Synthesis and characterization of nanosized ZnTiO$_3$ doped with reduced graphene oxide (RGO)

B L Martinov$^1$, A D Staneva$^1$, T E Vlakhov$^2$, S Slavov$^1$, D Dimitrov$^1$, Y G Marinov$^2$, G B Hadjichristov$^2$

$^1$ University of Chemical Technology and Metallurgy, 8 Kliment Ohridski Blvd., Bulgaria, BG-1756, Sofia, Bulgaria
$^2$ Georgi Nadzakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., BG-1784 Sofia, Bulgaria

E-mail: brsmartinov@gmail.com

Abstract. Composite materials based on nanosized zinc titanate (ZnTiO$_3$) doped with reduced graphene oxide (RGO) were obtained by means of ultrasonically assisted precipitation. In these composites, the concentration of RGO nanoparticles was varied from 1 wt.% to 20 wt.%. The ZnTiO$_3$ ceramic was produced by sol-gel method. RGO was prepared by a modified Hammers method and subsequent chemical reduction with sodium borohydride. Structural and phase characterization of the fabricated composites was performed by XRD, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). It was identified that for all of the studied samples of the RGO/ZnTiO$_3$ series, the two phases are uniformly distributed over the observed areas, which proves the formation of homogeneous nanocomposite materials. The electrical properties of the series of RGO/ZnTiO$_3$ samples were characterized by complex electrochemical impedance spectroscopy (EIS) in the frequency range from 0.1 Hz to 1 MHz. The results obtained by EIS for the electrical conductance of RGO-doped ZnTiO$_3$ as a function of the concentration of RGO nanoparticles were correlated with the data from structural studies.

1. Introduction

Even after decades of research, energy storage technology continues to be a major challenge for modern society. That is why development of small, light and environmentally friendly energy storage systems, including fuel cells, batteries, and supercapacitors are adapted and optimized with nanostructured components. In the field of nano-based energy storage devices, nanocapacitors are one of the most studied with potential application in the next generation of energy storage systems [1]. The need for more sustainable and efficient energy storage devices drives the demand for modern capacitor designs in which a set of experimental techniques and ideas that include nanotechnology play a crucial role [2].

Capacitors are devices that store electrical energy in the form of an electric charge accumulated on their plates. They have a low internal resistance and this capability is often used in systems that generate heavy loads when batteries cannot provide enough current.

Recent theoretical and experimental studies on graphene, carbon nanotubes and metal nanofibers have focused on the dielectric properties of these structures and the formation of thin layers that can serve as ideal metal plates for energy retention. In previous studies, high capacitance values per unit area have been achieved for capacitors with electrodes consisting of pure graphene and multilayer reduced graphene oxide [3].
The ZnO-TiO2 structure still attracts research attention, and finds application in microwave devices (including mobile phones and satellite communication systems) as high-quality microwave dielectric resonators. Capacitors and filters are also in development, thanks to the promising dielectric properties of these materials [4]. Graphene is a 2-dimensional, crystalline-allotropic form of carbon in which the carbon atoms are in the sp2 hybrid state [5]. High quality graphene is a strong, light, almost transparent, and an excellent conductor of heat and electricity. Its interaction with other materials, optical properties and two-dimensional nature make it a material with unique properties. Its surprisingly easy synthesis allows for a vast and growing field of research [6]. Andre Geim and Konstantin Novoselov of the University of Manchester won the 2010 Nobel Prize in Physics for "innovative experiments in two-dimensional material - graphene". A single carbon layer of the graphite structure can be considered as the final member of fused polycyclic aromatic hydrocarbons series and thus the term graphene should be used to denote the individual carbon layers of the graphite compounds [7].

Graphene oxide (GO) is a layered material obtained from the oxidation of graphite. GO research is an important part of the history of graphene, which dates back to more than 170 years [8]. The earliest report on GO was published in 1840, when the German scientist Schafhaeutl reported the intercalation and exfoliation of graphite with sulfuric and nitric acid [9]. In 1859, the British chemist Brody used modified methods to measure the atomic weight of graphite using strong acids (sulfuric and nitric) and oxidants (KClO3) [10]. The use of new chemicals not only improves the intercalation of graphite, but also chemically oxidizes its surface and leads to the formation of GO.

