Synthesis of Cu-GPNs/Polyvinyl chloride (Cu-GPNs/PVC) nanocomposite for application as an electromagnetic wave reflecting material

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Received 2 Oct. 2024; Revised 19 Nov. 2024; Accepted 2 Dec. 2024; Published 25 Dec. 2024.

DOI: https://doi.org/10.54939/1859-1043.j.mst.100.2024.83-89

ABSTRACT

This article presents a method for synthesizing Cu-GPNs/PVC nanocomposite materials. Cu is synthesized from $CuCl_2$ *salt using ascorbic acid as a reducing agent. Graphene nano sheet (GPNs) was synthesized using the oxidation method of graphite, then reducing it at high temperatures. The characteristics of Cu nanoparticles, graphene were determined using Field Emission Scanning Electron Microscopy (FE-SEM), Transmission Electron Microscopy (TEM), Energy-dispersive X-ray spectroscopy (EDX), and X-ray diffaction (XRD). With a mass ratio of 5% nano Cu and 10% graphene, the Cu-GNPs/PVC nanocomposite film with a thickness of 0.6 mm can reflect from 86.89% to 90.78% at a frequency of 8-12 GHz.*

Từ khóa: Graphene; Cu nanoparticles; Reflective; Electromagnetic.

1. INTRODUCTION

The future battlefield will be defined by the use of high-tech weapons combined with current reconnaissance equipment and technology capable of detecting targets under complicated weather circumstances. As a result, finding and implementing ways to improve the effectiveness of camouflage and deceiving actions is critical for reducing damage to forces, vehicles, weapons, and equipment. Deceive actions are a technique for displaying the traces of a real target in order to confuse the reconnaissance of attackers and damage equipment, therefore protecting and improving the real survivability of the target. Decoy solutions use materials, models, fake structures, fake activity traces, and fake signal-generating devices to look like the target activity traces and confuse reconnaissance and guidance equipment.

Decoy targets are false structures and models such as roads, bridges, cars, airplanes, tanks, artillery, and battlefields. The deception targets are intended to resemble combat vehicles for ground, aerial, optical, thermal, and radar reconnaissance. Decoy targets are used in operations to confuse and fool the opponent while protecting actual targets from detection and damage [1]. To directly camouflage real targets, decoys must have corresponding signatures, such as surface signatures, activity, and distribution, be compatible with operational tactics, be lightweight, easy to assemble, move, and install quickly, and be made from readily available natural materials at a low cost. In a modern battlefield, radar has emerged as an important sensor for the detection and targeting of enemy military assets. Radar is a system that uses electromagnetic wave radiation frequencies ranging from 3 MHz to 300 GHz to detect and determine the distance of objects, speed, and position. In the military, radar is commonly utilized for navigation of ships, boats, and aircraft, as well as weather monitoring, reconnaissance, detection, and target localization.

Polymer materials have been frequently employed in the creation of camouflage models for technical equipment weaponry because of their lightweight, great mobility, and variety of forms and shapes. However, most polymer materials are electrically insulating and visible to electromagnetic radiation, making it impossible to achieve radar invisibility standards. Many scientists have expressed interest in research approaches that combine polymers with conductive materials like graphene and metal nanoparticles to address the decoy issue for targets in the X-band frequency range of 8 to 12 GHz. Graphene has numerous outstanding properties, including high electron mobility, a large specific surface area, and good electrical and thermal conductivity. It has been used in a variety of subjects, including the reflection and shielding of electromagnetic waves. In 2018, Kangar and coworkers investigated the synthesis of epoxy coatings containing 50% graphene by weight. The authors discovered that just 0.002% of the electromagnetic wave energy passed through, with the majority being reflected at the surface of the coating [2].

Metallic nanoparticles with special size effects also attract significant attention from many researchers in the field of manufacturing electromagnetic wave reflection films. Using a combination of graphene and metal nanoparticles dispersed in a polymer matrix can achieve effective electromagnetic wave reflection. Another study by Kumar et al. (2020) dispersed graphene (25% by weight) and TiO_2 (25% by weight) into epoxy resin. The membrane has an electromagnetic wave reflection efficiency of 70 - 80% [3].

