples.

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2. NANOPARTICLES TRANSPORT CONCEPT

The nanoparticles transport concept (NPT) proposed in this paper is a nontrivial combination of manufacture technologies of porous ceramics and ceramic matrix composites [2, 10] and microcapsules transport techniques used in biomedical applications for targeting nanoparticles drugs delivery [4]. Over the past years, considerable advances were made to improve the physical, electrical and functional properties of piezoelectric ceramics using composite approaches [10]. Numerous composite technologies were developed and a novel design ideas was applied to develop functional piezoelectric ceramics [2, 10, 11].

The original microstructural design concept (MSD) for ceramic matrix composites was proposed in [2]. The MSD concept offers a brand-new range of polymer-free piezocomposite materials with parameters that are adjustable over a wide range. The MSD concept is based on controllable substitution during composite formation of separate crystallites or crystallite groups making a polycrystal by pores, crystallites with other composition and/or structure, or amorphous substances, all with preliminary choice of chemically, thermally and technologically compatible components and with FEM modeling of polycrystalline composite properties. The distinctive peculiarities of the MSD concept is the transition to a micro- or nanoscale level of separate crystallites and the use of the full set of technological approaches at particular stages of synthesis, preparation of initial materials (powders, solutions, suspensions, gels), granulation and compacting of a green bodies, sintering and the-post sintering treatment of a composites.

The MSD concept offers an innovative range of polymer-free piezocomposite materials (micro-, mesa- and macroporous piezoelectric ceramics, piezocomposites ceramics/ceramics and ceramic/crystal, and CMPC) with properties combining better parameters for PZT, PMN, PN and PT type ceramics and 1-3 composites [2, 10, 11].

Porous piezoceramic is composite material composed of two phases: a piezoelectrically active (piezoceramic) phase and a passive (porous) phase. The piezoelectrically active phase forms a three-dimensional matrix, in which the passive phase exists in the form of isolated and/or interconnected inclusions. The case of isolated inclusions corresponds to 3-0 connectivity while the interconnected inclusions case, to 3-3 connectivity type (closed and open porosity, respectively) [11, 12]. The microstructure of porous ceramics is unequivocally defined by the fabrication method and by the initial chemical composition of the piezoceramic phase. The structure and properties of porous ceramics are controlled by their processing.

The resulting elastic, dielectric, and piezoelectric properties of porous piezoceramics are defined by the properties of its piezoceramic matrix: that is, the porosity, type of connectivity, shape, and size of pores.

All existing methods of porous ceramics fabrication can be divided into two basic approaches: subtractive processes and processing limitations. In subtractive processes, certain elements of an original structure are selectively removed to create pores. In processing limitations, technological processing regimes are

modified to form porous structures [11, 12]. Porous ceramics with an open cell structure are usually formed by replicating a polymer foam/sponge. Closed cell porous ceramics are usually formed by adding porosifiers to ceramics powders.

A simpler technique for production of highly porous compacts was proposed in [11] with sintered mixtures of burnable plastic spheres (PMMA) and PZT powders. A series of further process for the preparation of porous ceramics and composites with 3-3 connectivity were subsequently introduced [2, 10, 12].

The universal manufacturing method suitable for mass production of a wide range of porous piezoceramics and piezocomposite materials based on burning out of burnable particles (polymer, organic substances or salts) proposed in [2, 10, 11] was used in the NPT concept.

Nanoparticles transport techniques using microgranules or microcapsules as a delivery means are intensively developed and widely used now for targeting drugs delivery and other biomedical and chemical applications [4]. A fabrication techniques of polymeric microgranules coated or filled (microcapsules) by nanoparticles of a various chemicals are well developed and different types of microgranules are commercially available [5]. The preparation and properties of microgranules for different applications as well as the properties of particular types of nanoparticles were described elsewhere [6, 7].

In the NPT method, proposed in this paper, polymeric nano- and microgranules coated or filled with nanoparticles of various chemicals are used as a porosifier agents for modified porous ceramics fabrication process. Thereby, polymeric nano- and microgranules act as a delivery means for targeting transport of nanosubstances into ceramic matrixes with closed nanopores.