Chemical modification of the graphite surface has proven to be valuable for several purposes, such as the preparation of GO and other similar materials [6, 11]. Functionalization of the graphite surface reduces the Van-der-Waals forces between the bonds, so that the oxidized layers can be easily separated by ultrasonic, thermal or other energetic conditions. In 1962, Boehm et al. found that GO can be chemically reduced in dilute alkaline media with hydrazine, hydrogen sulfide or iron salts [12].

In 2004, Novoselov et al. obtain graphene by mechanical exfoliation (ME) of graphite on a silicone pad. The thin layer of graphene was observed by optical microscopy, and the thickness of the sample layer was found to be 0.8 nm by atomic force microscopy (AFM) [13]. This discovery made mechanical exfoliation a very important method for the production of high quality graphene for the study of its properties [14]. Many interesting properties of graphene have been discovered in the last few years [15]. Mechanical strength, high Jung modulus and high breaking strength. Good optical properties, incredible high theoretical specific surface area. The charge carriers behave like massless relative particles. Very low resistance of graphene sheet ~ 10^{-6} \ \Omega \ \text{cm}, less than the resistance of silver, and excellent thermal conductivity (3000 \ \text{W/m K}).

The development of newly discovered nanomaterials provides an ideal opportunity for development in various fields due to their structures, composition, and properties [16]. Graphene has some advantages over other materials such as, two surfaces, it is easy to modify, and have no toxicity (compared to, for instance, metal particles). In recent years, metal oxide nanoparticles have attracted much interest in their application in battery electrodes. This is mainly due to their natural abundance, environmental compatibility and low cost, as well as good electrochemical properties. Despite the fact that most metal oxides have low conductivity, graphene, with its unique two-dimensional shape and numerous attractive properties, promises a remarkable increase in energy density and power density of electrochemical energy storage devices, like popular lithium-ion batteries and supercapacitors.

The maximum energy density of graphene for supercapacitors and ways for future improvements have been calculated. The synthesis of graphene in macrostructures allows the design of batteries and supercapacitors with many new functions that do not exist in current technologies [17].

A simple method for the preparation of a nanocoating of a composite of graphene/activated carbon (AB) is proposed for the building of a highly efficient electrode material for a supercapacitor. The composite has a relatively high relative density of 0.3 g/cm³ and a large specific surface area, and utilizes an organic electrolyte. These results indicate that the porous graphene/AB composite obtained by hydrothermal carbonization and chemical activation can be applied to high performance supercapacitors [18, 19].
Zinc titanate (ZnTiO₃) is a functional inorganic material, well known for its numerous applications in industry, such as pigment, sorbent, catalyst and others. Recent research also confirms that this is a ceramic material with low dielectric losses and stable resonance-frequency-temperature ratio, and can be a useful candidate for low-temperature co-fired ceramics used in microelectronics, in devices that have resistors, capacitors, transformers and are also a suitable candidate for gas sensors (for Ethanol, NO, CO, etc.) [20]. Also, thanks to their photocatalytic properties, there is a growing interest in using them to decompose organic pollutants.

Zinc titanate is also used as an antibacterial agent. High antibacterial activity of newly developed cubic ZnTiO₃ against suspensions with a high concentration of E. coli has been demonstrated [21, 22].

The various applications and properties of Graphene and ZnTiO₃ described above and the lack of sufficient study of the properties of composites with their participation provoked interest in obtaining and studying a nanocomposite with Graphene/ZnTiO₃ composition.

The aim of the present work was to investigate the electrical resistance and capacitance of a series of composites based on ZnTiO₃ and RGO.

2. Experimental

2.1. Synthesis

Graphene oxide is obtained by the Hammers method from purified natural graphite powder. The resulting graphene oxide is subjected to ultrasonic treatment with sodium borohydride (NaBH₄) to exfoliate the graphene layers. Of the reducing reagents, NaBH₄ was selected as one of the strongest. Sodium borohydride is most effective in reducing C - O bonds, but is low to moderately effective in reducing epoxy groups and carboxylic acids; alcohol groups also remain after reduction [23].

