Functional energy nanocomposites surfaces based on mesoscopic microspheres, polymers and graphene flakes

S A Alekseev¹, A S Dmitriev¹², A A Dmitriev², P G Makarov² and I A Mikhailova²

¹NanoGraphene Group, 67 35th Street C250 Brooklyn, NY 11232, USA
²National Research University «Moscow Power Engineering Institute»
Russia, 111250, Moscow, Krasnokazarmennaya 14

Abstract. In recent years, there has been a great interest in the development and creation of new functional energy materials, including for improving the energy efficiency of power equipment and for effectively removing heat from energy devices, microelectronics and optoelectronics (power micro electronics, supercapacitors, cooling of processors, servers and Data centers). In this paper, the technology of obtaining a new nanocomposite based on mesoscopic microspheres, polymers and graphene flakes is considered. The methods of sequential production of functional materials from graphite flakes of different volumetric concentration using polymers based on epoxy resins and polyimide, as well as the addition of a mesoscopic medium in the form of monodisperse microspheres are described. The data of optical and electron microscopy of such nanocomposites are presented, the main problems in the appearance of defects in such materials are described, the possibilities of their elimination by the selection of different concentrations and sizes of the components. Data are given on the measurement of the hysteresis of the contact angle and the evaporation of droplets on similar substrates. The results of studying the mechanical, electrophysical and thermal properties of such nanocomposites are presented. Particular attention is paid to the investigation of the thermal conductivity of these nanocomposites with respect to the creation of thermal interface materials for cooling devices of electronics, optoelectronics and power engineering.

1. Introduction
Over the past decade, graphene research has attracted increasing interest from researchers in physics, materials science, chemistry, etc. Graphene consists of an unusual single-layer honeycomb lattice of C atoms, which differs from all other materials of this element. More specifically, the C atoms of graphene are sp²-bonded and densely packed in a crystal lattice. This closely resembles the basic building block found in graphitic materials of different dimensionalities. It has been demonstrated that graphene exhibits some special characteristics, such as a high electron mobility of up to 230 000 cm²/V·s at low temperatures, an exceptional thermal conductivity approaching 5000 W/m·K and superior mechanical properties with a large Young’s modulus, exceeding 1.0 TPa the latter being comparable to those of single-walled nanotubes and even diamonds. With these intriguing physical and chemical properties, it is not surprising that graphene has been intensively investigated to exploit its functions as a promising material for future applications. Typical examples of graphene research focus are: the synthesis of pristine graphene in inorganic chemistry, the chemical modification of graphene, gra-
phene characterization (its properties and functions), the investigation of graphene–polymer composites, and graphene and inorganic materials either exclusively combined or in integrated electronic and energy systems with other components.

Graphene nanocomposites, in which graphene flakes are dispersed in a matrix (either polymer, ceramic or metal), have found numerous applications (energy, electronics and optoelectronics) that demand low weight with good mechanical as well as thermal performance [1-6]. The performance of composites is often limited by poor coupling between graphene flakes and matrix. For example, thermal transport through a composite can be dominated by thermal resistance at the interface that results primarily from phonon scattering due to mismatched phonon spectra in the two phases (graphene flakes and matrix) and from interfacial defects. The resistance is further increased by process-induced interfacial irregularities such as voids and interfacial stress, which result from graphene flakes surface roughness, poor adhesion between graphene flakes and matrix and dissimilarities in thermal expansion coefficient between graphene flakes and the surrounding matrix. Aside from the possibility of improving the overall mechanical properties of the composite, improved graphene flakes – matrix coupling would reduce interfacial thermal resistance and enhance heat conduction. Such an enhancement would have positive implications for a variety of applications, ranging from aircraft skins to lightweight heat exchangers.