This article presents a method for fabricating Cu nanoparticles and graphene nanosheet composite films on a PVC substrate, aimed at applications in decoy materials and electromagnetic wave reflection in the X-band frequency range from 8 to 12 GHz.

2. EXPERIMENT

2.1. Chemicals

- Anhydrous copper chloride ($CuCl_2$, Macklin) was used as a precursor for the preparation of copper nanoparticles. Ascorbic acid ($C_6H_8O_6$, Macklin) was used as a reducing agent. Polyethylene glycol (PEG, Macklin) was used as a dispersant and coating agent, and deionized water was used as a solvent. Sodium hydroxide (NaOH, Macklin) was used as a pH modulator.
- Graphite powder (99%), H_2SO_4 (98%), H_3PO_4 (85%), HNO_3 (63%), $KMnO_4$ (99%) were used in the synthesis of GO.
- N-hexane used as a solvent, liquid PVC resin (d = 1,13 g/mL, solid content = 20%) was used as a film-forming agent, and dioctyl phthalat (DOP) was used as a plasticizer.

All chemicals are used without further purification.

2.2. Preparation of nanocomposite Cu-GNPs/PVC

Synthesis of Cu nanoparticles

Typically, 0.33 g of anhydrous copper chloride and 2 g of polyethylene glycol (PEG) were dissolved in 100 mL of deionized water, resulting in a blue aqueous solution. Subsequently, 0.5 g of sodium hydroxide was dissolved in 50 mL of deionized water as well. The produced sodium hydroxide solution (0.25 M) was gradually added to the copper chloride solution at room temperature temperature while being stirred vigorously (pH = 12). The solution turned out to be a blue suspension. Then, 0.88 g of ascorbic acid was solubilized in 100 mL of deionized water, and a transparent solution formed. Next, the ascorbic acid aqueous solution was slowly introduced into the above blue suspension while maintaining vigorous stirring. The color of the suspension changed from blue to green; finally, a reddish suspension was obtained after 30 min of reaction. The as-prepared products were centrifuged from the solution at 4000 rpm for 30 minutes. The derived products were washed with deionized water three times and dried in N_2 gass, 4 hours and 60 ^{o}C for characterization.

Synthesis graphene nanosheets (GPNs)

GO was synthesized from graphite powder by chemical oxidation via the improved Hummer's method reported in 2010 by Marcano et al. [4]. Briefly, 1.0 g graphite powder was added into 100 mL of a mixture of concentrated acid H_2SO_4 and H_3PO_4 (90 mL and 10 mL) under vigorous stirring. Then 6.0 g $KMnO_4$ was added slowly. The oxidation reaction was carried out at 50 ^{o}C with continuous stirring for 3 hours. After that, 100 mL of water with H_2O_2 (30%) was added to the mixture, and the color of the solution turned from brown to yellow. The precipitate was centrifuged off, washed several times with distilled water, and then sonicated for 1 hour to form GO. Annealing GO in an N_2 gas environment for 2 hours, 800 ^oC with a heating rate of 10 ^oC/min, yields graphene, denoted as GPNs.

Synthesis of Cu-GPNs/PVC nanocomposite film

Powder nano copper and graphene samples were used directly to fabricate film reflecting electromagnetic waves without any further modification. A mixture of 10 wt% graphene powder, 5 wt% nano copper, 80 wt% of liquid PVC resin, 5 wt% of DOP were mixed well with an adequate amount of n-hexane solvent in a ball mill for 6 hours to form a homogeneous slurry. The slurry was then balde cast onto polyester fiber fabric. After being dried at 80 ^oC for 2 hour, the film was cut into square of 30 cm of length, which were utilized as reflection material test. Ater drying, the thickness of film is 0.6 mm and measured with an Ecometer device.