The NPT concept comprises:

- nanoparticles, nano- and microgranules preparation;
- filing or coating of nano- and microgranules with nanoparticles;
- characterization of the nanoparticles and microgranules;
- porous ceramics and CMPC fabrication process;
- resulting porous ceramics aor CMPC characterization.

The full-scale use of the NPT concept will results in a new generation of nano- and microporous ceramics and composite materials derived from technologically simple processing, whilst offering a unique combination of piezoelectric, magnetic and electrets properties along with a possibility of controllable changes of the main properties. The developed technology of nanoparticles fabrication and transport can be used also for advanced medical applications such as gene and drug delivery, cancer and neurodegenerative decease therapy etc.

3. EXPERIMENTAL SCENARIO

3.1 Polymer Microgranules and Nanoparticles Preparation

Four types of polymeric microgranules were used for "pilot" porous ceramics and CMPC samples

fabrication:

- pure polystyrene microgranules (PS);
- polystyrene microgranules (PS) filled with magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) and NiO nanoparticles;
- pure polytetrafluoroethylene nanogranules (PTFENG);
- polytetrafluoroethylene nanogranules (PTFENG) coated with metal-containing (Fe, Co, Ni, Cu, Pt and Pd) nanoparticles (MCNP).

Magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) nanoparticles 10-40 nm in diameter were prepared by chemical deposition of solid phase from Fe-salts solutions. NiO nanoparticles 10-30 nm in diameter were prepared by thermal decomposition of and Ni-salts (NiCO_3). PS microgranules 80-100 nm in diameter were prepared from polystyrene/magnetite or polystyrene/NiO colloidal fluids with successive polymerization [5].

PTFENG microgranules 150-500 nm in diameter were fabricated by the thermal gas-dynamic method [6]. MCNP nanoparticles 3.5-6.5 nm in diameter have been synthesized and immobilized on the surface of polytetrafluoroethylene nanogranules via thermal decomposition of metal-containing precursors on the surface of PTFENG in mineral oil, as described in [9].

To produce MCNP from MRn precursors ($M=\text{Co}, \text{Fe}, \text{Cu}, \text{Ni}, \text{Pd}, R=\text{CO}, \text{HCOO}, \text{CH}_3\text{COO}$), well-developed thermal decomposition processes have been used [7]. At PTFENG sizes from 100 to 500 nm, a fluidized bed of microgranules was formed over the surface of heated oil. This behavior of microgranules was used to immobilize MCNP. In the course of deposition, the nanogranules became progressively heavier, and some of them left the fluidized bed and settled in the oil. As a result, the MCNP on their surfaces stopped growing.

3.2 Characterization of the Nanoparticles and Microgranules

Polystyrene microgranules filled with magnetite or Ni nanoparticles were examined using transmission and scanning electron microscopy (TEM and SEM).

Exemplary micrographs of polystyrene microgranules containing magnetite nanoparticles are shown on Fig. 1.

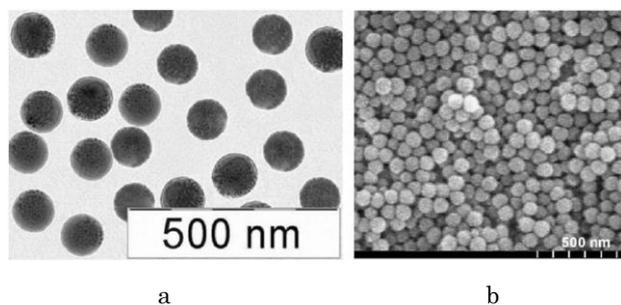


Fig. 1 – Micrographs of polystyrene microgranules containing magnetite nanoparticles: (a) – TEM, (b) – SEM. Magnetite mass content ~ 40 %, average diameter of microgranules ~ 100 nm

The MCNP nanoparticles were examined by X-ray diffraction (XRD), transmission and scanning electron microscopy (TEM and SEM), EXAFS spectroscopy, X-ray emission and Mossbauer spectroscopy [6, 7]. The results demonstrate that the nanoparticles with

average size 3.5-6.5 nm have a complex structure, are isolated from one another and are strongly bonded to the surface of the nanogranules.