In many cases, when discussing graphene thermal applications, we use the term graphene even when the actual material consists of a mixture of single layer graphene (SLG), bilayer graphene (BLG), and few-layer graphene (FLG). The latter is because for thermal applications the difference between SLG and FLG is not as important as for electronic applications. It is sometimes difficult to distinguish between FLG and graphite films or between FLG and graphite nano-platelets (GnP) or graphite nanoflakes (GnF) used in composite materials. The definition of SLG — a single atomic plane of sp²-bound carbon — is strict. The distinction between FLG and thin film of graphite or bulk graphite depends on the context. Investigating electrical properties one can consider the material to be FLG rather than graphite as long as it is thin enough for changing its carrier density via the electrostatic gating. In the thermal field, one can consider the film to be FLG as long as its Raman spectrum is different from that of bulk graphite.

It is important to note the possibility of using such hybrid nanocomposites as functional energy materials, for example, for lithium-ion batteries or materials with phase transitions. Development of high-power-density batteries, e.g., Li-ion batteries, enabled progress in mobile communications, consumer electronics, and automotive industries [7, 8]. Temperature rise beyond the normal operating range negatively affects Li-ion battery performance. If overheated, the battery can suffer thermal runaway, cell rupture or explosion. A conventional approach for thermal management of high-power-density-ion battery packs is based on the utilization of thermal phase change materials (PCMs). They reduce the temperature rise in the battery due to the latent heat storing and phase changes over a small temperature range [9, 10].

The common PCMs have very low thermal conductivity, with typical values in the range of 0.17–0.35 W/mK at RT [1, 3]. For comparison, the room-temperature (RT) thermal conductivity of Si and Cu are ~145 W/mK and ~381 W/mK, respectively. Conventional PCMs store heat from the batteries rather than transfer it away from the battery pack. The use of PCM in battery cells also serves the purpose of buffering the battery cell from extreme fluctuations in ambient temperature. This is different from thermal management of computer chips. To reduce the temperature rise in a computer chip, one uses thermal interface materials (TIMs) or heat spreaders that facilitate heat transfer from the chip to the heat sink [10]. The thermal conductivity of TIMs is in the range of 1–10 W/mK while that of solid graphite-based heat spreaders can be on the order of 1000 W/mK [1]. In this review we describe how these two different approaches for thermal management can be combined via the introduction of the hybrid PCM with graphene acting as filler for increased thermal conductivity. The properties that allow graphene to be an exceptional filler material are its high intrinsic thermal conductivity, and strong binding with various matrix materials.
In this work, we will demonstrate new types of hybrid nanocomposites based on graphene flakes and metallic monodisperse microspheres. We investigate contact angles on the surface of such composites and measure the heat conductivity of several types of hybrid nanocomposites.

2. Material and methods
In the work, hybrid functional materials were studied in relation to energy problems, made of metal microspheres, polymer (epoxy resin) and graphene flakes. The method of obtaining composite materials is as follows. Graphene flakes produced by NanoGrahpen Group were used to prepare a nanocolloid solution (nanofluid), for which graphene flakes of various volume were added to pure distilled water and stirring was conducted for 20-30 minutes in a rotating centrifuge. Graphene flakes with a size of 5-10 microns with 3-10 layers of graphene (few-layer graphene, FLG) were obtained. After that, the microspheres from Sn and Er$_3$Ni (production of the Moscow Power Engineering Institute) were placed in a Petri dish and a nanocolloid solution of graphene flakes was poured into it. After that, the Petri dish was placed on the heater and the water from it was evaporated at different temperatures (from 60 to 100 °C). After evaporation of the water, the microspheres covered with graphene flakes were heated to a temperature of 250 °C for 1-1.5 hours, which led to the effect of quenching the microspheres with graphene flakes on the surface. A general view of the microspheres covered with graphene flakes after drying and the quenching effect is shown in Figure 1 and Figure 2. It is not difficult to see that the microspheres were very homogeneous, with a good coating of graphene flakes. At the same time, the adhesion value of graphene flakes to metal microspheres was very high, which made it possible to mix microspheres without destroying the graphene coating.

