Electric properties of new composite materials based on RGO, nanosized ZnO and Cu nanoparticles

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Abstract. Graphene nanostructures combine properties that make them an attractive material for various technical applications. The objective of this study is to obtain a series of composites based on Reduced graphene oxide (RGO), nano-sized ZnO and Cu nanoparticles. RGO is synthesized by a modified Hammer’s method and chemical reduction after sonication. ZnO nanoparticles are obtained by the Sol-Gel method. The composites’ phases and structures are characterized by XRD, SEM, TEM, and EDX analysis. It is shown that ZnO is monophasic with a particle size of 48 nm. A series of composite materials based on RGO, ZnO and Cu nanoparticles is obtained by ultrasonic treatment. Electrical and dielectric properties are measured by Impedance analyser and RLC bridge. For comparison, the conductivity for 100% RGO is 309.513 S/m and for 100% Cu nanosized is 0.0056 S/m. Therefore, it should be initially concluded that increasing the RGO in the mixture will increase the conductivity, and increasing nanosized Cu will decrease it. The presence of cluster regions in the composites with different conductivity is found: 1) nano grains of conductive copper which are partially or completely surrounded by 2) low-conductivity shells of copper oxide and a minimal number of RGO sheets. The present work shows promising results for future research for the creation of new composite materials with controlled shape and size of copper oxide - RGO clusters. Dielectric measurements for RGO/ZnO composites are made in range from 5 mass% to 100 mass% content of RGO, the composites show variable conductivity. For lower concentration of RGO, selected samples are dielectrics.

1. Introduction
Graphene and graphene nanostructures combine properties that make them an attractive material for technical applications, and the development of composites with their participation with new properties [1, 2].

Reduced graphene oxide (RGO), a monolayer sp² carbon atom and two-dimensional honeycomb lattice structure, has high mobility of electric charges and conductivity [3], high optical properties [4], mechanical flexibility [5], chemical stability, and high specific surface area [3]. These excellent features of the material can be utilized in numerous applications [3-5], such as photovoltaics, super capacitors, fuel cells, and nanofluids. High electrical conductivity, mechanical strength, thermal conductivity, and good optical properties of graphene are a prerequisite for promising applications in portable electronics and hybrid electric cars, new generation batteries, supercapacitors, and more. Lithium-ion batteries, the most commonly used, cannot meet varied requirements in different practical situations, due to their low energy density [3-6]. On the other hand, electrolytic capacitors exhibit extremely high energy density, but are unable to power high-power electronic devices.
Supercapacitors, also called ultra-condensers or electrochemical capacitors, attract attention as promising power source to fill the gap between electrolytic capacitors and batteries. They can achieve higher power output than electrolytic capacitors, have good longevity (> 10^5 charging cycles), ultra-fast charging and drain process that takes from few seconds to few minutes) [7]. Modern energy sources based on the next-generation graphene supercapacitors are integrated into energy storage devices to meet the needs of today's renewable energy generation and hybrid electric cars. Graphene, a material with the thickness of a carbon atom [8], attracted interest after the discovery of Novoselov et al. in 2004 [8]. Significant efforts have been devoted to the development of graphene for new high-performance electrodes for supercapacitors [9]. They are motivated by the exceptional electrical conductivity, high theoretical specific surface of 2620 m²/g, excellent mechanical properties and the theoretical capacity of 550 F/g [10]. Graphene supercapacitors have qualities such as high voltage, shape diversity, miniaturization that integrate seamlessly with the needs of portable electronics [9, 10].

Copper (Cu), one of the widely used metals, has useful properties such as high electrical and thermal conductivity, as well as a relatively affordable price. Recently, as an alternative in electrical devices, considerable attention has been designated to graphene / Cu composites, which have good mechanical and electrical properties. To incorporate graphene into copper powders, currently are available two main groups: ex-situ and in-situ methods [11].

Graphene and its derivatives are suitable for copper reinforcements due to their high thermal conductivity values in-plane (4000-5000 W/m K) and through-plane (10-20 W/m K), excellent mechanical strength, electrical conductivity, and large specific area (SSA-500-1200 m²/g) [12].