The metal content of the samples was determined by elemental analysis. TEM images were taken on a JEOL JEM-100B at an accelerating voltage of 100 kV.

Fig. 2 shows a representative TEM image of as-prepared PTF-ENG/MCNP [9].

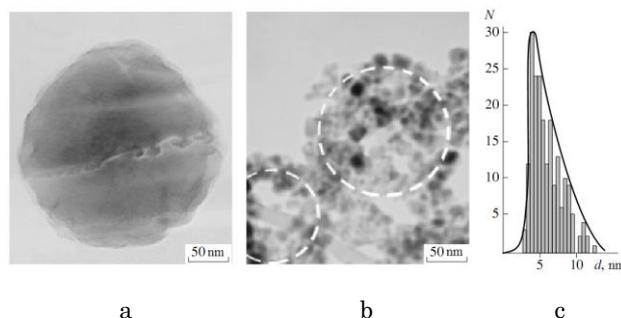


Fig. 2 – Exemplary TEM image of initial PTFENG (a), as-prepared PTFENG/MCNP (b) and their size distribution (c)

As seen in Fig. 2, MCNP are distributed rather evenly throughout the PTFENG surface. It easily to see that all the nanogranules are covered with nearly monodisperse MCNP. From the TEM image in Fig. 2, the average size of the MCNP [$\text{c-Fe}_2\text{O}_3$ prepared from $\text{Fe}(\text{CH}_3\text{-COO})_3$] was determined to be ~5 nm, with a narrow size distribution. The average sizes of Ni- and Pd-containing nanoparticles were 3.5 and 7.5 nm, respectively. Although the number of MCNP surrounding each PTFENG varied from sample to sample, we were able to control the total amount of the deposited metal per nanogranule by varying the precursor concentration in the solution.

3.3 Porous Ceramics and CMPC Fabrication Processes

Schematic illustration of the technological processes used for porous ceramics and CMPC fabrication are shown on Fig. 3.

Standard sequence of porous ceramics technological processes (mixing, compacting, burning out and sintering) were used for CMPC fabrication. Polymer nanogranules, coated or filled with a various chemicals, were used as as porosifier agents. Resulting CMPC were composed by super lattices of closed pores filled or coated by nanoparticles of metals, oxides, ferromagnetics etc. embedded in piezoceramic matrix.

Special regimes of wet and dry mixing were used for homogeneous distribution of polymer nanogarnules in piezoceramic raw powders. Burning out was fulfilled at 700 °C to provide full decomposition of polymer components. Sintering was carried out at optimal temperature for each piezoceramic composition.

Special anti-oxidation nanoparticles additives (SiC and C, as an examples) were be embedded in polyer nanogranules simultaneously with matall or oxide nanoparticles in proper mass proportion, to prevent undesirable oxidation of metal nanoparticles or to deoxidize metal oxides during ceramics sintering process.

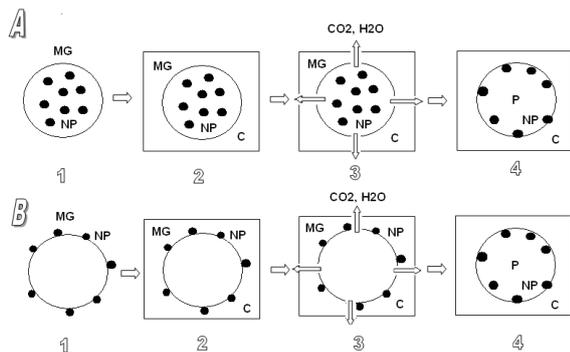


Fig. 3 – Schematic technological process for nano- and microporous piezoceramics and CMPC fabrication using polymer microgranules filled (A) and coated (B) with nanoparticles:

- 1 – preparation of microgranules (MG) filled (A) and coated (B) with nanoparticles (NP);
- 2 – embedding of microgranules (MG) in ceramic matrix (C) by means of mixing and compacting;
- 3 – burning out (thermal decomposition) of polymer microgranules (MG) and deposition of nanoparticles (NP) on a pore surface;
- 4 – sintering of porous ceramic matrix (P) and covering internal pores surface with nanolayers of metals or oxides, local doping or modification of stoichiometric composition of surface layer of piezoceramics (C).