Zinc titanate was prepared by the sol-gel method using Titanium ethoxide and Zinc acetate as precursors. 6.5 g of Titanium ethoxide are dissolved in 50 ml of Ethanol. 1.7 g of citric acid is dissolved in 50 ml of ethanol and 6.8 g of zinc acetate is added to the solution. The two solutions are mixed; 5 ml of ethylene glycol are added. The solution is stirred for two hours at 60°C, after which the sample is dried at 110°C. The thus obtained xerogel is transferred to a crucible and baked at 550°C for 3 hours - calcination step.

The pre-synthesized precursors for RGO/ZnTiO₃ composites are mixed in the proportions shown in (figure 1). Ethanol is added, followed by sonication for 2 hours and drying at 70°C for 5 hours. The obtained samples are placed on a watch glass and a plasticizer – 3 % aqueous solution of PVA is added. Stirring is applied until the components are evenly moistened, after which they are placed in a hydraulic press to produce a tablet with a diameter of 12 mm and a thickness of 2 mm. All tablets are treated in an oven at 140°C for 3 hours.

2.2. Characterization and measurement of electrical properties

All samples were characterized by powder XRD using Bruker D8 Advance powder diffractometer with Cu Kα radiation and a LynxEye detector. The data collection was performed in the range of 10 to 90°2θ with step 0.03°2θ, with a counting time 57 s/step.

The samples are also characterized by scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) analysis. The instrument used is a dual beam scanning electron/ focused ion beam system (SEM/FIB LYRA I XMU, TESCAN), equipped with EDX detector (Quantax 200, Bruker, spectroscopic resolution at Mn-Ka and 1 kcps 126 eV. Electronic source: tungsten filament, resolution - 3.5 nm at 30 kV, accelerating voltage - 200 V to 30 kV. Electrical measurements are performed by two-electrode method and application of silver electrodes. An RLC bridge with an operating frequency of 1 kHz was used. The dielectric constant, conductivity, and dielectric loss are measured in the 1 kHz-100 kHz range.
3. Results and discussion

3.1. The X-ray diffraction results

The X-ray diffraction of the obtained materials (figure 1) show the presence of the two main phases - RGO and ZnTiO₃ in all obtained composites. The wide peak of 2θ = 25.28 corresponds to RGO’s (002) plane. Also the synthesized single-phase ZnTiO₃ shows peaks corresponding in shape and values of angle θ to those in the literature [24]. There is a sharp decrease in the intensity of the ZnTiO₃ peaks with increase of RGO content, respectively the particle size also decreases. This effect may be due to the uniform distribution of the zinc titanate layers between the reduced graphene oxide layers, i.e. the alternation of the layers of the two phases. The crystallite size of ZnTiO₃ in all tested composites was determined by Scherer's formula to be 5 nm.

3.2. Scanning electron microscopy (SEM) of the obtained materials

3.2.1. Reduced graphene oxide

The microstructure of the synthesized RGO was observed by SEM at different magnifications (figure 2 a), b), c)). At 143 000 × (3c) magnification, the exfoliated graphene layers are clearly visible. From the EDX analysis, it can be concluded that only carbon and minimal amounts of oxygen are present in the sample.

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Figure 1. XRD analysis of the synthesized composites and the starting components.

Figure 2. SEM images of RGO, with different magnifications a) 20 kx; b) 100 kx; c) 143 kx.
3.2.2. Zinc Titanate (ZnTiO₃)

The SEM of the ZnTiO₃ synthesized by us at similar magnifications as in RGO shows the morphology of the obtained particles. At a magnification of 140 k×, a very fine structure of the obtained crystals is observed (figure 3).

The EDX analysis shows the presence of only the elements Zn, Ti and O in a percentage corresponding to the theoretical ratio for ZnTiO₃ phase. The SEM images of the composite materials show a uniform distribution of nanosized ZnTiO₃ crystallites on the well-exfoliated graphene layers.