In their experiment, Maharana, H.S., Rai, P.K. & Basu, investigated the surface-mechanical and electrical properties of coatings, based on graphene oxide, chemically reduced graphene oxide (RGO), and thermally reduced graphene oxide (TRGO) incorporated into a copper matrix [13]. Cu–TRGO composite coatings show excellent electrical conductivity as compared to GO- and RGO-reinforced composite coatings due to removal of oxygen-containing groups after a thermal reduction process.

Layered graphene composites where zinc oxide particles are interlaid between graphite sheets are also developed [14]. There are no reports of systematic studies of volumetric graphene composites containing zinc oxide nanocrystals. With preliminary experiments, it is found that the deposition of zinc oxide nanocrystals prevents graphene sheet aggregation, resulting in a significant increase in the specific surface area of the nanocomposites, which is directly related to the increase in their conductivity.

The aim of the present study is to develop new composites and appropriate technological schemes to reach a high specific surface by introducing nanoparticulate zinc oxide into volumetric graphene composites. This would help prevent the aggregation of the graphene sheets, which is a major problem with graphene materials. According to our preliminary experiments, the inclusion of nanoparticulate zinc oxide leads to a significant increase in the specific surface and the fuller utilization of the valuable properties of the graphene composites: high mobility of electrical charges, good electrical conductivity, good mechanical and optical properties [15-17].

2. Experimental

2.1. System RGO-ZnO

2.1.1. Synthesis of graphene oxide

Synthesis of graphene oxide is made by applying the modified Hammer’s method by oxidation of graphite powder and ultrasonic treatment [18] In brief, fine graphite powder (10 g) and NaNO₃ (5 g) was vigorously stirred in combination of H₂SO₄/H₃PO₄ in ratio 4:1 (200 ml/50 ml). KMnO₄ (30 g) with d.H₂O (460 ml) was added slowly with stirring in an ice bath to avoid the temperature from exceeding 20°C. After that, the mixture was heated on magnetic stirrer to 80°C for 60 min. Next step is the addition of peroxide solution (760 ml distilled water and 30% H₂O₂ (30 ml)) drop by drop at standard conditions under constant stirring. The product was filtered by standard filter paper through Buchner funnel and washed several times with 1M HCl and water/ethyl alcohol mixture. The filtrate was dried under vacuum
(60ºC) for 12 h., and complete exfoliation of graphite oxide into monolayer graphene oxide is accomplished by sonication. The chemical reduction of the graphene oxide sheets can be achieved with sodium borohydride (NaBH₄), ascorbic acid, and others green reducing agents [19, 20]. This synthesis is known for its reliability, reproducibility, scalability and cost-effectiveness. Furthermore, the possibility of modifying this method in order to influence the structural characteristics of the graphene materials obtained is of importance.

2.1.2. Synthesis of ZnO nanosized particles
Various working schemes are proposed in which zinc acetate or zinc nitrate are commonly used as precursors, as well as suitable solvents. The solvolysis method affects the particle size and morphology of ZnO particles [17]. In the present work, submicron ZnO powder is synthesized by applying aqueous acetal gelling method which is a modification of the techniques proposed by several collectives.

Zinc Acetate (Zn (CH₃COO)₂·2H₂O), isopropanol (C₃H₈O) and acetic acid (CH₃COOH) are mixed in a beaker. The mixture is stirred for 1h at a temperature of 60ºC, after which the temperature is raised to 100ºC to begin evaporation. When the solution is gelled, it is placed in a crucible and dried at 140ºC. The dried gel is then further annealed in 2 steps: First step: Heating at 220ºC for 3 hours. Second step: heating for another 5 hours at 420ºC.

2.1.3. Preparation of composites based on reduced graphene oxide (RGO) and ZnO nanoparticles.
A series of zinc oxide and graphene oxide (ZnO-RGO) based composites (varying by 10w.%) were prepared. The pre-synthesized RGO and nanoparticulate ZnO were mixed in the ratios presented in figure 1. The as prepared compositions are dispersed (5mg/ml) in absolute ethyl alcohol and are subjected to ultrasonic treatment for 2 hours. Then they were dried at 100ºC in a laboratory drier. The resulting samples were placed in a manual press with a hydraulic mechanism. At a pressure of about 260 MPa, tablets with a diameter of 12 mm and a thickness of about 2 mm are produced.

