GRAPHENE OXIDE-SILVER NANOWIRES COMPOSITES FOR PROTECTION AGAINST MODERN POLLUTION – ELECTROMAGNETIC WAVES

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Abstract
With the development of the electronic industry, telecommunication, transportation, energy storage devices, and wireless technologies, the need for materials that are able to block electromagnetic waves (EMWs) in low-frequency regions of the spectrum is increasing. A new type of pollution named pollution by EMWs is an inevitable component of modern life. Although materials efficient in blocking the propagation of EMWs are developed, these materials show drawbacks regarding durability and mechanical properties, as well as a high production price and processability. Thus, new eco-friendly and durable materials are needed. Herein, we produced composites based on graphene oxide and silver nanowires to create an efficient shielding barrier for low frequencies (0-15 GHz) EMWs.

Introduction
The industrial progress and development of new electronic devices made everyday life more simple and conformable. At the same time, all devices that generate, transfer, and use electrical energy, emit in the area around them Electromagnetic Waves (EMWs). In this way, a new type of environmental pollution, so-called EMW pollution becomes an inevitable component of everyday life [1].
Current research laboratories and researchers across the world are facing issues with EMW inferences which lead to prolonged measurements, shortening of the equipment lifetime, and unwanted signal and noise [2].
Thus, there is currently a large demand for efficient EMW shielding materials. The efficiency of the materials to block EMW propagation is related to reflected (SE_R), absorpted (SE_A), and multiple reflected EMWs (SE_{MR}) [3]. The total shielding efficiency of material (SE_T) is the sum of these three components and it is expressed in dB. Commercial applications demand a SE_T of 20 dB is considered an acceptably efficient material since it blocks 99% of the total incident energy [4].
Common shielding materials are metals such as Cu, Al, and Ag [5], but they are hard to process, chemically unstable, and rigid which makes them unfavorable for current technological requirements. Another group of shielding materials is conducive polymers (CPs) with high SE_T, lightweight, good mechanical properties such as flexibility and resistance to humidity [6]. But, CPs showed the issues regarding processability [7]. Particularly interesting and highly efficient shielding materials are MXene due to its high electrical conductivity which is a key parameter for EMI shielding materials and it is between 5 S cm^{-1} to above 20,000 S cm^{-1} [8, 9].
Considering mechanical, chemical, and electrical properties, but also ecological and economic aspects of production, graphene and its derivates, are one of the promising materials for EMI

shielding [10]. Thanks to its mechanical strength, elasticity, lightweight, chemical stability, and tunable electrical properties, graphene derivates become a spotlight of shielding material [11]. Graphene was isolated from graphite using a simple experiment, an adhesive tape and graphite in 2004 [12], and later in 2010, Geim and Novoselov won a Nobel prize. Graphene is a single atomic layer of graphite and contains only sp^2 hybridized C atoms [12].
Since then, various methods for the production and modification of graphene have been reported, such as chemical vapor deposition (CVD), electrochemically exfoliated graphite, and Hummers oxidation of graphite followed by chemical reduction [11].
Herein, we prepared graphene oxide by oxidizing graphite with an improved Hummers method [12] and produced silver nanowires (AgNWs) by chemical reduction of Ag ions with ethylene glycol in the so-called polyol method [13]. After, two separately produced nanomaterials were mixed in different mass ratios and deposited using vacuum filtration producing homologous and uniform free-standing films. The efficiency of these films in blocking EMWs was studied.