2.3. Characterization

The crystal structure of the Cu nanoparticles was identified by a powder X-ray diffractometer (XRD) employing radiation (λ = 1.5418 Ao) at 50 kV and 200 mA. The surface morphology of materials was observed by a field emission scanning electron microcopy (FE-SEM, Hitachi S4800, Japan) at 5 kV and by a high-resolution transmission electron microcopy (HRTEM, Philips TECNAI F30) at 200 kV. Particle size was analyzed by the laser scattering method on the DLS 9500 device.

The Cu-GNPs/PVC nanocomposite film was tested to determine its radar-reflective properties. The test setup is shown in figure 1.

The signal generator is used with a power level of 20 dBm. The frequency of electromagnetic reflective effectiveness values of Cu-GNPs/PVC nanocomposites film were determined in the X-band (8 to 12 GHz) frequency. The measurements were taken using a vector network analyzer (VNA). A graded dielectric radar absorbers were used on the floor to only allow reflections from the test area. The experiment was performed in an anechoic chamber to further eliminate the interference effects of antenna back and sidelobes. Initially, an aluminum plate of known size was kept as a reference object, and the measurements from 8 to 12 GHz were re-recorded. Then the plate was replaced with a flat piece of reflective material of the same dimensions, and the measurements were repeated. Both these measurements were plotted on the same plot for comparison.

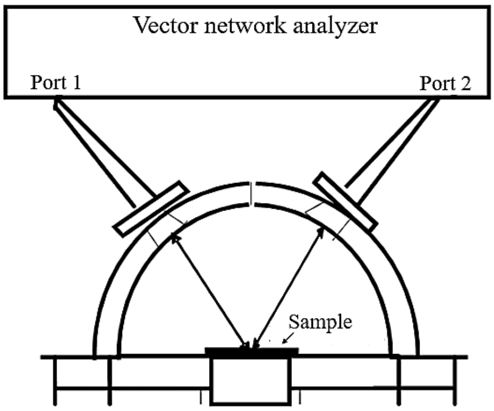

***Figure 1**. Test setup for measuring radar reflectivity of the film.*

3. RESULTS AND DISCUSSION

3.1. Synthesis of Cu nanoparticles

The crystal structure of Cu nanoparticles was analyzed using X-ray diffraction (XRD), and the results are presented in figure 1.

As shown in XRD patterns of Cu nanoparticles in figure 1, there are clear diffraction peaks at $2\theta = 43.7^o$, $50.7^{o,}$ and 74.3^o which are indexed to (111), (200) và (220) planes of metal copper. This indicates that metal copper had been prepared in composites. In addition, the diffraction peak of copper oxide can be found in XRD pattern at $2\theta = 36^o$ related to (111) plane of Cu_2O material. The cause may be due to a small portion of Cu nanoparticles being oxidized to form Cu_2O. The redox equation is shown as follows [5].