2.1.4. X-ray analysis of the resulting composites
The results of the XRD (figure 1) show that in the composite two phases are present RGO and ZnO. An increase in ZnO peak intensity was observed with an increase in its sample content coupled with the corresponding decrease in the intensity of the RGO peaks.

2.1.5. Scanning Electron Microscopy (SEM) of the materials obtained
Through SEM analysis, the microstructure of the synthesized RGO (figure 2) as well as the selected composite (RGO/ZnO - 50/50) (figure 3) is observed at various magnifications.

The SEM images in figure 2 and 3 show at different magnifications the highly layered structure characteristic of graphene materials. EDX analysis shows the presence of mainly carbon in the test sample with a minimum oxygen content. The size of ZnO nanorods observed in the SEM images is with a diameter of about 48 nm (calculated from XRD data using the Scherer formula).
Figure 2. SEM of the obtained RGO at different magnifications: A-40 kx, B-80kx.

Observed morphology under SEM analysis of the selected composite (RGO/ZnO - 50/50) shows well exfoliated carbon layers, incrusted with well distributed ZnO nanoparticles (figure 3). This proves the formation of nanocomposite material.

Figure 3. SEM analysis of selected composition-RGO/ZnO - 50/50 at various magnifications: A-13 kx, B-22 kx

2.1.6. TEM analysis of selected composite RGO/ZnO (50/50 mass%)
The bright field (BF) TEM images and the corresponding selected area electron diffraction (SAED) pattern of RGO flakes are presented in figure 4 a). It is demonstrated that the procedure of graphite layers exfoliation is successful. figure 4 b) presents BF TEM images, High Resolution (HR) TEM image and SAED pattern for ZnO nanoparticles. As it is seen, the nanoparticles are different in shape and size and tend to aggregate during the drying process of the preparation for TEM analysis procedure. Some of them are elongated, rod-like features, while others possess more isotropic shapes. Their dimensions vary between 20 and 200 nm. The particles are crystalline with hexagonal structure of ZnO with cell parameters a= 3.24170 Å and c= 5.1876 (#96-210-7060), as reveal SAED pattern indexing and HRTEM image. In the composite (RGO-ZnO) sample, two type morphologies are visualized by BF TEM images in figure 4 (a, b). The large and more electronically dense particle (figure 4 c)) is consisting of ZnO nanoparticles attached to a poorly exfoliated graphite. The second type of composite particles exhibit a morphology close to that of graphene and characterized by higher electronic transparency. The aggregate of ZnO nanoparticles attached to the graphene flake is also visible.
2.1.7. Electrical properties

In order to measure the electrical and dielectric properties with an Impedance analyzer and RLC bridge (figure 5), the composites were prepared into 12×2mm tablets in a hydraulic press. For the RGO/ZnO composite materials dielectric measurements the samples with composition ranges up to 5 mass% RGO are dielectric due to dielectric behavior of ZnO. For further increasing of RGO concentration (more than 5%) selected samples are conductive (up to 10^2 S/m).

2.2. System GO-ZnO-Cu NPs

2.2.1. Synthesis of composites GO-ZnO-Cu NPs

A series of composites with GO-ZnO-Cu nanoparticles is synthesized with varying compositions (figure 6) by using the same methodology specified in point 2.1.3. of this article.

2.2.2. XRD, SEM, EDX analysis of composites GO-ZnO-Cu NPs

The as prepared series of nanocomposite material compositions in the GO-ZnO-Cu system are characterized by X-ray diffraction (figure 6), SEM and TEM (figure 7) analysis. The presence of the initial phases in the composites has been proven. The morphology and microstructure of the obtained composites were well characterized by SEM and TEM analysis. Well exfoliated graphene layers and evenly distributed nanoparticles are observed. It is evident from the presented diffraction in figure 6 that in all composites GO is present in predominant amounts, and the other phases - ZnO and Cu are ill defined. The reason is that these phases constitute a small part of the prepared composite and are therefore difficult to identify by XRD. Therefore, other methods of analysis are applied - SEM and TEM in order to identify the respective nanoscale phases - ZnO and Cu. Figure 7 shows TEM images of a selected composite (70GO.10ZnO.20CuNPs) at different magnifications.
Nanoparticles of different shapes, located on the highly folded graphene oxide layers, are very well distinguished. It is observationally evident that at the nano scale, a relatively uniform distribution of nanoparticles in the well-exfoliated graphene structures has been obtained.