Experimental

For GO synthesis, graphite powder (KS6, TIMREX®, Bodio, Switzerland) was used as a starting material [12]. First, graphite powder was sonicated in ccH_2SO_4 in a concentration of 43 mg mL^{-1}, and then three times the larger amount of $KMnO_4$ was carefully added while the temperature was kept at 4 °C, for 30 min, followed by heating at 40 °C for 30 min. In the next stage, a double volume of water was gradually added, and for another 15 min, the temperature was kept at 90 °C. The reaction was stopped by pouring the mixture into water. GO was cleaned from residual acid and ions using centrifugation (3500 for 30 min) till a pH of 7. The precipitate was then dried under reduced pressure and GO in the form of powder was collected.
Separately, AgNWs were produced using a previously described method [13].
To produce GO-AgNWs composites, GO powder was dispersed in water at a concentration of 1 mg mL^{-1}, while AgNWs were sonicated shortly in ethanol at the same concentration. Then, different volumes of both dispersions were mixed at room temperature for 30 min. The mass ratio of GO and AgNWs varied from 20:80 to 50:50. Samples were named GO-AgNWs 20:80 and 50:50. After mixtures were stabilized, they were transferred in a system for vacuum filtration to produce free-standing films. For each dispersion, the same volume (15 mL) was poured. After drying, samples were detached from the membrane surface.
For reduction, films were heated at 90 °C for 8 hours in a water solution of L-(+)-ascorbic acid (AA, 15 mM) [11]. After reduction, films were washed in 400 mL of water and dried.
To analyze the morphology of the surface of free-standing films, a scanning electron microscope (SEM) was used. All measurements were performed in a high vacuum. A high-resolution scanning electron/focused ion beam (dual-beam) microscope Tescan® LYRA 3 FEG / XMH SEM was used. Images were captured using a secondary electron detector. The acceleration voltage was 10kV.
Tetmogravimetic analysis of composites was conducted using the Mettler Toledo TGA/DSC 3+ instrument. The samples were heated from ambient to 700 °C at a scan rate of 5 K min^{-1}, under nitrogen purge (20 mL min^{-1}).
Shielding properties of free-standing films were characterized in the microwave regime using a homemade dedicated coaxial test cell operating in reflection and transmission mode. In its essence, the test cell consists of two semi-rigid coaxial cables that sandwich the free-standing film. Special attention is paid to minimizing RF crosstalk and parasitic RF radiations using grounded metallic structures. The test cell is connected to a Keysight Technologies Streamline P5008A Vector Network Analyzer (VNA), with operating frequency set to 150 KHz-18 GHz, input RF power of -15 dBm, at 25 °C. The test cell is connected to the VNA using highly stable coaxial cables.

Results and discussion

Morphology of samples was investigated using SEM and images are presented in Figure 1. In Figure 1a), a cross-sectional view of GO film is presented, showing lamellar morphology and a thickness of around 12.58 μm. In the case of composites GO-AgNWs, the bright, rodlike structures packed between graphene sheets could be observed. These images indicated that GO sheets are closely wrapped around AgNWs and located in the middle of the composite (Figure 1c and d). TGA measurements (Figures 1e and f) showed better thermal stability of composites after reduction (red curves). The weight loss between 100 and 231 °C could be attributed to the removal of the labile oxygen groups (such as carboxylic and aldehydes groups) and residual water [15] and it is 13.67% for GO-AgNWs 50:50 and 4.73 % for GO-AgNWs 20:80. After reduction, these values were 2.52% and 1.05%, respectively. These changes indicated successful chemical reduction with AA. The second weight loss between 260 and 460 °C is a result of the decomposition of stable oxygen groups as epoxides [15]. At 460 °C weight loss for GO-AgNWs 50:50 was 71.87% and 90.50% after reduction, while for GO-AgNWs 20:80 was 87.29%, and after reduction 95.46%. The results indicated the removal of epoxy groups.