4. EXPERIMENTAL RESULTS

4.1 Method of Measurements

The basic techniques for finding material constants of piezoelectric materials are outlined in the IEEE Standard on Piezoelectricity (1987) [11]. These methods work for many of the most widely used commercial piezoceramics based on lead-titanate-zirconate (PZT) compositions that are high- Q_M and high-coupling coefficient piezoelectric materials. However, there is a general agreement that their use in many new piezoelectric materials such as porous ceramics, piezoelectric polymers or piezoelectric composites may lead to significant errors. Furthermore, the current IEEE Standard does not comprehensively account for the complex nature of material coefficients, as it uses only the dielectric loss factor ($\tan \delta$) and the mechanical quality factor (Q_M) to account for loss.

Numerous techniques using complex material constants have been proposed to take into account losses in low- Q_M materials and to overcome limitations in the IEEE Standard [12-17]. Iterative methods [12-15] provide a means to accurately determine the complex coefficients in the linear range of poled piezoceramics from complex impedance resonance measurements.

The Piezoelectric Resonance Analysis Program (PRAP) automatic iterative method [18] was proposed for complete complex characterization of a wide range of materials with very high and moderate loss factors. The PRAP software analyses impedance spectra to determine complex material properties. This software uses a generalized form of Smits's method to determine material properties for any common resonance mode, and a generalized ratio method for the radial mode valid for all material Q 's. By analyzing on each harmonic, PRAP can determine complex material

properties as a function of frequency. The software always generates an impedance spectrum from the determined properties to indicate validity of the results.

New nanoporous piezoceramics and CMPC are lossy and direct use of IEEE Standards for material constant evaluation can lead to significant errors, therefore the PRAP automatic iterative measurement method was applied to the full set of standard geometries and resonance modes needed to complete complex characterization of the pilot samples.

Measurements of electric parameters were made using the Solartron Impedance/Gain-Phase Analyzer SL 1260 and Agilent 4294A Impedance Analyser. Pulse-echo and through-transmit measurements of ultrasonic transducers were made using LeCroy digital oscilloscope and Olympus pulser/receiver. Piezoelectric modulus was measured using APC d₃₃ tester. The microstructure of polished, chemically etched, and chipped surfaces of composite samples was observed with optical (NeoPphot-21) and scanning electron microscopes (SEM, Karl Zeiss).

4.2 Microstructure of Nanoporous Ceramics and CMPC

A pilot samples of nano and microporous ceramics and CMPC were fabricated using different piezoceramics compositions (PZT, lead-potassium niobate and lead titanate) as a ceramic matrix and PS and PTFENG microgranules as a porosifier agents.

Fig. 4 shows SEM micrograph of chipped surface of PZT nanoporous piezoceramics prepared as a result of pure PTFENG microgranules burning out and sintering. It is obvious that PTFENG microgranules are prevent compacting of PZT powder and lead to intercrystalline nanopores formation.

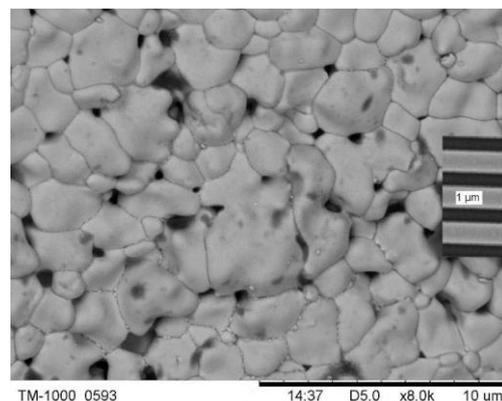


Fig. 4 – SEM micrograph of chipped surface of PZT nanoporous piezoceramics with closed intercrystalline nanoporosity

Fig. 5 shows optical micrograph of lead-potassium niobate (PKN) ceramics microstructure with closed intra-crystallite nanopores filled by magnetite microgranules burning out and sintering. Resulting piezo-magnetic CMPC demonstrate notable magnetic properties at retained piezoelectric characteristics of initial PKN ceramics.