$$CuCl_2 \rightarrow Cu^{2+} + 2Cl^- \quad (1)$$

$$Cu^{2+} + C_6H_8O_6 \rightarrow CuCl + C_6H_7O_6^- + HCl \quad (2)$$

$$CuCl + C_6H_7O_6^- \rightarrow Cu^o + C_6H_8O_6 + HCl \quad (3)$$

$$4\ Cu^o + O_2 \rightarrow 2\ Cu_2O \quad (4)$$

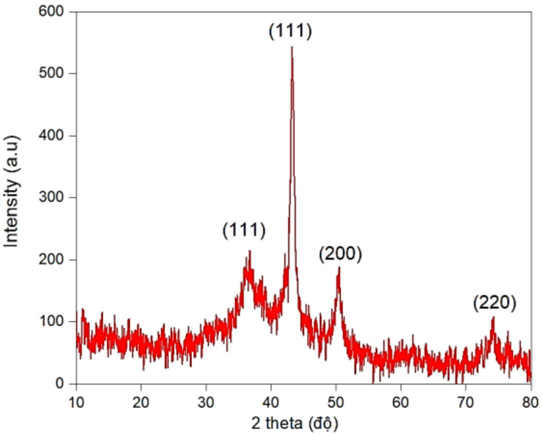

Figure 2. *X-ray diffraction pattern of Cu nanoparticles.*

The morphology of Cu nanoparticles was investigated through FE-SEM/EDX. Figure 3 shows fabricated powders FE-SEM and their corresponding EDX analysis. In terms of Cu nanoparticles, it is observed that spherical particles are formed. The particles are quite small, about 30-40 nm. The elemental composition of Cu nanoparticles was analyzed using X-ray energy dispersive spectroscopy (EDX). The EDX spectrum indicates the presence of the elements O and Cu. The results in figure 2 show the presence of Cu with energy peaks appearing at 0.81, 8.04, and 8.90 eV. Observing the energy peak of O appearing at 0.52 eV confirms the existence of a small amount of Cu_2O. The results show that in addition to the main component Cu, which accounts for 93.15% by weight, there is a small amount of O that accounts for 6.75% by weight. This proves that a small amount of Cu has been oxidized to Cu_2O.

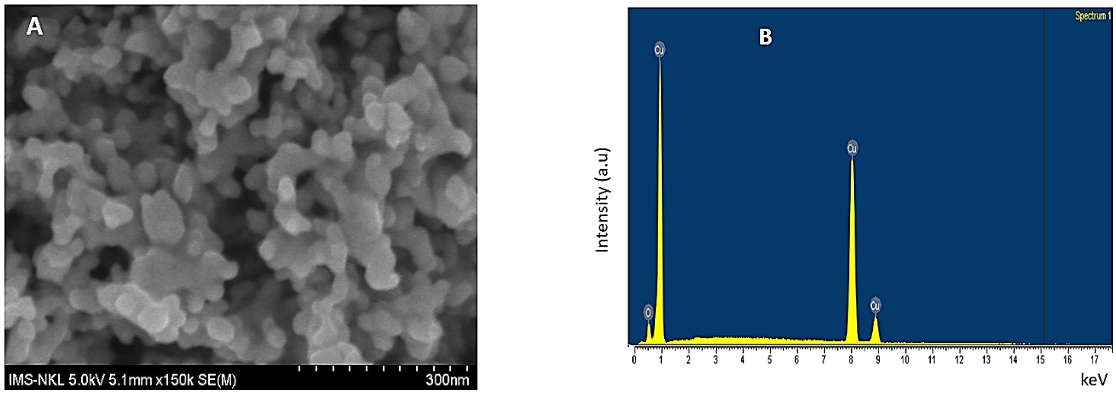

Figure 3. *FE-SEM image and the corresponding EDX measurement of Cu nanoparticles.*

The percentage by mass and atomic of the elements were averaged from 5 different points and presented in table 1.

Table 1. *The element of Cu nanoparticles.*

Sample	Element	% Atomic	% Weight
Cu nanoparticles	Cu	87.81	93.15
	O	12.19	6.75

The morphologies of typical nanoparticles were analyzed by TEM image, and the results are presented in figure 4A. The nanoparticles exhibit typical spherical morphology with a size means diameter of 30 nm, the particles are quite evenly distributed. The particle size distribution results (figure 4B) show that the particle size distribution of Cu nanoparticles is very concentrated, represented by a high peak and a narrow base. The average particle size is 40 nm, with the cumulative percentage of particles concentrated in the size range of 30-50 nm accounting for 65% of the total particle volume.