![Figure 6](image1.png)

**Figure 6.** X-ray diffraction patterns of composites from the GO-ZnO-Cu NPs system.

![Figure 7](image2.png)

**Figure 7.** TEM images of a composite 70GO.10ZnO.20CuNPs at different magnifications.

### 2.2.3. Electrical measurements

Electrical measurements are made by two-electrode method and application of silver electrodes. An RLC bridge with an operating frequency of 1 kHz is used. Selected samples from the GO/ZnO/Cu system (table 1) were measured for their dielectric characteristics. Examining the dielectric characteristics of samples of the tertiary system GO-ZnO-Cu. The dielectric constant (figures 8, 9), conductivity (figure 10) and dielectric loss (figure 11) are measured in the 1 kHz-100 kHz range. Samples 1, 2 and 4 show identical dielectric constant values (both real and imaginary). Increasing the ZnO contents leads to a decrease in dielectric loss with increase of frequency in all samples (figure 11). It is noteworthy that Sample 2 shows weak frequency dependency, while the other samples are heavily dependent on frequency (figure 11). It is possible, due to formation of cluster regions with different
conductivity - nano grains of conductive copper and low-conductivity shells of copper oxide and a minimum number of GO layers which surround them partially or completely.

**Table 1.** Sample composition ratios of GO-ZnO-Cu nanocomposites.

| Composition          | GO  | ZnO | Cu  |
|----------------------|-----|-----|-----|
| Sample 1 (GO/Zn/Cu)  | 80  | 10  | 10  |
| Sample 2 (GO/Zn/Cu)  | 70  | 20  | 10  |
| Sample 3 (GO/Zn/Cu)  | 70  | 10  | 20  |
| Sample 4 (GO/Zn/Cu)  | 90  | 5   | 5   |

Possibly, with increasing GO content, the shape and size of the copper oxide - GO clusters change significantly, which influences the configuration of the partial volume conductivity. Increasing ZnO contents to 20 % leads to a reduction in dielectric losses and to stabilization of the parameters in the studied frequency range. At a fixed ZnO content in the GO-ZnO-Cu nanoparticle system, the increase in the content of copper nanoparticles slightly changes the frequency characteristics of dielectric parameters and leads to reduced dielectric losses.

**Figure 8.** Graphical representation of the frequency dependence of the real part of the dielectric constant of selected GO-ZnO-Cu composites against frequency.

**Figure 9.** Graphical representation of frequency dependence of the imaginary part of the dielectric constant of selected GO-ZnO-Cu composites.

**Figure 10.** Graphical representation of frequency dependence of conductivity in selected GO-ZnO-Cu composites.

**Figure 11.** Graphical representation of the frequency dependence of dielectric loss selected GO-ZnO-Cu composites.
3. Conclusions

For the RGO/ZnO composite materials dielectric measurements the samples with composition ranges up to 5 mass% RGO are conductive. For higher concentration of RGO (more than 5%) selected samples are dielectrics.

Preliminary expectations for the GO-ZnO-Cu nanoparticle system in general, are that the addition of ZnO allows for better control of the properties of graphene composites. Increasing ZnO contents to 20% leads to a reduction in dielectric losses and a stabilization of the parameters in the studied frequency range. At a fixed ZnO content in the GO-ZnO-Cu nanoparticle system, the increase in the content of copper nanoparticles slightly changes the frequency characteristics of dielectric parameters and leads to reduced dielectric losses. It is probable that the dielectric behavior of the studied composites is due to the peculiarities of the microstructure of the GO components when mixed with copper and formation of cluster regions with different conductivity is likely.

The present work is promising for future research in which to create promising new composite materials based on RGO-ZnO and Go-ZnO-Cu with controlled shape and size of copper oxide-RGO clusters.

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