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Lecture Proceedings

GAMMA IRRADIATION AS A TOOL FOR MODIFICATION OF GRAPHENE OXIDE-SILVER NANOWIRES COMPOSITES

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Abstract
Graphene oxide (GO) was produced using the Hummers' method while silver nanowires (AgNWs) were obtained by polyol synthesis. Composite was produced by simple mixing of GO and AgNWs dispersions. The composite was produced in a form of free/standing films by vacuum filtration and exposed to gamma irradiation in an oxygen-free atmosphere. After irradiation, without any additional cleaning, the structure, morphology and electrical properties were investigated. Gamma irradiation was shown to be an efficient tool to induce a chemical reduction of GO, and it was able to improve the electrical conductivity of produced composites. Due to avoiding the usage of reagents and solvents, this method belongs to green chemical approaches.

Introduction
Graphene oxide (GO) is a water-dispersible derivate of graphene [1]. While graphene is built from only benzene aromatic rings, it is highly hydrophobic and hard to disperse in polar organic solvents and water, GO has a large amount of polar, O-containing functional groups in the amount of 33.6 at% [2], made GO dispersible in water and polar solvents. On the other side, when O-functional groups are incorporated into graphene sheets, they disrupt the delocalized π-electronic cloud, responsible for extraordinary electrical properties of graphene such as electrical conductivity, and increased the resistance of 14.8 MΩ [2]. Thus, GO is more processable than graphene, but it does not have graphene's electrical properties.
Due to this condition, GO was often reduced using different chemical reactions, such as reaction with hydrazine monohydrate, H_2, sodium borohydride, or HI [2-5]. These reactions demand the use of dangerous, hazardous reagents as well as organic solvents to remove residual reagents and side products. Due to the price of chemicals and appropriate handling and storing of toxic waste, these procedures are both ecologically and economically unfavorable.
Herein, we investigated the possibility of using gamma irradiation in the reduction of GO in a composite based on GO and silver nanowires (AgNWs). These composites attract scientific attention due to their good electrical conductivity and electromagnetic shielding efficiency [6-8]. Studies have shown that the electrical properties of GO-AgNWs can be improved by chemical reduction. In this paper, we explored the effects of different doses of gamma irradiation onto GO-AgNWs under an oxygen-free atmosphere. Gamma irradiation of GO at a dose of 35.3 kGy was able to reduce the sheet resistance from 10^7 Ω □$^{-1}$ to 100 Ω □$^{-1}$ [9]. During the exposure, gamma rays induce radiolytic decomposition of the medium and, if oxygen is present, oxidative, oxygen-containing free radicals species were produced and caused the oxidation of the material [10], while in the case when the medium for irradiation is oxygen-free or contained quenchers of oxygen free-radicals [11, 12], the chemical reduction will occur.

Thus, in this study we selected doses of gamma irradiation up to 35 kGy and an oxygen-free atmosphere.

Experimental

GO was produced using a previously described modified Hummers' procedure [13]. AgNWs were obtained according to the polyol method [14]. Composite GO-AgNWs were prepared by simply mixing the same volumes of GO dispersion in water (1 mg mL^{-1}) and AgNWs (1 mg mL^{-1}) in ethanol. A magnetic stirrer was used for homogenization and after 1 h of mixing, the dispersion was deposited onto the membrane filter (*Isopore* membrane filter, polycarbonate, hydrophilic, pore size 0.22 μm) using a vacuum filtration system. The composite was peeled off from the membrane after drying, and collected as a free-standing layer and named GO-AgNWs 1:1. The samples were then exposed to gamma irradiation. Argon atmosphere was selected as an irradiation medium. Samples were exposed to irradiation doses of 15, 25 and 35 kGy and named GO-AgNWs $1:1^{15}$, GO-AgNWs $1:1^{25}$, and GO-AgNWs $1:1^{35}$, respectively. Structure, morphology and electrical properties were investigated before and after gamma irradiation.