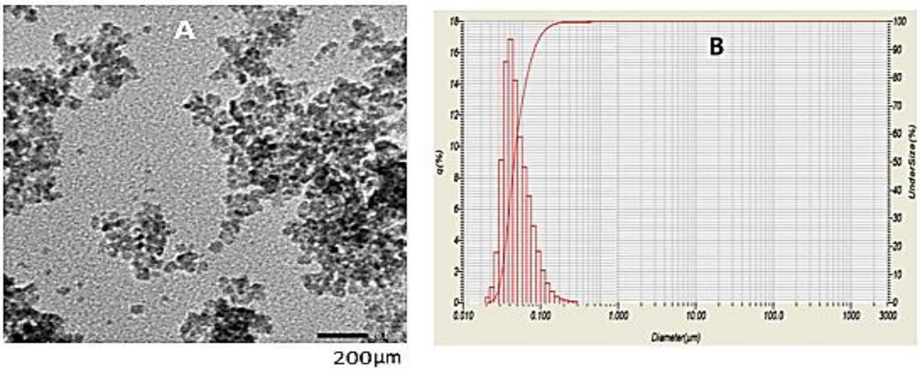

Figure 4. *(A) TEM image and (B) particle size of Cu nanoparticles.*

3.2. Synthesis of graphene nanosheet (GPNs)

The morphology of GPNs was investigated through an FE-SEM image. As can be seen in figure 5A, GPNs contain nanosheet structure. The micrographs show wrinkled sheets of GPNs.

Raman spectroscopy is a powerful equipment for the determination of defect rate. Raman spectra of GPNs are displayed in figure 5B. There are two typical peaks at 1350 and 1590 cm^{-1} in Raman spectra, corresponding to D and G peaks of carbon. The D peaks represent the defects and the disorder in carbon. The G peak is associated with the vibration of in-plane sp^2 hybridization. The intensity ratio of D and G peaks (I_D/I_G) reflects the graphitization degree of carbon-based materials. Based on the test results, the I_D/I_G values of GPNs are around 1.02, indicating disorders and defects in the structure of GPNs.

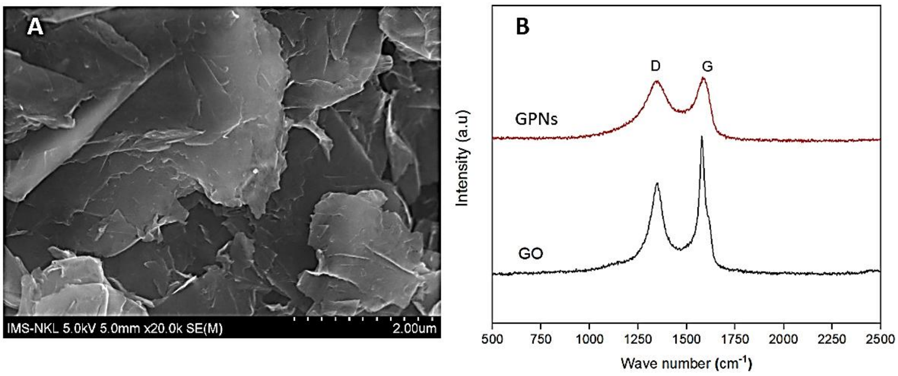

Figure 5. *(A) FE-SEM image and (B) Raman spectra of GPNs material.*

3.3. Synthesis of Cu-GPNs/PVC nanocomposite film

Morphologies of the Cu-GPNs/PVC nanocomposites film were analyzed by FE-SEM image. figure 6 presents the surface (A) and the cross (B) image of the nanocomposite film.

Observing the surface of the film sample, it is noted that materials such as Cu nanoparticles and GPNs are evenly dispersed in the PVC resin. From the cross-sectional images, the structure of graphene in the coating can be observed. The ingredients are evenly distributed, and the film has a tightly structured composition. This structure can enhance the efficiency of electromagnetic wave reflection compared to a PVC film.

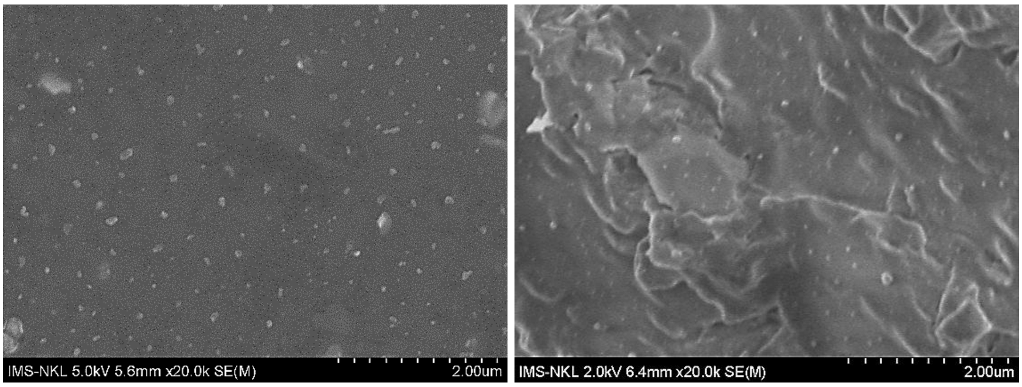

Figure 6. *FE-SEM image (A) surface and (B) cross of Cu-GPNs/PVC nanocomposite film.*