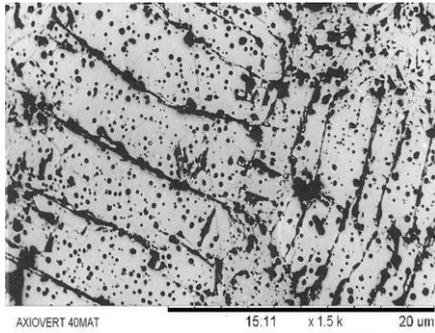


Fig. 5 – Optical micrograph of PKN piezoceramics with closed intracrystalline nanoporosity filled by magnetite nanoparticles

4.3 Dielectric and Piezoelectric Properties

The distinctive peculiarity of a new family of nano- and microporous piezoceramics and CMPC are the possibility of controllable changes of the main properties within a wide range along with a possible combination of piezoelectric, magnetic and electrets properties:

- acoustic impedance $0,1Z_{AC} \leq Z_A \leq 2Z_{ACMPC}$, where Z_{AC} – impedance for initial ceramics;
- dielectric constant $0,1\epsilon_{33}^{T_C} \leq \epsilon_{33}^T \leq 5\epsilon_{33}^{T_C}$, where $\epsilon_{33}^{T_C}$ – dielectric constant for initial ceramics;
- electromechanical coupling factors $0,1k_{pC} \leq k_p \leq k_{pC}$, $k_{tC} \leq k_t \leq 1,5k_{tC}$, where k_{pC} and k_{tC} radial and thickness for initial ceramics;
- piezoelectric modulus $d_{33C} \leq d_{33} \leq 2d_{33C}$, $0,1d_{31C} \leq d_{31} \leq d_{31C}$, where d_{33C} and d_{31C} longitudinal and thickness for initial ceramics.

It is obvious that the nanoporous ceramics technology results in increasing of piezoelectric anisotropy, removal of internal mechanical stress, increasing of mechanical durability, preventing of cracking and finally, allows production of stable in time elements of such "technologically difficult" ceramics as lead metaniobate with excellent and reproducible properties.

Dielectric and piezoelectric parameters of piezoceramic-metal nanoporous CMPC (lead titanate piezoceramics with closed nanoporous covered by Ni nanoparticles layers) are shown in Table 1.

Table 1 – Piezoelectric properties of piezoceramic-metal nanoporous CMPC

Parameter/Material	PbTiO ₃ /Ni <i>P</i> = 20 %	PbTiO ₃ /Ni <i>P</i> = 40 %
Electromechanical coupling factor for planar mode, <i>k_p</i>	0	0
Electromechanical coupling factor for thickness mode, <i>k_t</i>	0.55	0.6
Piezoelectric modulus, <i>d₃₃</i> (10 ⁻¹²), C/N	150	275
Dielectric constant, $\epsilon_{33}^{T/\theta}$	250	480
Dielectric loss $\tan \delta$, %	2	4
Mechanical quality factor for thickness mode, <i>Q_M^t</i>	< 12	< 10
Density, ρ (10 ³), g/cm ³	6,4	4,8
Curie temperature, <i>T_C</i> , °C	490	480
Frequency constant, <i>N_t</i> , kHz·mm	1200	800

We can see from Table 1 that electromechanical and piezoelectric activity as well as dielectric constant of nanoporous CMPC "piezoceramic-metal" increase with relative porosity, and consequently with metal content grows. This behavior is in good conformity with the theoretical and FEM modeling results [19] predicting grows of dielectric constant and piezoelectric modulus in the vicinity of dielectric-metal percolation threshold. The electromechanical behavior of CMPC with hollow metal spheres (pore with metalized internal surface) is drastically differs from the solid metal sphere case, because of practically infinite elastic compliance of pores.