![Microspheres Sn covered with graphene flakes after drying and the quenching effect](image)

Figure 1. Microspheres Sn covered with graphene flakes after drying and the quenching effect

A micrograph of transmission electron microscopy of graphene flakes is shown in Figure 2.
Figure 2. Transmission electron microscopy (TEM) of graphene flakes

In some experiments, isolated flakes were homogeneously dispersed in epoxy matrix and almost no large agglomerates or bundles were observed. The strong interfacial adhesion between oxygenic groups on the of GnF and epoxy molecular chains led to high embedding and tight binding of GnF in the matrix. For this reason, these wrinkled and isolated GNPs effectively prevents direct contact between graphite nanoparticles in the composite, which give advantages for forming a large microcapacitor network and suppressing the leakage current.

3. Investigation of the properties of hybrid graphene nanocomposites

Various properties of hybrid nanocomposites based on microspheres and graphene were investigated. In some cases, microspheres coated with graphene were placed in a polymer matrix. For the experiments, tablets were prepared in the form shown in Figure 3. For all types of samples, contact angles and thermal conductivity were studied. To determine the angle of wetting of drops on the surface of samples of a hybrid nanocomposite, Kruss EasyDrop measuring system.

Figure 3. Hybrid nanocomposites samples

Investigation of thermal conductivity of graphene hybrid nanocomposites includes experiments on the measurement of thermal conductivity by two methods: the method of thermal resistance of a layer and the method of laser flash (LFA-laser flash analysis). The laser flash method is a more accurate method, so the results of these methods will be compared with each other. In the interaction of microspheres covered with graphene with water drops, microspheres moved, forming a monolayer on the drop surface (Figure 4, left). The contact angle varies greatly with the volume fraction of graphene flakes. In the absence of graphene flakes on the surface of microspheres, the contact angle is about $\theta \sim 104^\circ$. In the range of variation in the concentration of graphene flakes from zero to about 0.25%, the angle is about $\theta \sim 155^\circ$. With a further increase in the concentration of graphene flakes, the contact angle does not actually change.
Measurements of the thermal conductivity of hybrid nanocomposites were carried out for dilute samples. In the first series of experiments, samples based on a freely lying layer of microspheres coated with graphene flakes were investigated. At the same time, the volume fraction of the graphene fraction changed. The results of measurements in the first series of samples are shown in Figure 5. In the second series of measurements, the thermal conductivity of densely packed microspheres coated with multilayer graphene was studied (Figure 5).

It is important to note that the dependence of thermal conductivity on the volume fraction of graphene flakes has a sharp increase with a volume fraction of about 2.5-3%. Thus, the graphene layers near the microspheres play an important role in the process of heat transfer - with increasing amounts of graphene flakes, thermal conductivity sharply increases. This fact can be used to control heat transfer in various nanocomposites, in particular, used as thermal interface materials.
The results of the thermal conductivity show that there is an optimal volume fraction of graphene flakes in the range 2.5 - 10%. For large values of the volume fraction, the thermal conductivity practically does not increase. Apparently, physically this means that the observed percolation in this range of the mating fraction and the further increase in the amount of graphene flakes does not affect the mechanism of phonon heat transfer. The following series of experiments were carried out on the samples shown in Figure 3. These samples were hybrid nanocomposites - the inclusion of graphene flakes in the polymer matrix of the epoxy, as well as the hybrid nanocomposite microspheres + graphene flakes inside the epoxy matrix. The dependences of the thermal conductivity of such hybrid nanocomposites are presented in Fig.6. In addition, the thermal conductivity of a polymer matrix (epoxy resin) is shown here. With increasing temperature, the thermal conductivity of all samples decreases, which is associated with an increase in phonon scattering at the boundaries of graphene flakes. It is important to note that the use of graphene coated microspheres greatly increases the thermal conductivity. This indicates the possibility of using hybrid nanocomposites with microspheres as functional energy materials.

Conclusions
In this paper we presented the results of the properties of new hybrid nanocomposites based on graphene flakes, metal microspheres and epoxy polymers. The obtained data on the contact angles on the surface of such composites and their thermal conductivity at room temperature make it possible to draw conclusions about the potential use of these materials as functional energy materials. In particular, for practical applications of graphene nanocomposites are outlined in an example using thermal phase change materials for thermal management of high-power battery packs.

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