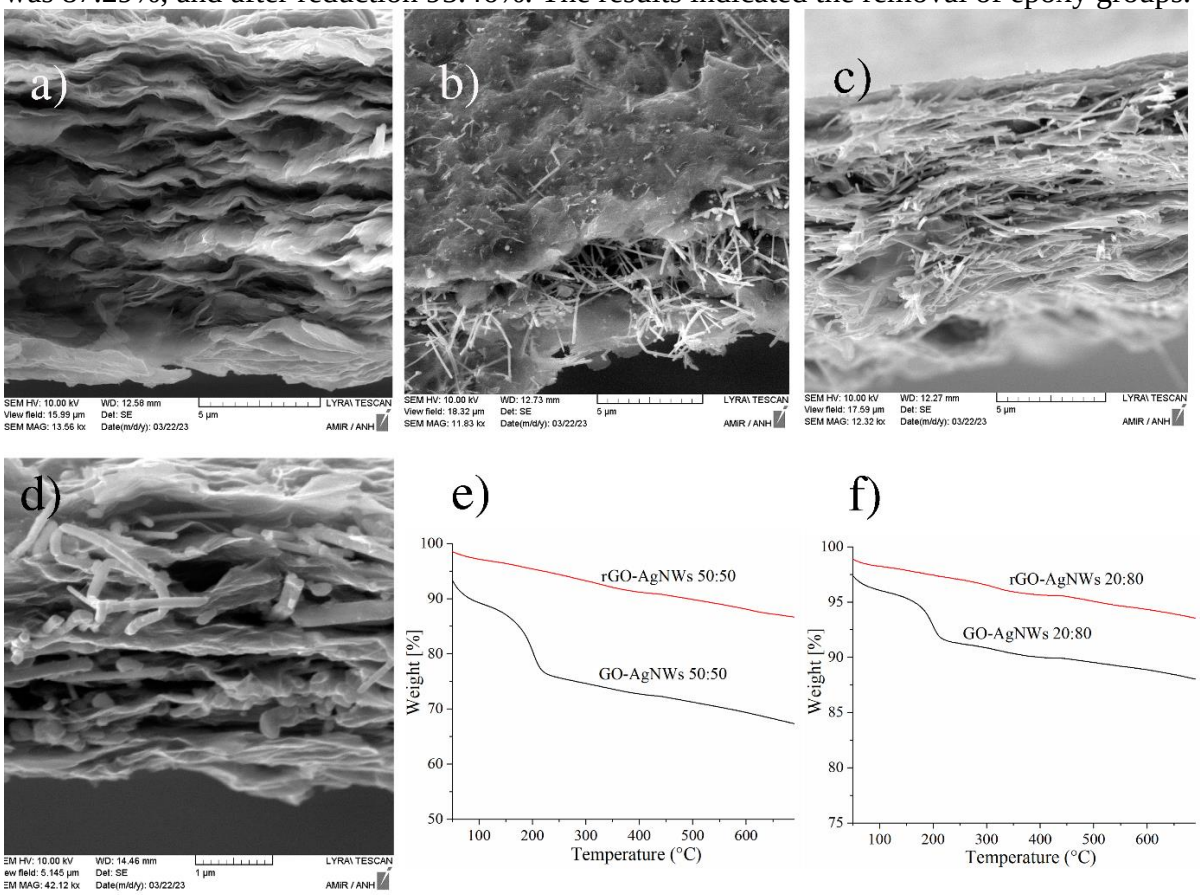

Figure 1. SEM images of GO (a), top (b) and cross-sectional view (c) of GO-AgNWs 50:50, and rGO-AgNWs 50:50 (d), TGA of (r) rGO-AgNWs 50:50 (e) and (r)GO-AgNWs 20:80 (f).

Results obtained by investigating the shielding properties of rGO-AgNWs 20:80 are presented in Figure 2.