The effectiveness of electromagnetic wave reflection was performed on the vector network analyzer. The result is presented in figure 7 and table 2.

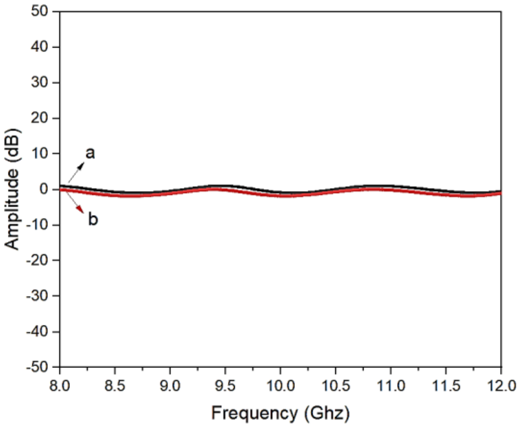

Figure 7. *Test results of radar reflectivity of (a) alumina plate and (b) Cu-GPNs/PVC nanocomposite film.*

Table 2. *The reflection efficiency of Cu-GPNs/PVC nanocomposite film.*

Sample Cu-GPNs/PVC film	**Frequency (GHz)**				
	8	9	10	11	12
Reflection loss (dB)	-0.61	-0.92	-0.52	-0.85	-0.42
Reflection coefficient (%)	86.89	80.9	88.71	82.29	90.78

The test results are indicated in figure 7. The 7a plot indicates a reflected signal from the aluminum plate, while the 7b plot indicates a signal from radar-reflective material. From the result in table 2, it can be seen that the material presented very good reflective properties for radar waves over the complete frequency range of 8 - 12 GHz. In the X band, the radar wave reflection efficiency achieved ranges from 86.89% to 90.78%.

4. CONCLUSIONS

In the present work, the feasibility of using graphene and Cu nanoparticles as reflection material has been examined. NanoCu and nanographene powder samples were added to the liquid PVC resin to make the film with ratios of 5% and 10% by weight, respectively. The effectiveness of reflective material for radar was investigated through a vector network analyzer in the frequency range of 8 -12 GHz. Based on the result obtained, it can be concluded that reflective material can provide effective camouflage against radar.

Acknowledgment: *This research is funded by the project VKHCNQS-2023.*

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TÓM TẮT

Tổng hợp nanocomposite Cu-GPNs/polyvinyl clorua (Cu-GPNs/PVC) ứng dụng làm vật liệu phản xạ sóng điện từ

Bài báo này trình bày phương pháp tổng hợp màng nanocomposite Cu-GPNs/PVC. Nano Cu được tổng hợp từ muối $CuCl_2$ *sử dụng axit ascorbic làm tác nhân khử. Graphen (GPNs) được tổng hợp bằng phương pháp oxy hóa graphite rồi khử ở nhiệt độ cao. Các đặc tính của nano Cu, graphen được xác định phương pháp kính hiển vi điện tử quét phát xạ trường (FE-SEM), kính hiển vi điện tử truyền qua (TEM), phổ nhiễu xạ tia X (XRD) và phổ tán sắc năng lượng tia X (EDX). Với hàm lượng nano Cu chiếm 4% khối lượng, graphen chiếm 10% khối lượng, màng nanocomposite Cu-GNPs/PVC có độ dày 0,6 mm đạt hiệu quả phản xạ từ 86,89% đến 90,78% ở tần số từ 8 đến 12 GHz.*

Từ khoá: Graphene; Nano Cu; Phản xạ; Sóng điện từ.