![Figure 3. SEM of the synthesized ZnTiO₃ a) 40kx; b) 80kx; c) 144kx.](image)

3.2.3. RGO-ZnTiO₃ composites

![Figure 4. SEM images of selected composite (1 % mass RGO/99 % mass ZnTiO₃) a) 25 kx; b) 30 kx; c) 60 kx](image)

![Figure 5. EDX and colour maps of composite 1 % mass RGO/99 % mass ZnTiO₃.](image)

The synthesized composites are studied by SEM and EDX, and elemental distribution colour maps of the composite materials is also produced (figures 4 and 5). In all of them, a uniform distribution of ZnTiO₃ on the well-exfoliated graphene layers is observed. The EDX of the composite shows the presence of the elements C, Ti, Zn and O, and the color maps show their even distribution in observed
area. Although the RGO in the sample (figure 4) is only 1% by weight, it is clearly visible on the SEM images, tightly and consistently covered with clusters of ZnTiO$_3$. This is observed in the EDX analysis of the sample 1% mass RGO/99% mass ZnTiO$_3$ (figure 5).

3.3. Electrical measurements of the synthesized ZnTiO$_3$ and composite materials

The diagram of the electrical properties of the sample with pure ZnTiO$_3$ (figure 6) show that it has two orders of magnitude higher resistance than all composites containing RGO. It’s also visible that that with increasing frequency up to 22 kHz (input energy from the electric field), the resistance decreases. Further increasing the frequency leads to a gradual increase in resistance. This behavior is typical for the onset of volumetric polarization in the structure.

In (figure 7) is a diagram of the electrical properties of the synthesized composite materials. It is observed that with increasing RGO content in the composites, the resistance decreases significantly. In compositions with 1, 3 and 5% RGO, a much lower frequency dependence was observed compared to that of pure ZnTiO$_3$. In composites with 10 and 20% RGO and in pure RGO, frequency dependence of resistance is not observed, and the resistance value is below 1 kΩ. This characterizes them as conductive materials rather than dielectrics.

These results are also confirmed by the constructed dependences of the dielectric constant ($\varepsilon_r$) on the frequency in synthesized RGO/ZnTiO$_3$ composites.
constant. It can be seen that at low frequencies (around 20 kHz) the dielectric constant increases with increasing frequency, which is the opposite behavior compared to the samples with 1, 3, 5% RGO content.

From the frequency dependences of the resistance and dielectric constant of all obtained composites, it can be concluded that a composite with up to 10% RGO content has the best parameters for future dielectric applications. This gives us the motivation for a future in-depth study of new composites with RGO content of 1 to 5% to determine the type of conductivity, the influence of the number of RGO layers, the activation energy of conductivity and others.

4. Conclusions

A series of composite materials with varying compositions based on presynthesized RGO and ZnTiO₃ is produced. Structural and phase characterization of the obtained composites is performed by X-ray diffraction. It is proven that in all obtained samples the two main phases are present - RGO and ZnO. The crystallite size of all tested composites is determined by Scherer's formula to range between 5 and 6 nm. The microstructure of the synthesized RGO, ZnTiO₃, as well as of selected composites at different magnifications, is observed by SEM. The SEM images of the composite materials show a uniform distribution of nanosized ZnTiO₃ crystallites on the well-exfoliated graphene layers. In composite 5% mass RGO – 95% mass ZnTiO₃ aggregates are observed, densely covering the graphene layers. It is possible that this is what contributes to the further interesting result, which is observed in the electrical measurements. From the presented color maps of the distribution of the elements in a given area of the sample, it is evident that C, Zn and O are evenly distributed. This proves the formation of nanocomposite material. From the determined frequency dependences of the resistance and dielectric constant of all obtained composites, it concluded that a composite with under 10% RGO in its compositions is most promising for future dielectric applications. This gives us the basis for a future in-depth study of new compositions of composites with RGO content from 1 to 5% to determine the type of conductivity, the influence of the number of RGO layers, the activation energy of conductivity and others.

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