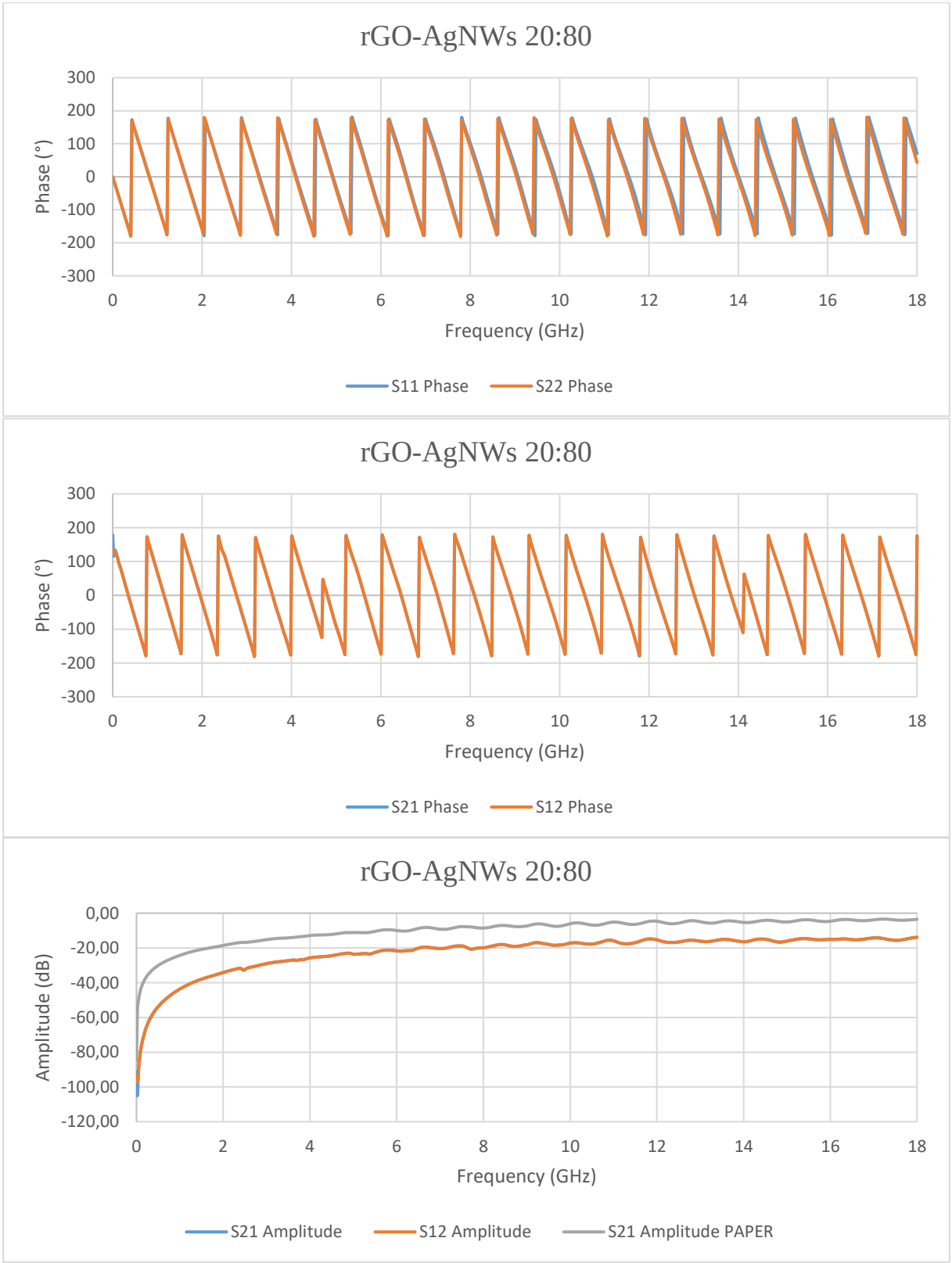

Figure 2. Measured amplitudes of the transmission coefficient of the coaxial test cell loaded with rGO-AgNWs 20:80 as shielding materials.

The measured complex reflection coefficients vary from 0 to 3.5 dB. As the set-up is calibrated at the output of the coaxial cables, the microwave paths in the test cell (from coaxial input up

to the coaxial aperture are not taken into account by the calibration procedure). In addition, each sample is inserted between two cellulose papers (named PAPER) that need to be taken into account to isolate the signature of the sample only. In particular, the PAPER only shows a variation of the amplitude of the complex reflection between 0 to 5.5 dB. Therefore, better reflection is observed between PAPER only and PAPER loaded with the material. In addition, the amplitude of the transmission coefficient falls when the PAPER is loaded with the material under test. For instance, the amplitude is shifted from around 20 dB at 2 GHz. These results indicated that the obtained composite is an efficient shielding material, considering that the shielding efficiency of 20 dB is acceptable for commercial applications [4].

Conclusion

A new type of environmental pollution caused by low-frequency range electromagnetic waves needs to be addressed urgently. In this paper, composites based on graphene oxide and silver nanowires were studied as a potential solution for the growing problem regarding EMW shielding. Composite rGO-AgNWs 20:80 showed a satisfying shielding efficiency to block the propagation of EMWs.

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