Quesant atomic force microscope (AFM, Agoura Hills, CA, USA) was used to investigate the morphology of films. It was operating in tapping mode, at room temperature. All measurements were done under the air atmosphere. Q-WM300, a monolithic silicon AFM probe was used. The non-contact mode was selected for obtaining the AFM images. We used standard silicon tips with a force constant of 40 N/m by NanoAndMore GmbH, Wetzlar, Germany. Gwyddion 2.53 software was used for image analysis [15].

Both GO and composite based on GO and AgNWs were investigated using scanning electron microscopy (SEM) with energy-dispersive X-ray (EDS) spectroscopy. The FEI ESEM Quanta 200 microscope (FEI Company, Hillsboro, OR, USA) was used. Free-standing films were scanned at the SEM microscope without any additional preparation of the surface of the sample (no metalization). A “low vacuum mode” was selected. EDS measurements were obtained focusing the analysis over an area of ca. 230x200 microns. Data were analyzed using the EDAX Genesis EDS microanalysis software (AMETEK, Inc., Berwyn, PA, USA).

Electrical properties of the material were investigated using a 4-point probe Jandel RM3000+ (Leighton Buzzard, UK) test unit. The probe spacing was 1 mm. Measurements were conducted in room conditions, each measurement was repeated at 3 different locations and the average values of sheet resistances and conductivities were calculated.

Results and discussion

Morphology of the composite before and after gamma irradiation was investigated using an AFM microscope and these results are presented in figure 1. It was calculated that the mean surface roughness was 376 and 210 nm for GO and GO-AgNWs 1:1, respectively, while for composites irradiated with a dose of 15, 25, 35 kGy, it was measured 237, 265, 219 nm, respectively.

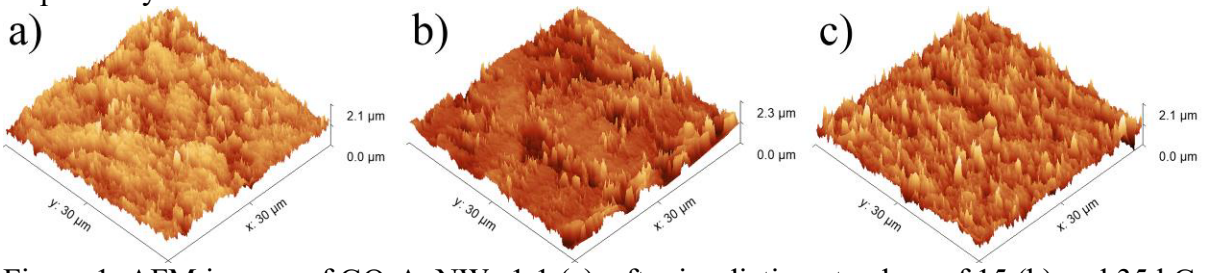

Figure 1. AFM images of GO-AgNWs 1:1 (a), after irradiation at a dose of 15 (b) and 35 kGy (c).

SEM-EDS was used to investigate both the morphology and chemical composition of GO and composite (figure 2.). It was detected GO free-standing film has a uniform, grainy surface (figure 2a and b), while the cross-section image showed that the thickness was around 12 µm. In the case of the composite, cylindrical objects were noticed (figure 2e and e), which were particularly clear at the cross-section image (figure 2g). The thickness of GO-AgNWs 1:1 was 17 µm. EDS spectra showed that C and O were dominant in GO film, while C, O and Ag were detected in composites (figure 2d and h).