Preliminary experiments on nanoporous CMPC "piezoceramic-metal" in low frequency range 10⁻⁵-10⁴ Hz confirmed also the theoretical predictions of giant dielectric relaxation and giant piezoelectric effect resulting from Maxwell-Wagner relaxation, as was foreshown in [19].

New generation of nano- and microporous piezoceramics, and ceramic matrix piezocomposites with unique chemical and electromechanical properties can be usefull for a variety of ultrasonic transducers, sensors and actuators applications. The developed technology of nanoparticles fabrication and transport can be used also for advanced medical applications such as gene and drug delivery, cancer and neurodegenerative decease therapy etc. [20].

5. CONCLUSION

New technology of nanoparticles transport using polymer nano- and microgranules for advanced material design and medical applications are presented.

Methods of fabrication and transport of polymer nano- and microgranules filled and/or coated by metal-containing nanoparticles in ceramic matrices were developed. It was shown, that the method of nanoparticle transport using polymer nano- and microgranules provides point-to-point delivery of nanoparticles of metal-containing compounds to specified regions of the target matrix. It was shown also that the pilot samples of nano- and microporous piezoceramics and ceramic matrix piezocomposites are characterized by a unique spectrum of the electrophysical properties unachievable for standard PZT ceramic compositions and fabrication methods and can be used in ultrasonic transducers for NDT and medical applications.

The developed technology of nanoparticles fabrication and transport can be used also for advanced medical applications such as gene and drug delivery, cancer and neurodegenerative deceases therapy etc.

ACKNOWLEDGEMENTS

This work was financially supported by the Ministry of Education and Science of the Russian Federation: the basic parts of the state task, themes №BP0110-11/2017-44 (12.5425.2017/8.9), №3.8863.2017/ITW (3.8863.2017/7.8) and The Russian Foundation for Basic Research (RFBR №16-58-48009-Ind-omi).

Транспорт наночастиц с использованием полимерных нано- и микрогранул: новый подход к проектированию новых материалов и медицинским применениям

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Представлены результаты практической реализации новой технологии транспорта наночастиц для проектирования новых материалов и медицинских применений. В качестве модельных объектов были выбраны пористые пьезокерамики и керамоматричные композиты. Для изготовления пилотных образцов использовались различные типы полимерных микрогранул, заполненных и/или покрытых наночастицами металлов. Полимерные нано- и микрогранулы исследовались с использованием трансмиссионной и сканирующей электронной микроскопии, а также с помощью EXAFS и рентгеновской эмиссионной спектроскопии. Полимерные нано- и микрогранулы, покрытые или заполненные различными химическими соединениями, вводились в синтезированные порошки керамики с последующими процессами получения пористых керамик и композитов. Изготовлены и исследованы экспериментальные образцы нано- и микропористой керамики и композитов на основе различных пьезокерамических композиций (PZT, ниобат свинца-калия и титанат свинца). Полученные керамоматричные пьезокомпозиты представляли собой суперрешетки замкнутых или открытых пор, заполненных или покрытых наночастицами металлов, оксидов, ферромагнетиков и пр., встроенных в пьезокерамическую матрицу. Диэлектрические и пьезоэлектрические параметры пилотных образцов измерялись с использованием метода пьезоэлектрического резонансного анализа. Новое семейство нано- и микропористых пьезокерамик и керамоматричных пьезокомпозитов характеризуется уникальным спектром электрофизических свойств, недостижимых для стандартных керамических композиций PZT и методов изготовления. Разработанная технология изготовления и транспортировки наночастиц может использоваться также для современных медицинских применений, таких как доставка генов и лекарств, лечение рака и нейродегенеративных заболеваний и т.п.

Ключевые слова: Транспорт наночастиц, Полимерные микрогранулы, Пористая керамика, Керамоматричные композиты, Сканирующая электронная микроскопия, Рентгеновская спектроскопия, Доставка лекарств.

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