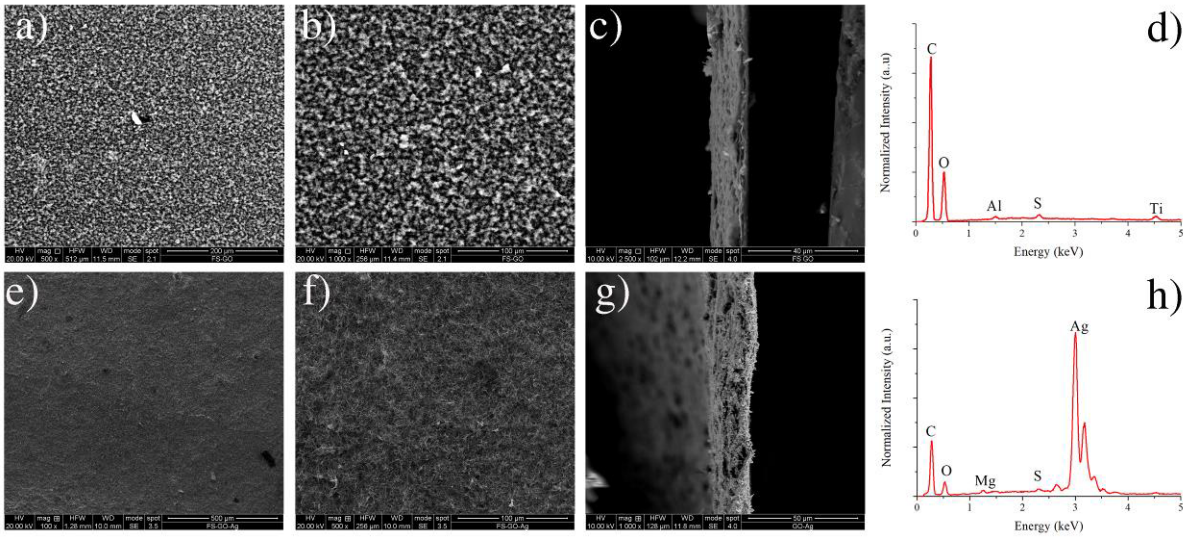

Figure 2. Top view (a, b) and cross-section SEM images of GO (c), and EDS spectrum of GO (d); and the same for composite GO-AgNWs 1:1: top-view (e, f), cross-section (g) and EDS (h), respectively.

In figure 3, photos of GO and GO-AgNWs 1:1 are displayed. As it can be seen, GO film was easily breaking upon bending while composite GO-AgNWs 1:1 was more elastic and mechanically stable.

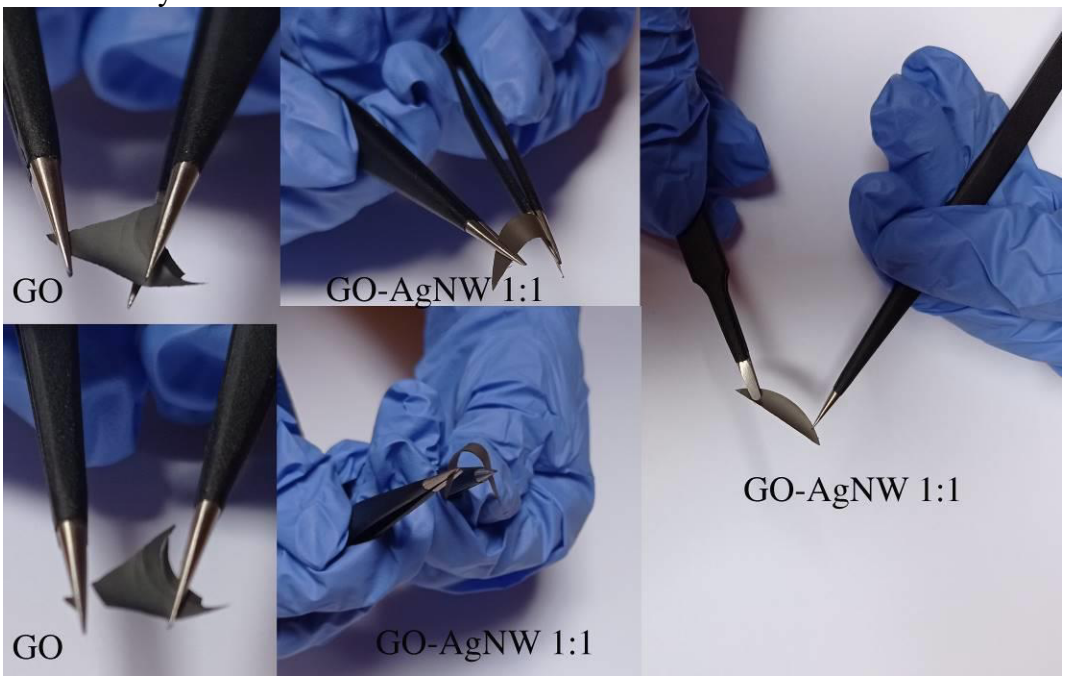

Figure 3. Photos of the free-standing film: GO and GO-AgNWs 1:1, as indicated.

When the composite was exposed to gamma irradiation, the changes in electrical properties were investigated using a 4-point probe. In figure 4a, conductivity vs. applied gamma irradiation dose is reported. At the lowest applied dose (15 kGy), conductivity was significantly increased, from 167 to 430 S cm^{-1}. At higher doses, 25 and 35 kGy, conductivity also increased, for 99.4 and 32.9%, respectively. These results can be explained by taking into account the chemical reduction of GO during gamma-irradiation, which leads to an increase of conductive, π-domains in graphene sheets [16, 17]. The conductive nature of the gamma-irradiated composite with the dose of 15 kGy was studied by analyzing the current (I)–voltage (V) curve (figure 4b). The current increased linearly with voltage (figure 4b).

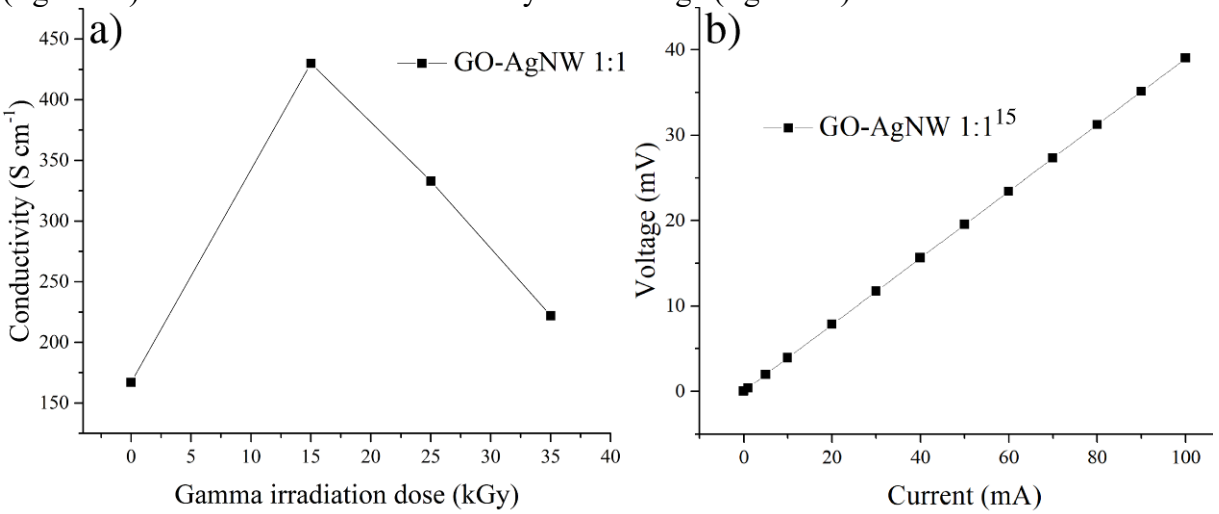

Figure 4. The conductivity of GO-AgNWs 1:1 vs. applied gamma-irradiation doses (a) and I-V curve for GO-AgNWs $1:1^{15}$ sample (b).

Conclusion

Although chemical reduction of GO and GO-based composites leads to improvements in the electrical conductivity of these materials, these procedures demand the usage of toxic and hazardous chemicals. Gamma irradiation showed to be a good alternative due to avoiding of usage of chemical reagents as well as no need for the cleaning stage. By simple gamma irradiation of free-standing GO-AgNWs composites under argon atmosphere, electrical conductivity increased by almost three times.

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